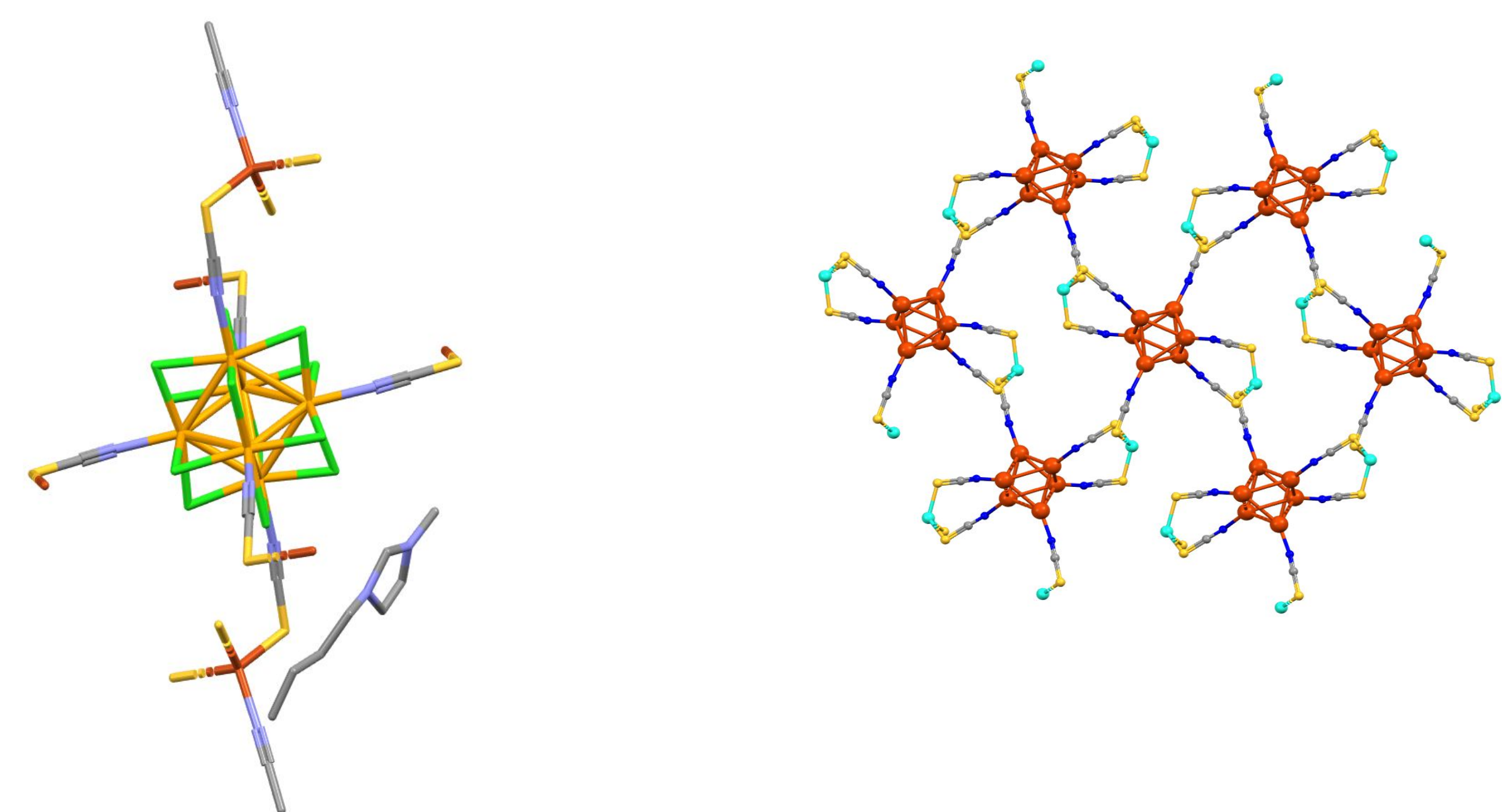


Natalie Husby, Akane Inoue, \*Hilary J. Eppley

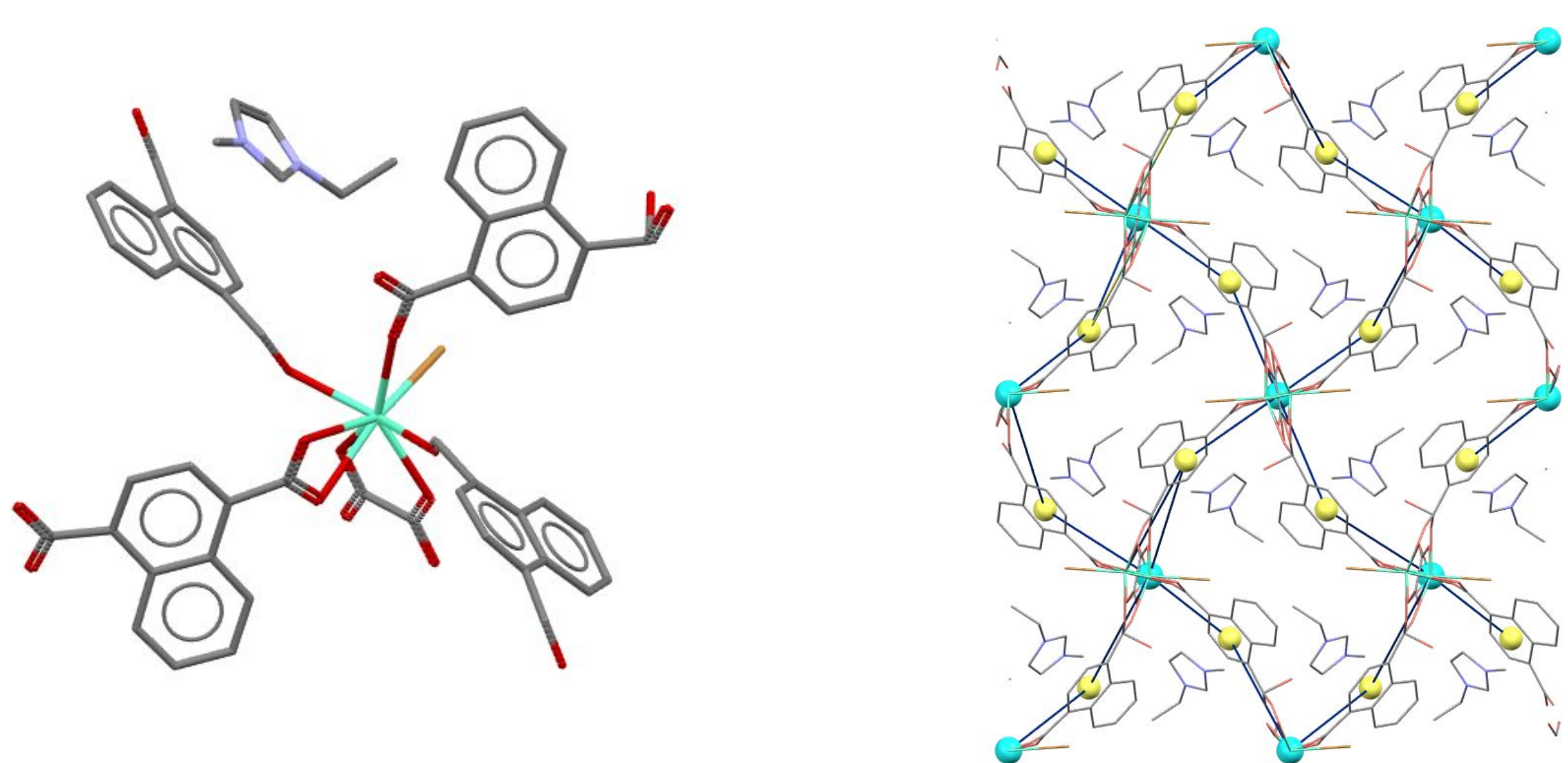
Department of Chemistry and Biochemistry, DePauw University, Greencastle, IN 46135

## Introduction

Synthesis of metal organic frameworks can result in different products based on the solvent that is used. One option is to use ionic liquids (ILs, or room temperature molten salts) to create novel metal organic coordination polymers.<sup>1</sup> Using databases such as Sci-Finder Scholar, and Cambridge Structural Database, our group analyzed metal organic polymers synthesized in ILs with the goal of cataloging the topology of the structures, the connectivity of the organic ligands, the overall net structures, and the roles of the ILs in the syntheses.



**Figure 2:** Structures from the Pigorsch et. al paper. The left photo shows the  $[BMIM][Nb_6Cl_{12}(NCS)_6\{Cu(CH_3CN)\}_2]$  monomer with the EMIM, whereas the right photo shows the net connections of of the polymer.



**Figure 3:** The left photo shows the  $\{(EMIM)[Eu(1,4-ndc)(ox)0.5Br]\}_n$  monomer centered around the EU atom and the photo on the right shows the net connections between the Eu atoms and the carbon rings

## References

- (1) Vaid, T. P.; Kelley S.; and Rogers, R. Structure-directing effects of ionic liquids in the ionothermal synthesis of metal-organic frameworks. *IUCrJ.* **2017**, *4*, 380–392.
- (2) Pigorsch, A. and Köckerling, M. *Cryst. Growth Des.* **2016**, *16* (8), 4240-4246.
- (3) Gao, M.; Wang, Y.; Cao, H.; Liu, Q.; Chen, L. *Zeitschrift Für Anorganische Und Allgemeine Chemie.* **2014**, *640*, 12-13, 2472–2476.
- (4) Huang, Y.; Qin, J.; Yang, X.; Wang, H.; Li, F.; Ma, L. *J. Solid State Chem.* **2020**, *285*, 121-252.
- (5) Qin, J.; Jia, Y.; Li, H.; Zhao, B.; Wu, D.; Zang, S.; Hou, H.; Fan, Y. *Inorg. Chem.* **2014**, *53*, 685-687.

## Methods

Our methods consisted of using three different databases: Sci-Finder Scholar, Conquest, and Mercury.

- |   |          |   |          |   |
|---|----------|---|----------|---|
| <p><u>Sci-Finder Scholar</u></p> <ul style="list-style-type: none"> <li>○ Used to find relevant papers</li> <li>○ Searched using keywords and phrases such as “Ionic liquid syntheses” or “Mixed ligand coordination Polymers”</li> </ul> | <p>→</p> | <p><u>Conquest (CSD)</u></p> <ul style="list-style-type: none"> <li>○ Used to find compounds from papers</li> <li>○ Could search for compound                     <ul style="list-style-type: none"> <li>■ Formula, structure, author</li> </ul> </li> <li>○ Would give us a ‘hitlist’ of results under six letter reference codes                     <ul style="list-style-type: none"> <li>■ Ex: OROKAJ</li> </ul> </li> </ul> | <p>→</p> | <p><u>Mercury</u></p> <ul style="list-style-type: none"> <li>○ Used ref code to find and edit structure</li> <li>○ Created net structures through connecting centroids</li> <li>○ Created centroids in Mercury and then turned them into “dummy atoms” in CIF file which allowed for creation of Net figures</li> </ul> |
|---|----------|---|----------|---|

Build Queries | Combine Queries | Manage Hitlists | View Results

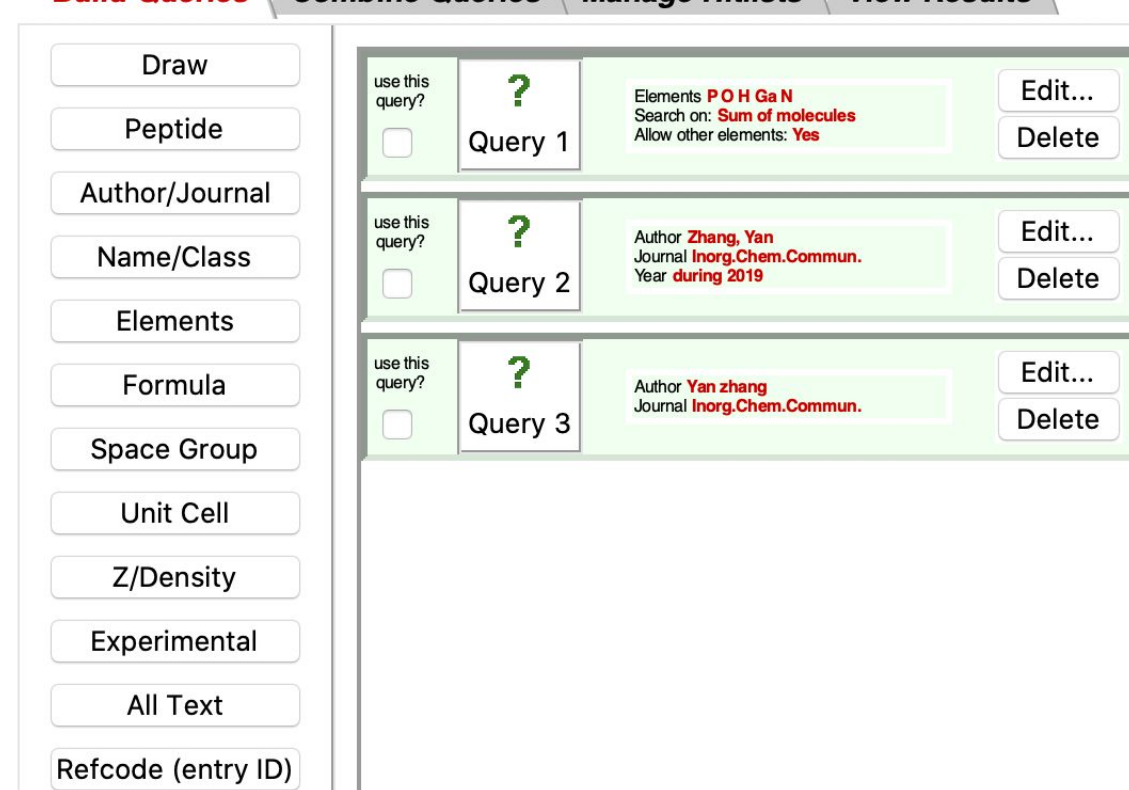


Figure 1a.

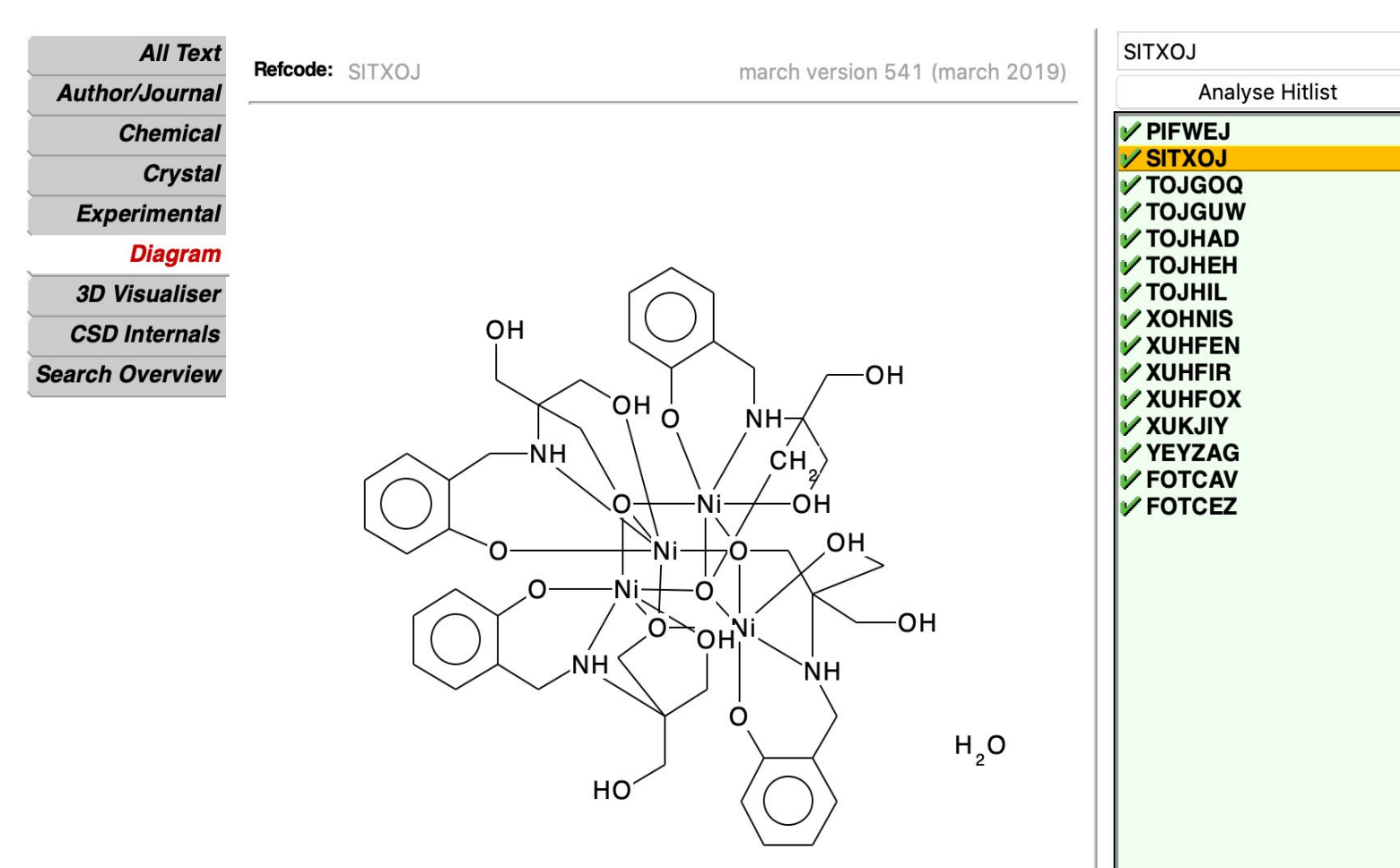


Figure 1b.

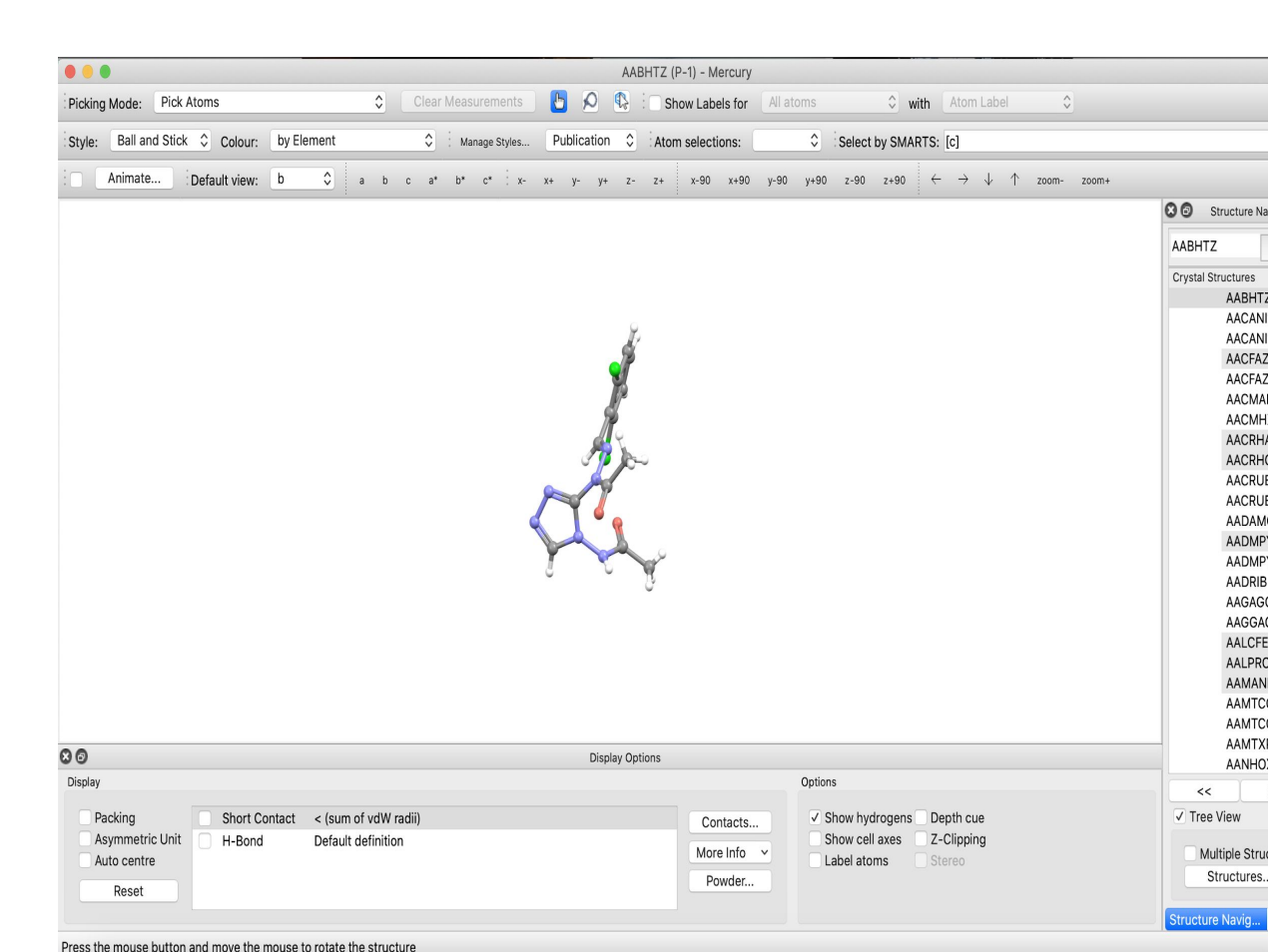


Figure 1c.

**Figure 1:** The databases used in our research. Figure 1a and 1b show the program conquest, and figure 1c shows the program Mercury.

## Results

Formula	Reference #	Ref code	IL	Role of IL	1D, 2D, 3D?	Ligand	Net	Interesting properties
$[BMIM][Nb_6Cl_{12}(NCS)_6\{Cu(CH_3CN)\}_2]$	2	OROKAJ	$[BMIM][PF_6]$	Cation/Medium	3D bridged compound	Isothiocyanato ligands n-bonded to cluster unit	Ligands n bonded to cluster units (cluster bound)	H-bonds between layers
$\{(EMIM)[Eu(1,4-ndc)(ox)0.5Br]\}_n$	3	EMUTUD	$[EMIM]Br$	Cation	2D layers that form 3D framework	Bromide ion as terminal ligand	6 connected PCU net	Exhibit lanthanide luminescence emissions
$[M_2(TBAPy)(H_2O)_2] \cdot (Guests)_x$ (M = Co, Zn)	4	KUJYUM	$[RMIM]Br$ (R = ethyl, propyl, butyl)	Medium (increases yield)	2D layers stack to form 3D network	TBAPy ligand bridging and monodentate to each metal	4,4 - net Square grid	Temperature dependent fluorescence
$[Mn_2(ptptp)(suc)_{0.5}(H_2O)_3] \cdot Br \cdot 0.5H_2O$	5	EFEFUS	$[BMIM]Br$ or $[P_{14}]Br$	Anion donor and structure regulator	1D helical structure forms 3D supramolecular network	Ptptp ligand and suc ligand are bridging	N/A	Anti-ferromagnetic properties

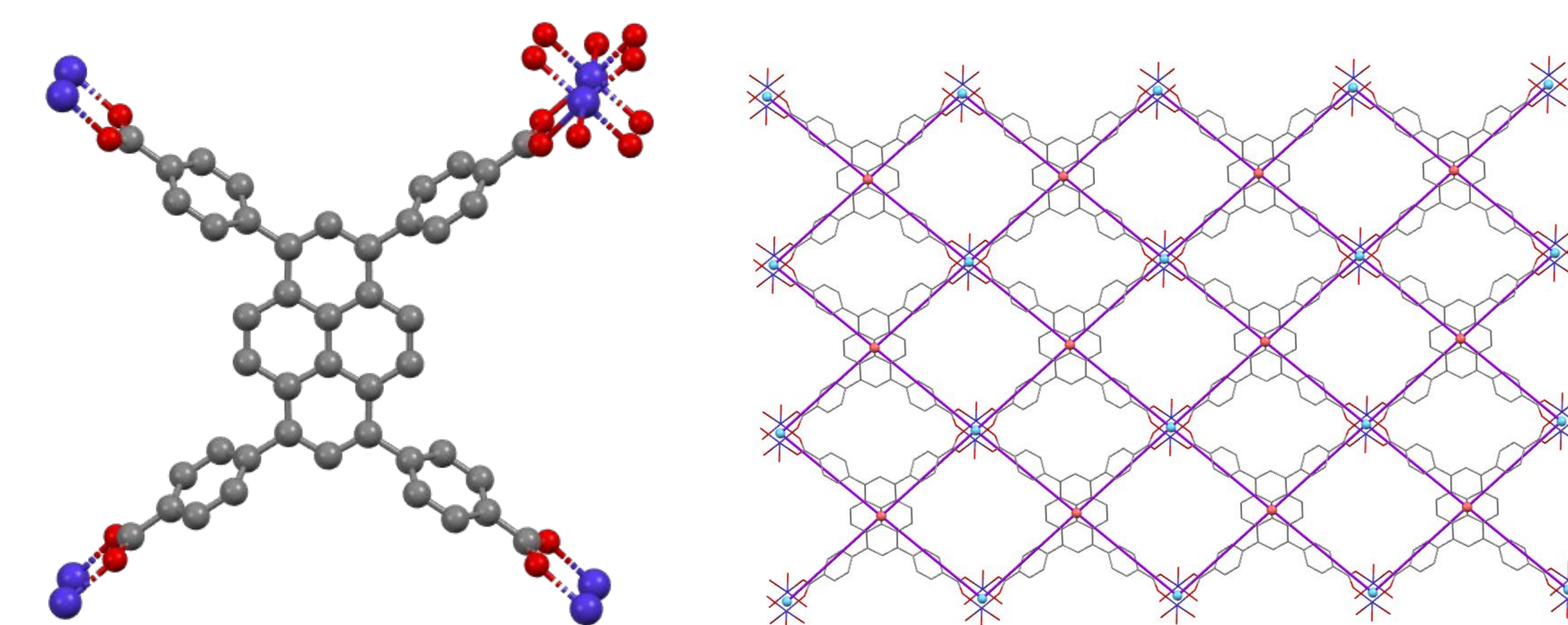
## Results discussion

- Role of IL divided into cation donor, anion donor, medium.
- Many compounds form 3D frameworks or networks
  - 2d structures can stack to form 3D layers
- Some have interesting properties that can be applied to useful things
  - Luminescence
  - Fluorescence

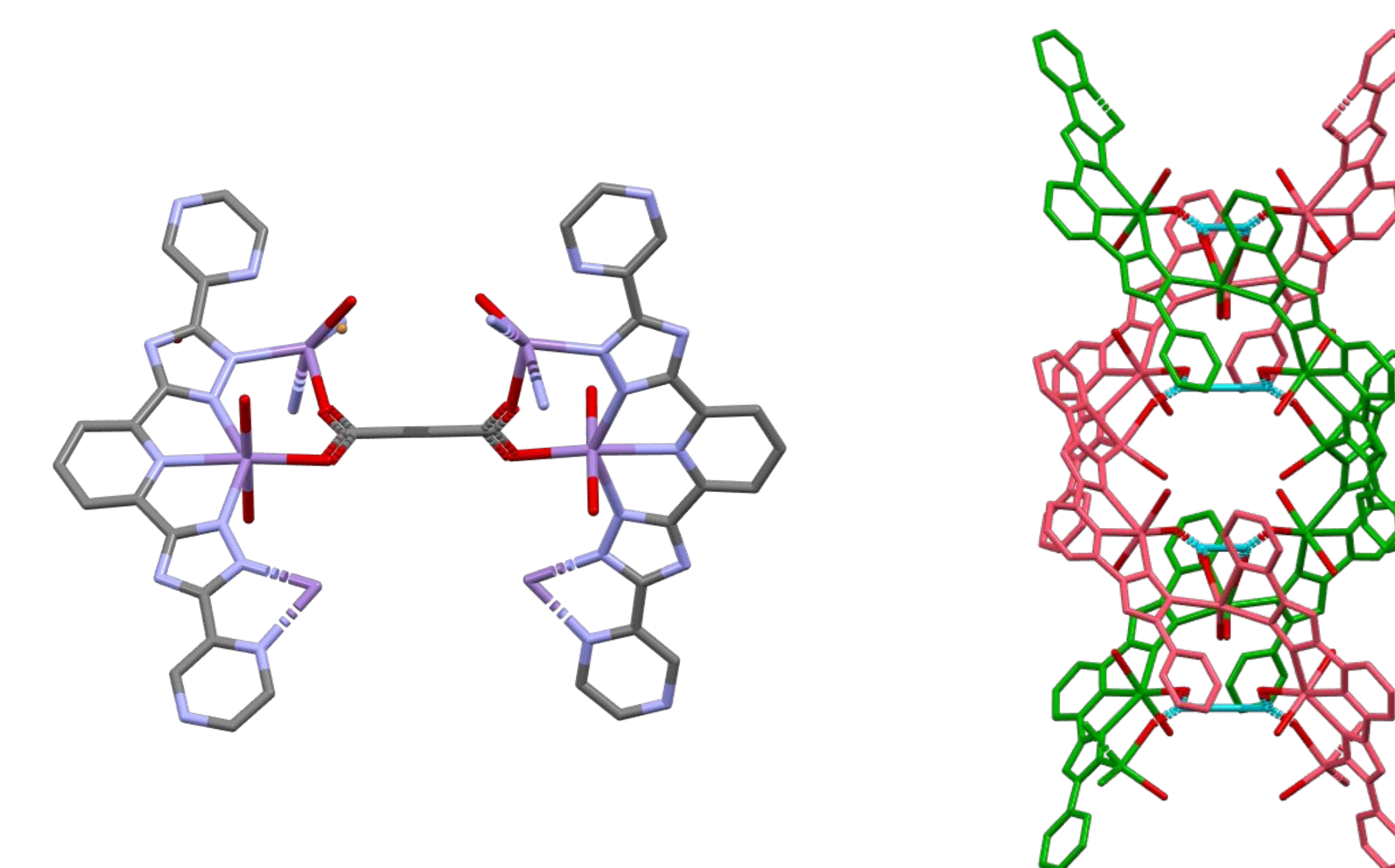
## Future Work

For our future work, we have two major projects:

1. Continue our work analyzing new structures synthesized in ionic liquids and to use the topology program TOPOS Pro as another tool to analyze the structures. We plan on writing a review paper incorporating the different structures using the visuals we created.
2. Identify systems with  $Na_3SIP$  ligands that can be adapted to ionic liquids in order to synthesize new products and to do those reactions in a lab setting.



**Figure 4:** Structures from the Huang et. al study. The left image is the  $[M_2(TBAPy)(H_2O)_2] \cdot (Guests)_x$  (M = Co, Zn) monomer. The right image shows how the monomers connect to form a 2D layer with 4,4 net square grid structure (as shown by the purple lines).



**Figure 5:** Structures from the Qin et. al study. The left image is the  $[Mn_2(ptptp)(suc)_{0.5}(H_2O)_3] \cdot Br \cdot 0.5H_2O$  monomer with two pieces of the helix held together by a suc ligand. The right shows the 1D helical structure. Green and pink show individual strands of the helix, with light blue ladder structure.

## Acknowledgments

We would like to express our gratitude and appreciation to the Department of Chemistry and Biochemistry, the Science Research Fellows Program, Caroline Gilson, Tiffany Hebb, and Gina Federighi for supporting this project.

# **Introduction**

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# Methods

Our methods consisted of using three different databases: Sci-Finder Scholar, Conquest, and Mercury.

## Sci-Finder Scholar

- Used to find relevant papers
- Searched using keywords and phrases such as “Ionic liquid syntheses” or “Mixed ligand coordination Polymers

## Conquest (CSD)

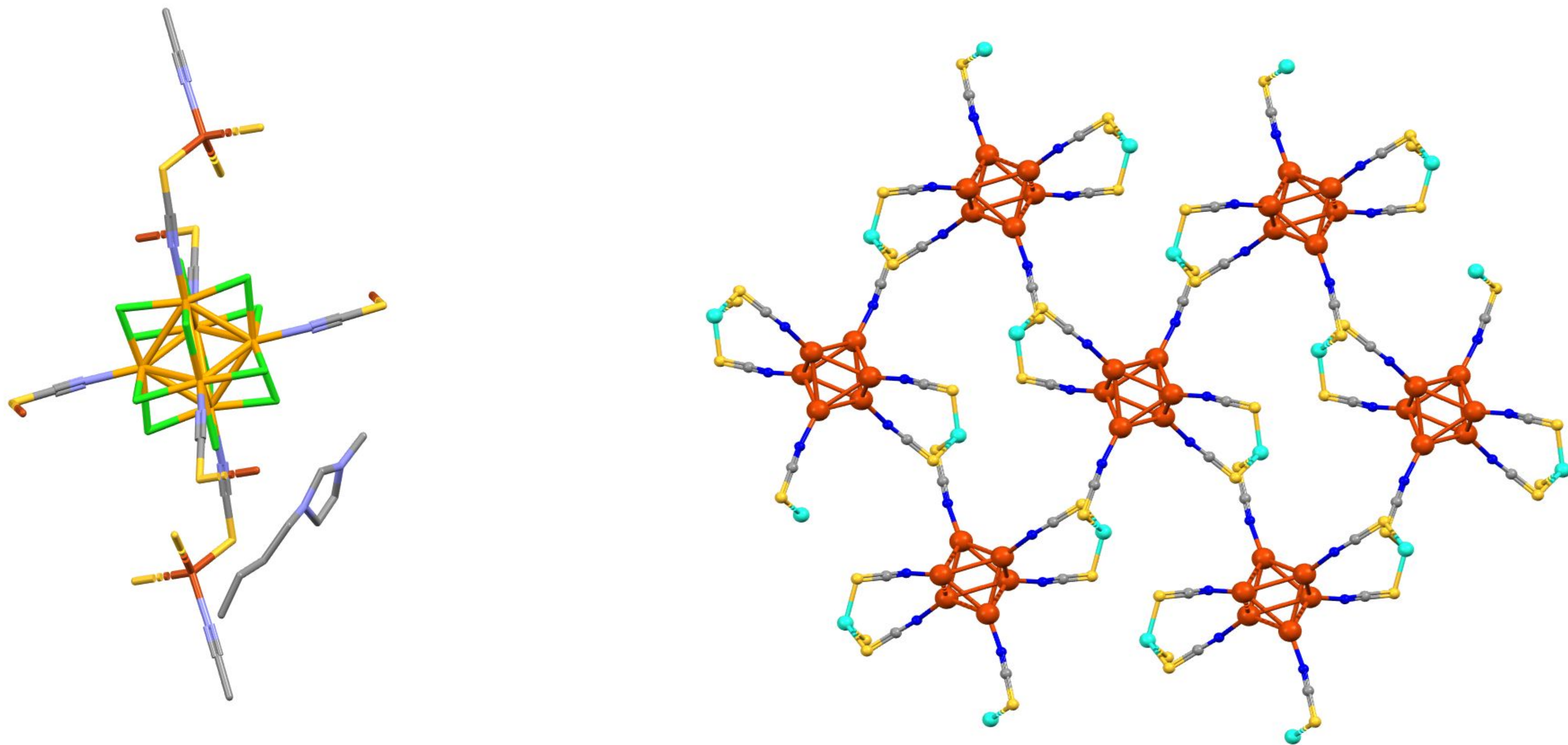
- Used to find compounds from papers
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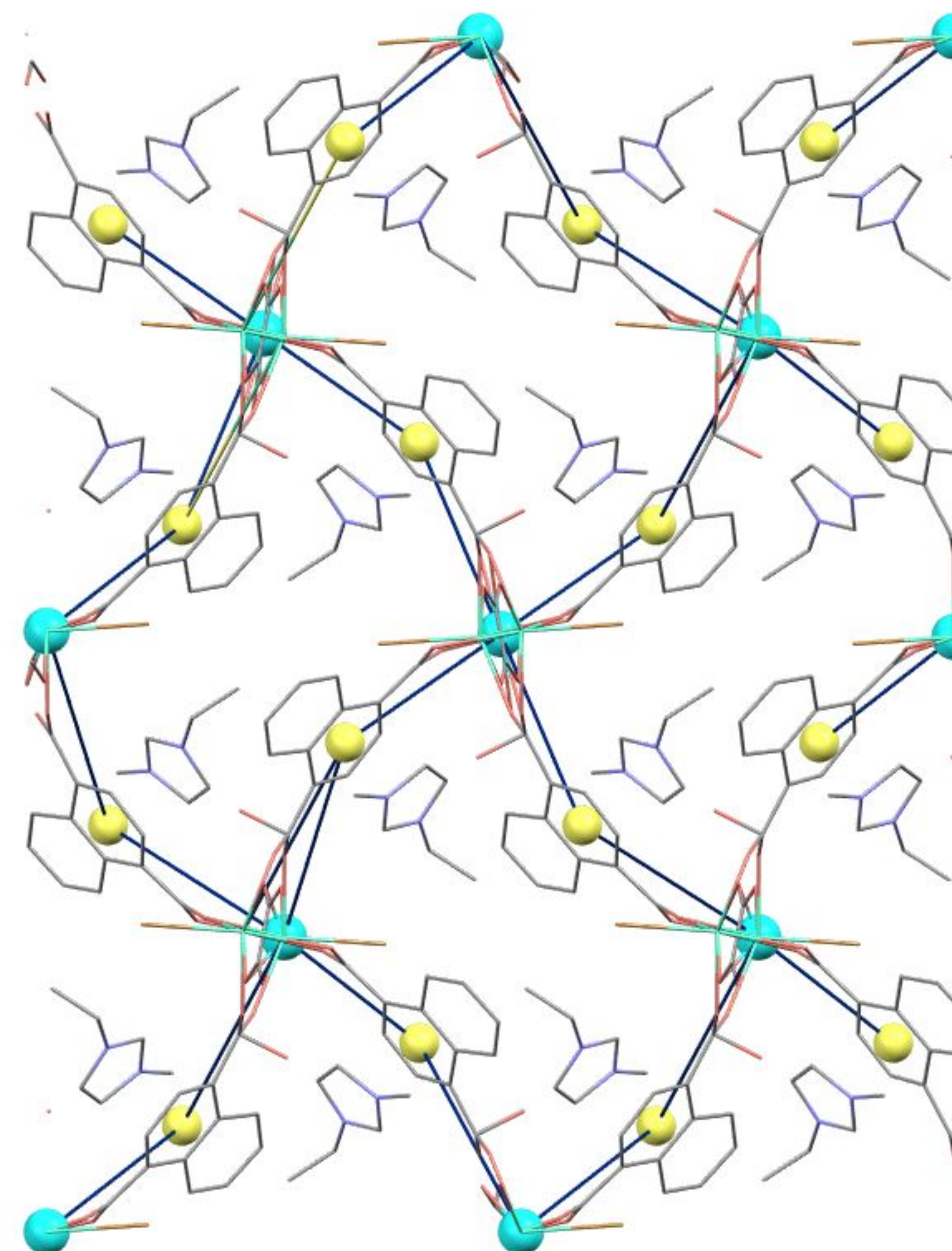
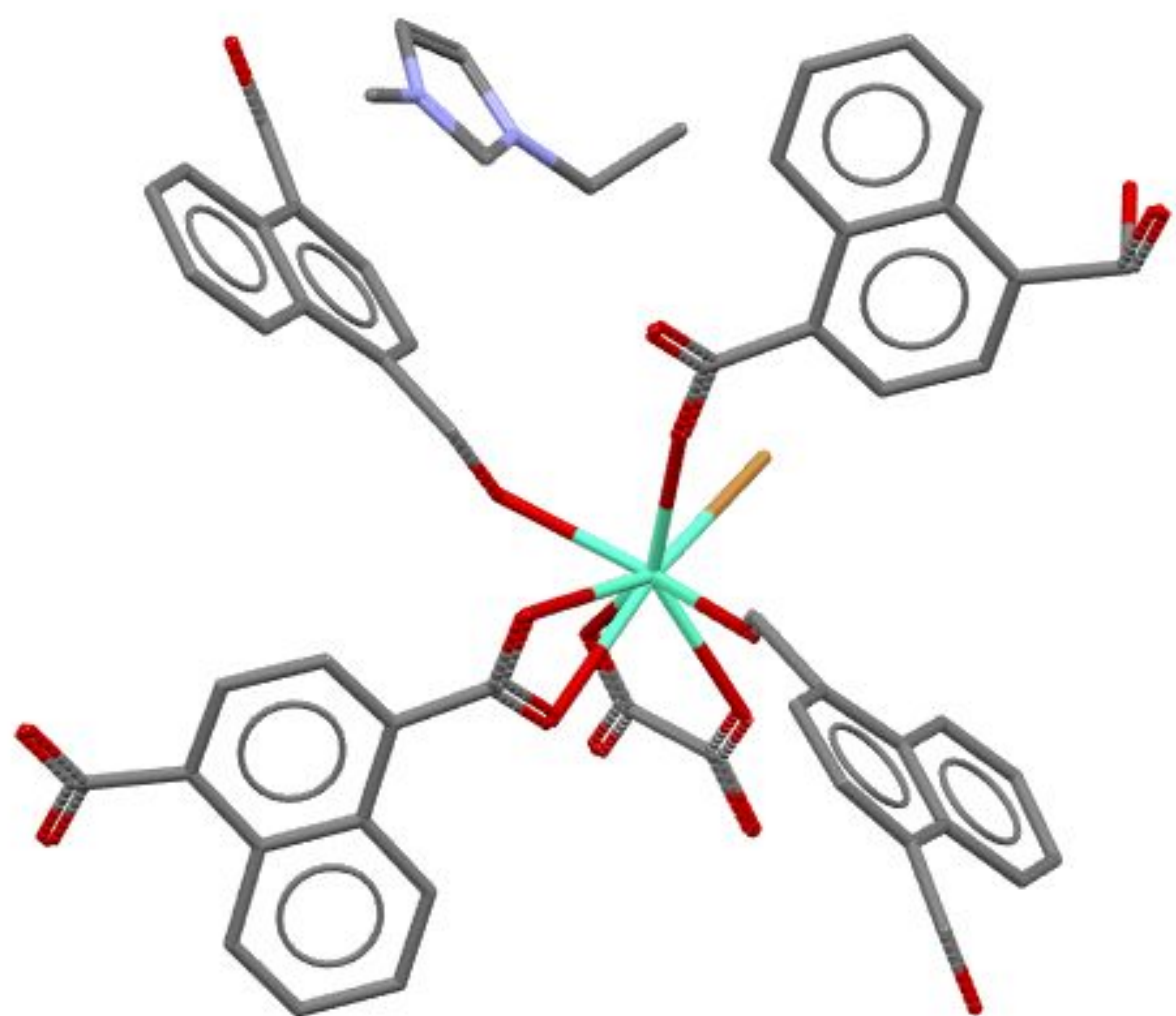
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# Results

Formula	Reference #	Ref Code	Ionic Liquid	Role of IL	1D, 2D, 3D?	Ligand	Net	Interesting properties
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$[\text{M}_2(\text{TBAPy})(\text{H}_2\text{O})_2] \cdot (\text{Guests})_x$ (M = Co, Zn)	4	KUJYUM	$[\text{RMIM}]\text{Br}$ (R= ethyl, propyl, butyl)	Medium (increases yield)	2D layers stack to form 3D network	TBAPy ligand bridging and monodentate to each metal	4,4 - net Square grid	Temperature dependent fluorescence
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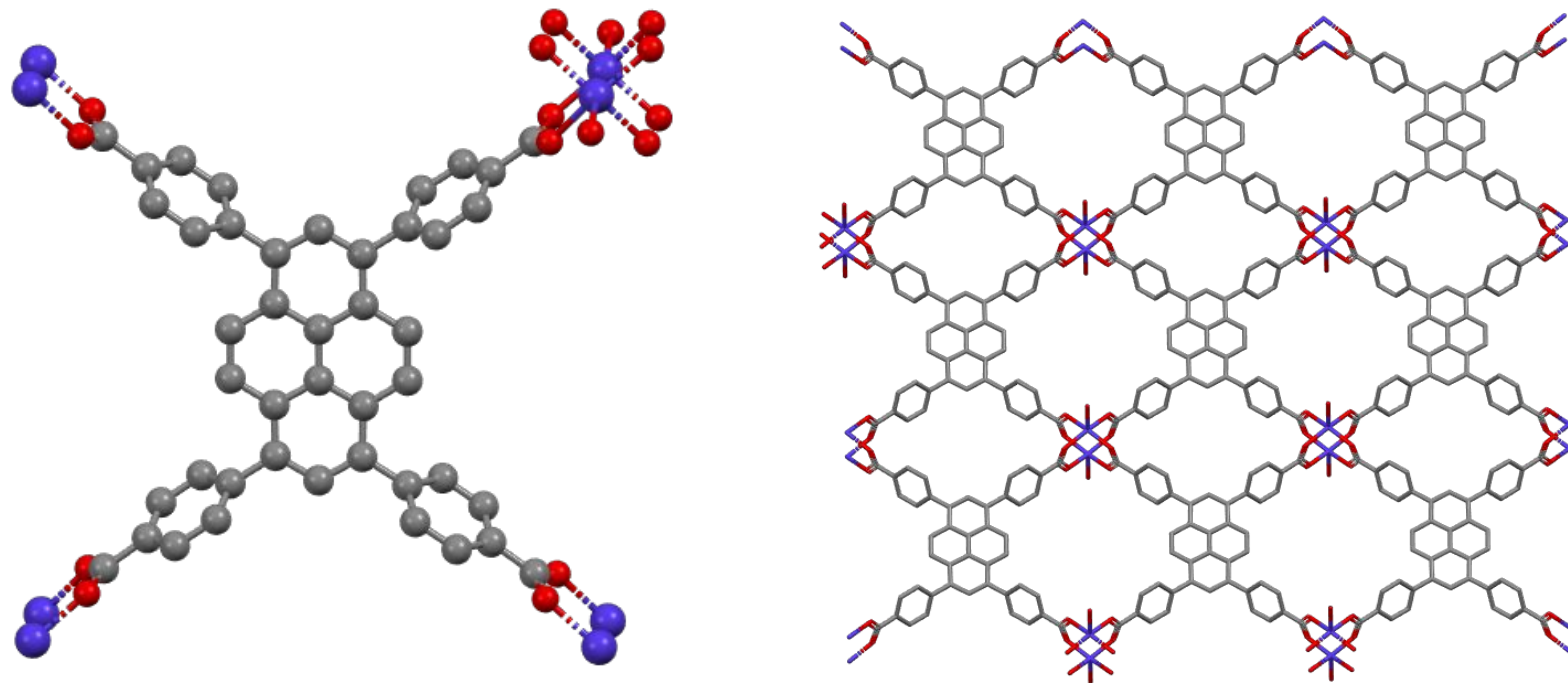
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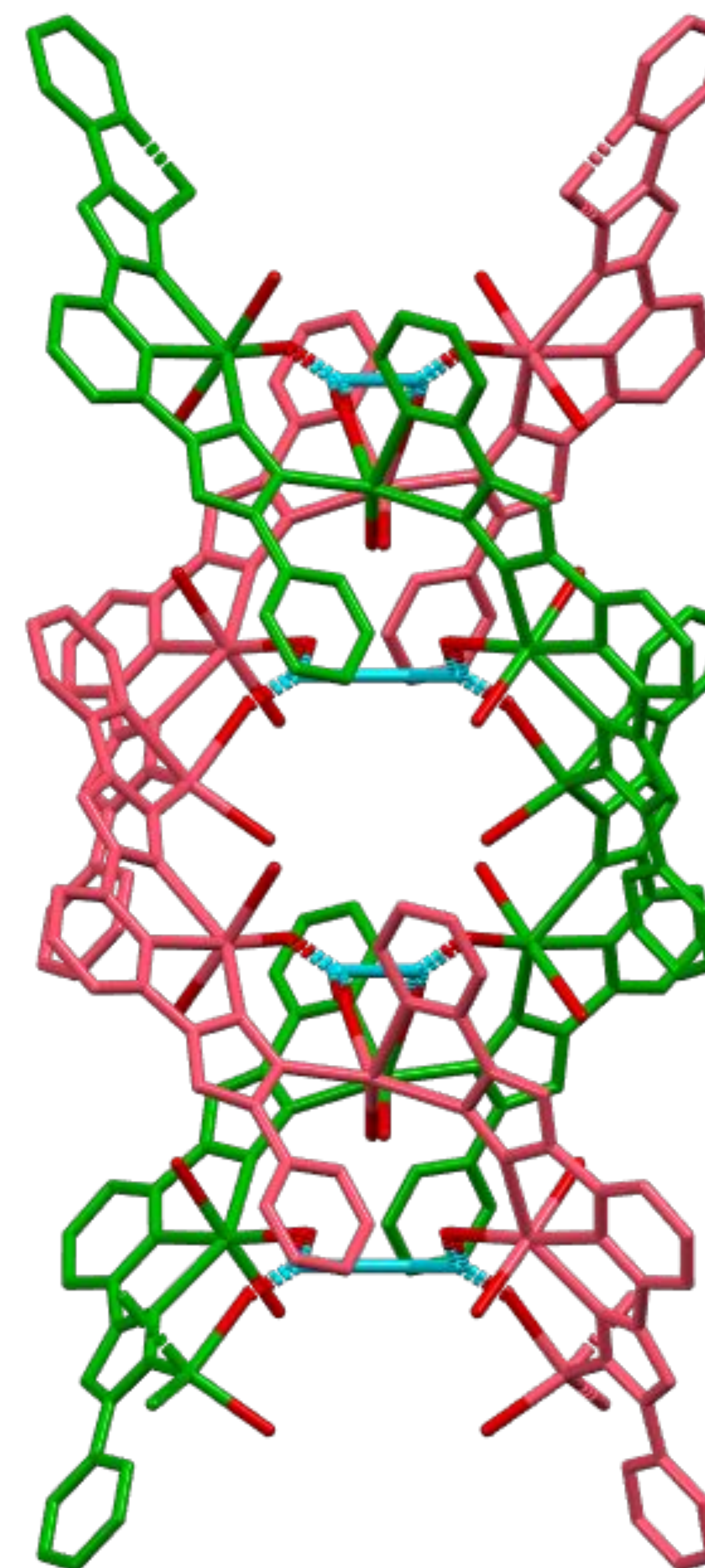
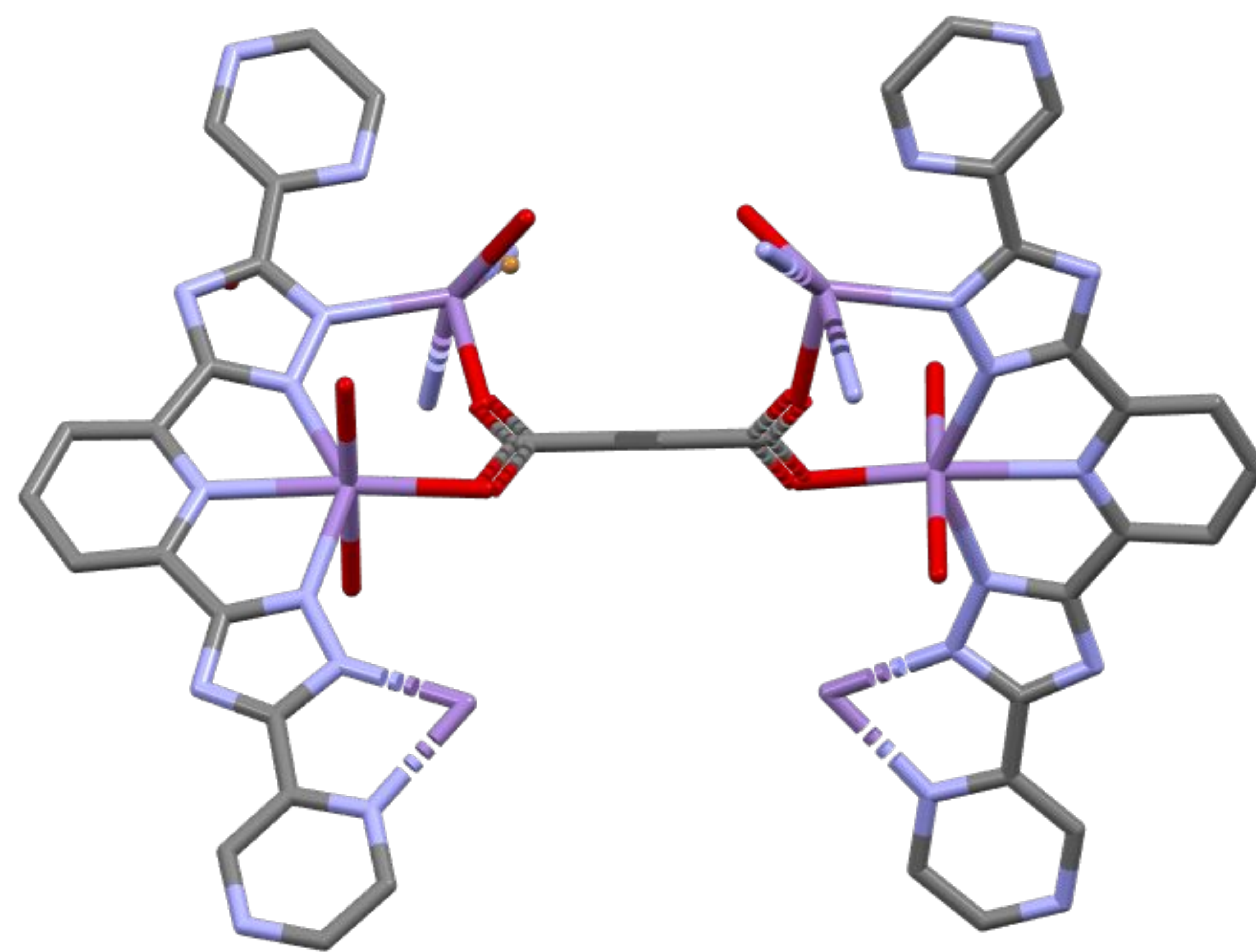
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