A Metalloligand Approach to Heterometallic Coordination Polymers

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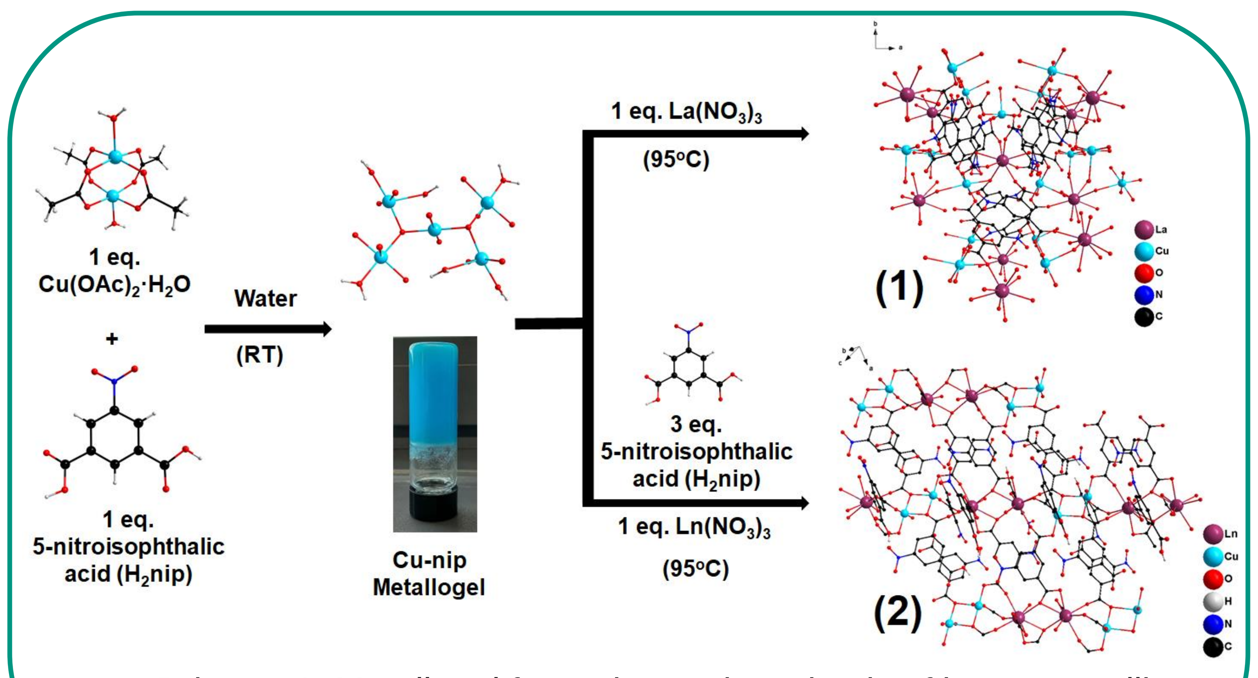
Introduction

The 3d-4f heterometallic clusters and frameworks have fascinating and diverse applications in catalysis, magnetism, energy conversion/storage, luminescent sensors etc.[1] Metal ions with different electronic properties in the same molecule can create synergistic effects and result in multifunctionality. This is achieved by many inorganic-organic hybrid systems, but is often difficult due to unpredictable coordination environments around metal ions and resulting properties. The synthesis of heterometallic systems can be achieved by a step-by-step process whereby firstly a single-metal metalloligand 3d/4f complex is made and then 4f/3d ions are introduced to form the bimetallic and multimetallic complexes. This approach provides better control over the final product and can yield materials with interesting properties for various applications. In this work, a metalloligand approach, based on a metallogel is discussed for the 3d-4f heterometallic coordination polymers.



Scheme 1. Metallogel formation and synthesis of heterometallic coordination polymers **1** and **2**.

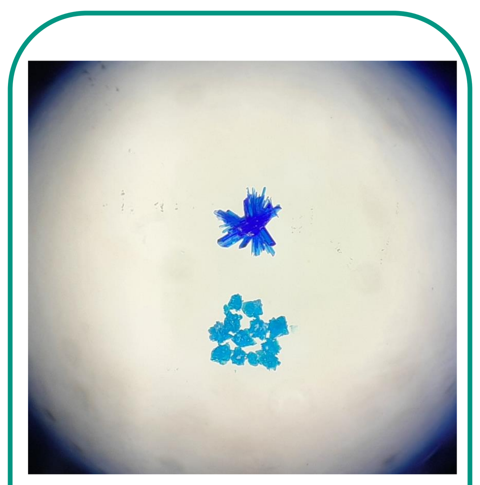


Figure 1. Crystals of **1** (top, dark blue) and **2** (bottom, blue) as viewed under optical microscope.

The reaction of copper acetate with 5-nitroisophthalic acid (H_2nip) in water gives a Cu-nip metallogel which is a Cu_5 – cluster.[2] This gel acts as a metalloligand to incorporate Ln^{3+} ions which leads to heterometallic coordination polymers. As shown in scheme 1, we get a three-dimensional network compound **1** $[\{La_2Cu_3(nip)_6(H_2O)_9\}{\cdot}8H_2O]_n$ and a two-dimensional compound **2** $[\{Ln_2Cu_2(nip)_2(Hnip)_6(H_2O)_4\}{\cdot}2H_2O]_n$, where Ln = La-Nd, depending on whether extra H_2nip ligand is added or not.

(a) (b) (c) (d) (e) (f) (g)

Figure 2. (a)-(g) Crystal growth of **1** from Cu-nip-La precipitate through Ostwald ripening over 64 hours.

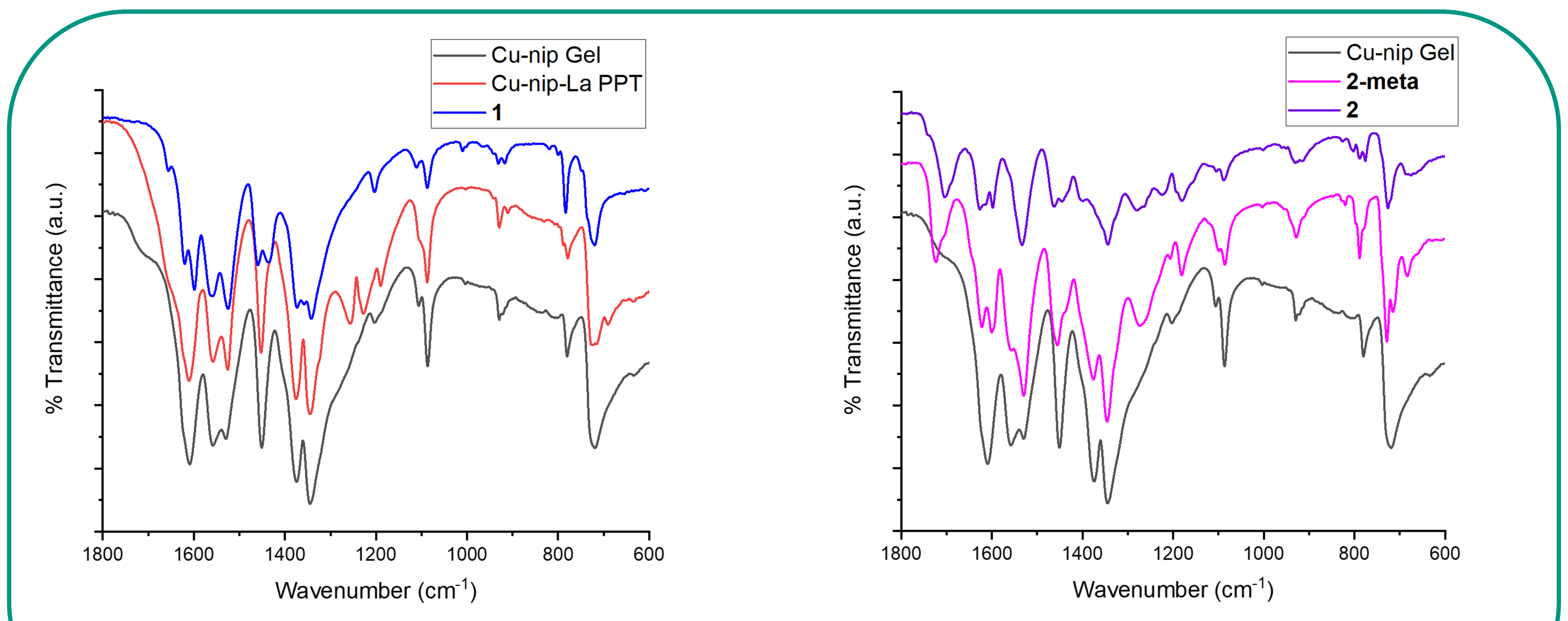


Figure 3. Comparison of FT-IR spectra of Cu-nip Gel, intermediates from which **1** and **2** grow as crystals.

The crystal growth is facilitated by Ostwald ripening[3], where a metastable intermediate phase is initially formed, which then partially dissolves and transforms into a chemically and thermodynamically stable state and this is observed as dark blue crystals of **1**, as shown in Figure 2 (a)-(g).

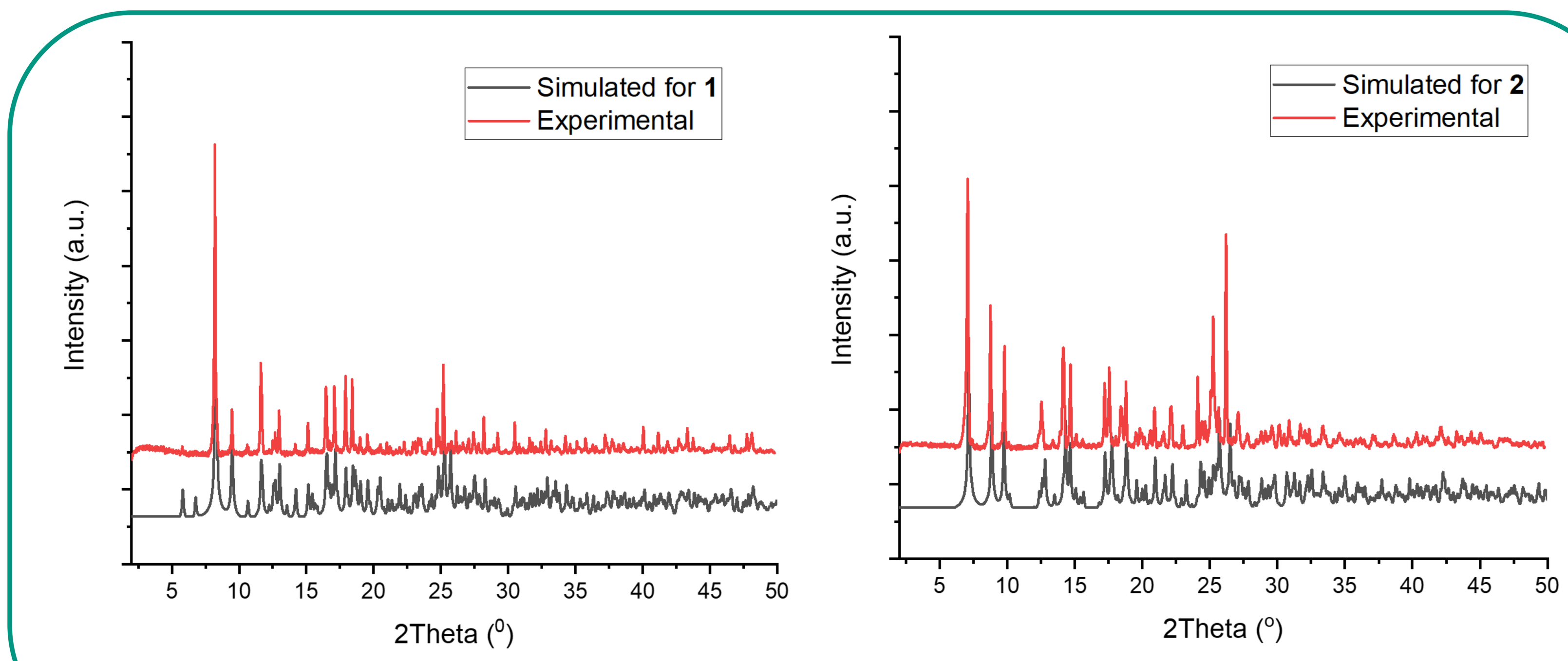


Figure 4. Simulated & Experimental PXRD patterns for **1** and **2**.

For the extra H_2nip ligand is added along with $La(NO_3)_3$ as for compound **2** with La_2Cu_2 as the secondarys building unit (SBU), the intermediate metastable compound **2-meta** $[\{La_4Cu(nip)_5(Hnip)_4(H_2O)_8\}]_n$ was isolated with a La_4Cu SBU. The crystals can be distinguished from the colour.

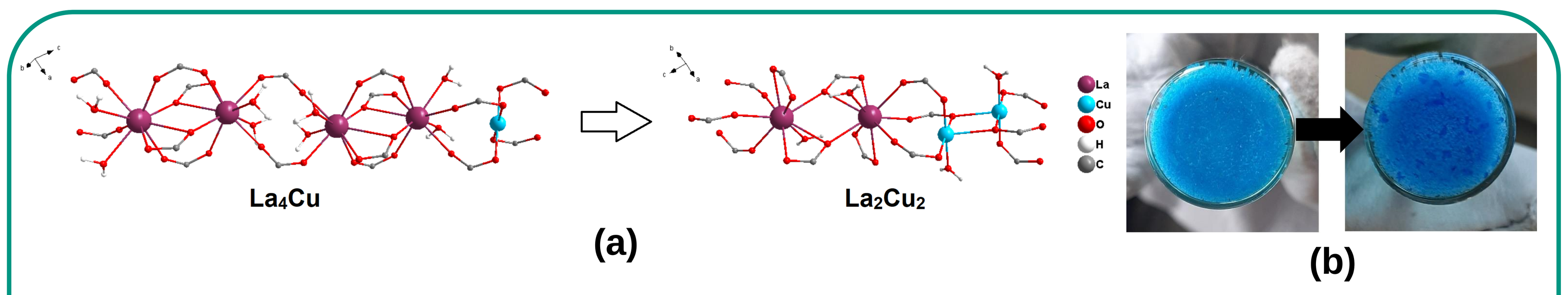
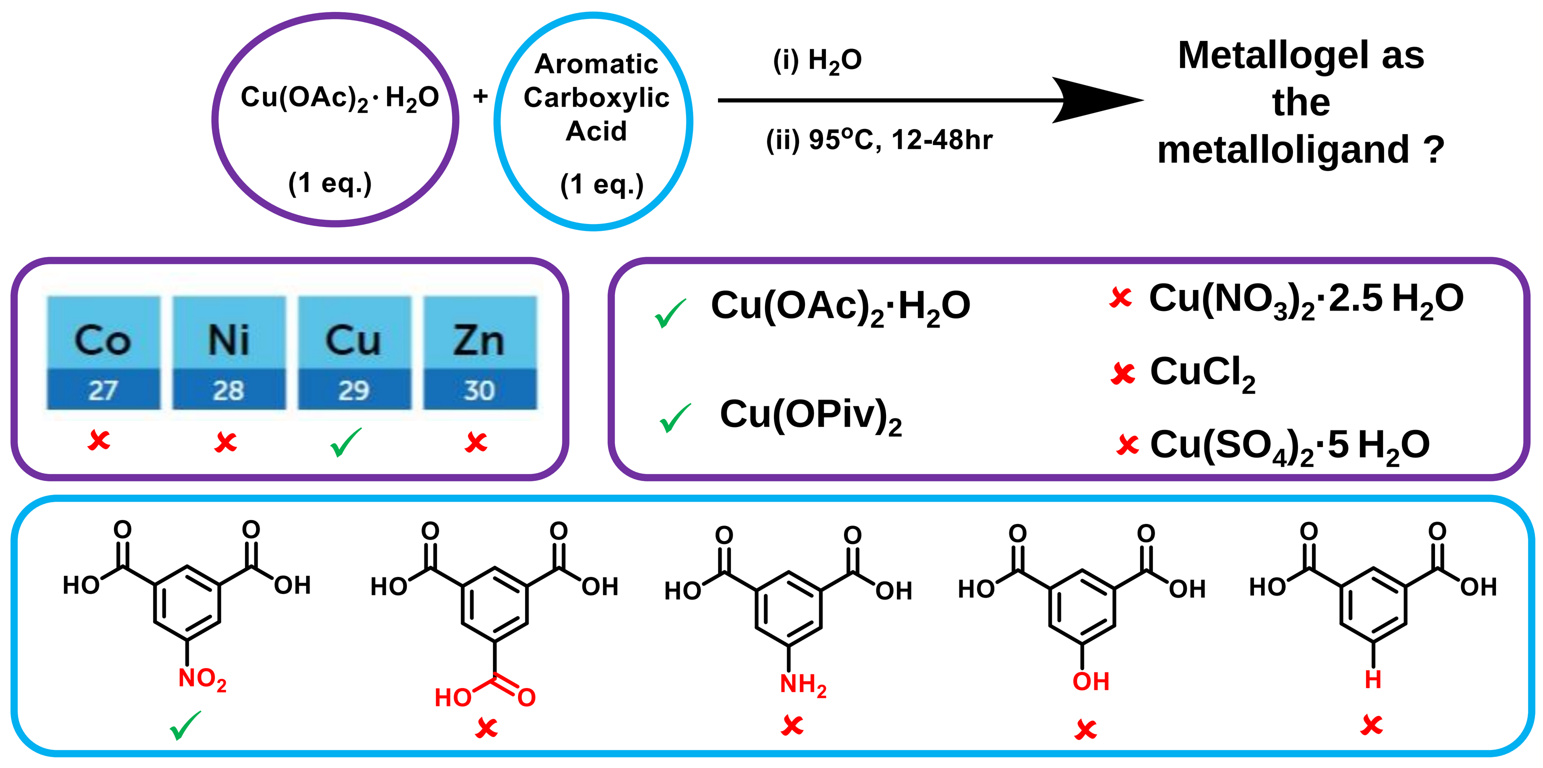


Figure 5. (a) Single Crystal to Single Crystal transformation of La_4Cu unit (**2-meta**) to La_2Cu_2 (**2**); (b) Crystal growth of **2** (blue crystals) through Ostwald ripening from **2-meta** (pale blue crystals).



Conclusion & Outlook

- The metalloligand approach is an effective method for synthesizing novel lanthanide containing heterometallic complexes/coordination polymers.
- Exploration of the catalytic and magnetic properties of the synthesized lanthanide-containing heterometallic complexes is currently underway.
- Changing small reaction parameters such as functional groups in organic ligands, source of metal ions etc. and noting how these parameters effects the self-assembly, directs the idea towards data collection for machine learning.

References

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