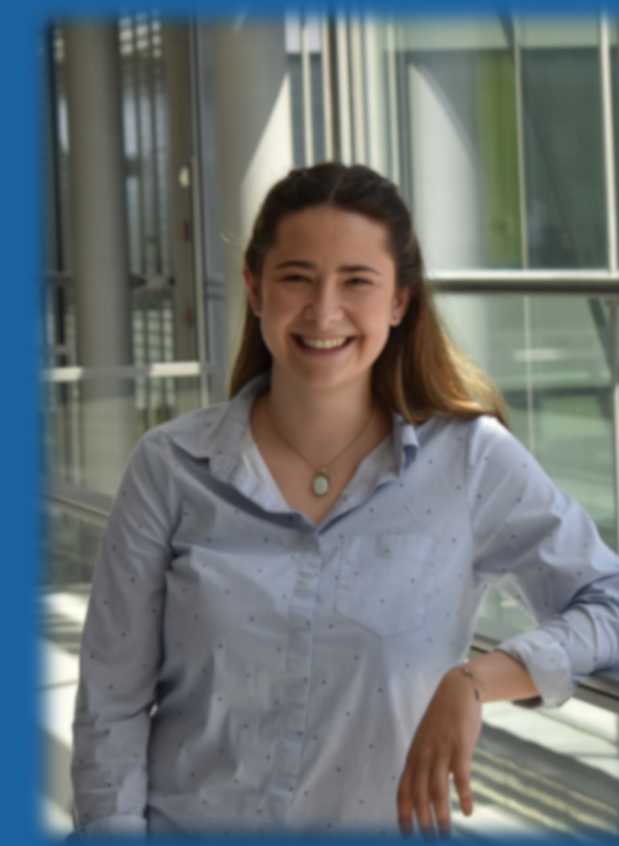


# Synthesis and Investigation of copper(I) complexes with a N<sub>3</sub>S-thioether ligand-system

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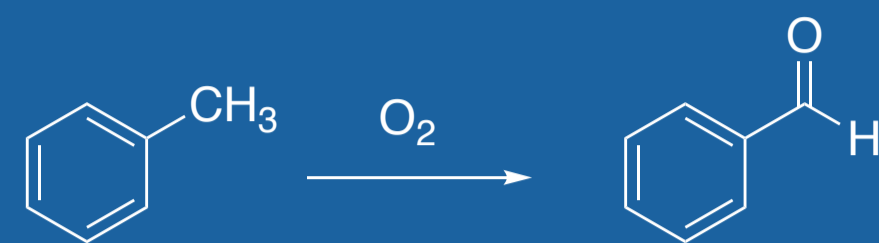
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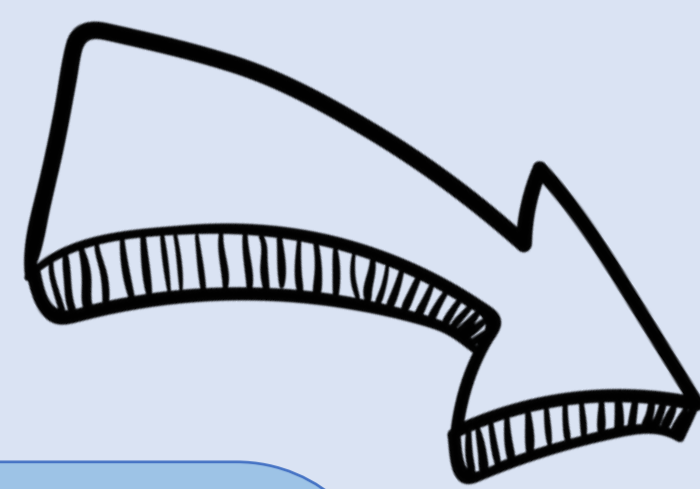


## Research Goal

aerobic aliphatic C-H oxidation<sup>[1]</sup>  
→ mild and environmental friendly (green) conditions<sup>[1]</sup>

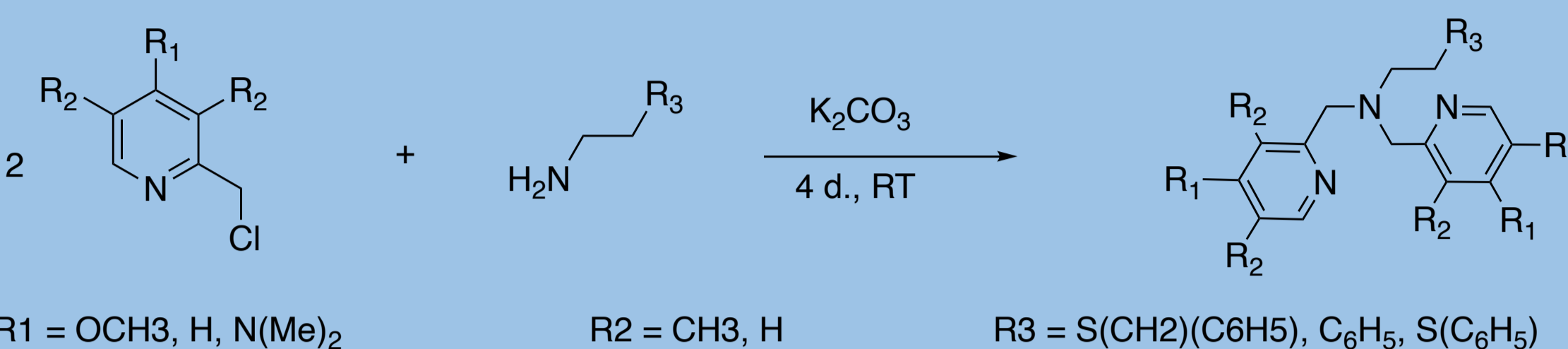


- **In nature:** activation of dioxygen and strong C-H by copper-containing enzymes<sup>[2]</sup>  
→ see PHM  
→ reactive species: end-on superoxido copper complex  
→ model system (with only N-donor atoms) has been developed<sup>[3]</sup>
- **State of the art:**  
→ role of the thioether in the active site is still unclear  
→ Investigation of ligands with N<sub>2</sub>S and N<sub>3</sub>S systems to mimic the active site of PHM<sup>[4,5]</sup>

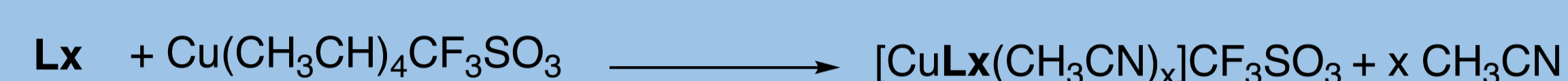


## Ligand and complex synthesis

selection of tripodal and tetrapodal ligands:



copper(I) complexes with all ligands:

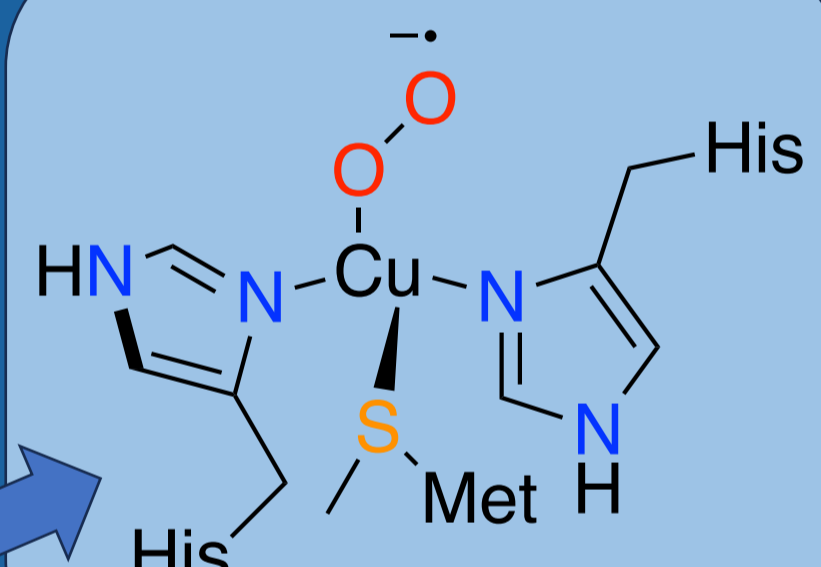
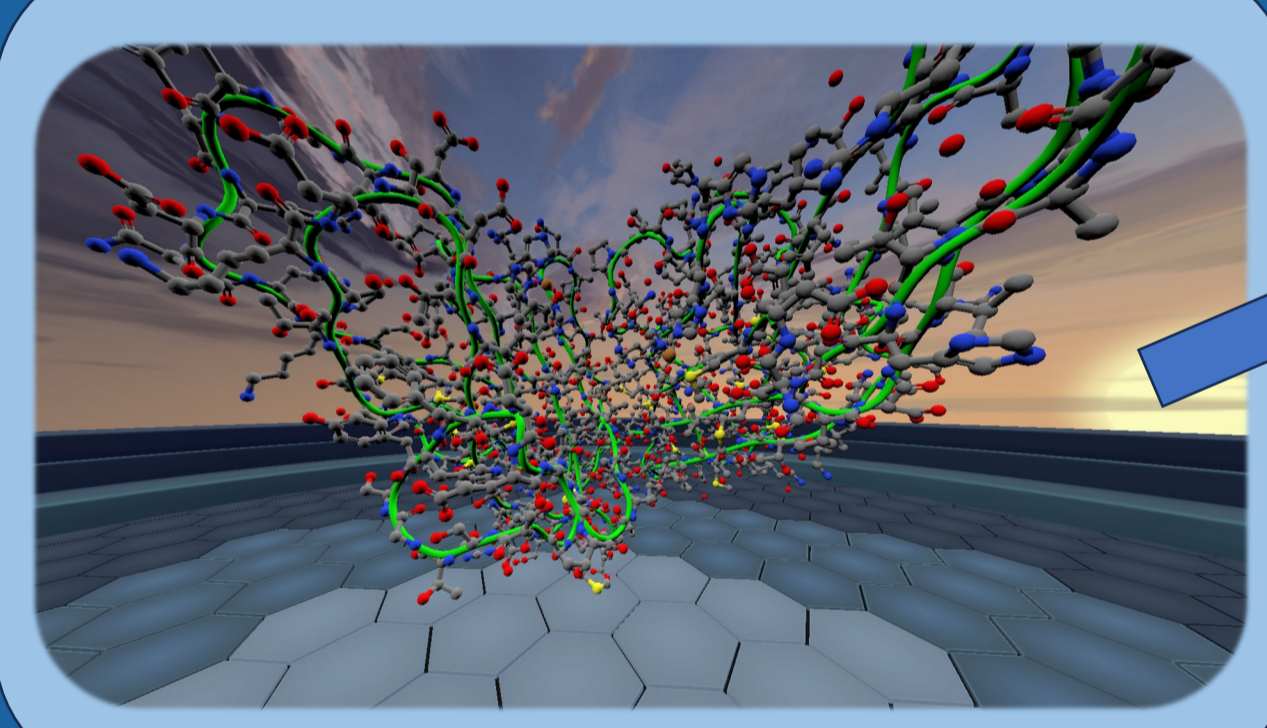


- ligands are dissolved in acetonitril
- copper(I)-salts (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> or [BAR<sub>4</sub>F<sup>-</sup>]) are added in solution
- solvent is removed → light green solid

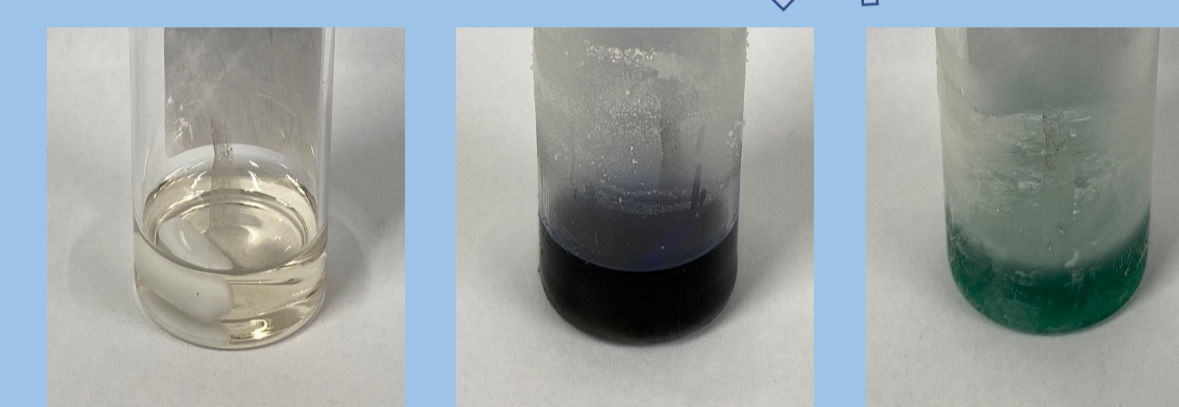
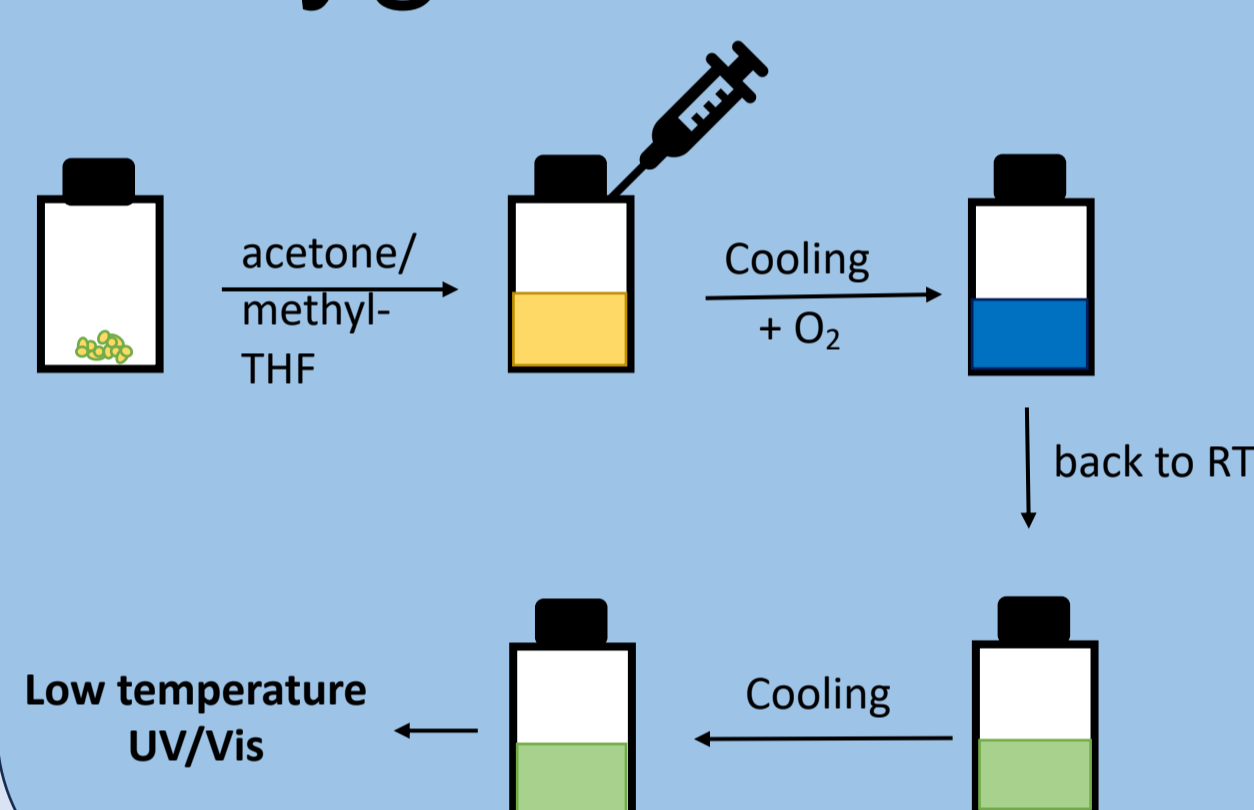
## See the Peptidylglycine α-hydroxylating monooxygenase in VR



You can see the active site of PHM also on YouTube here!



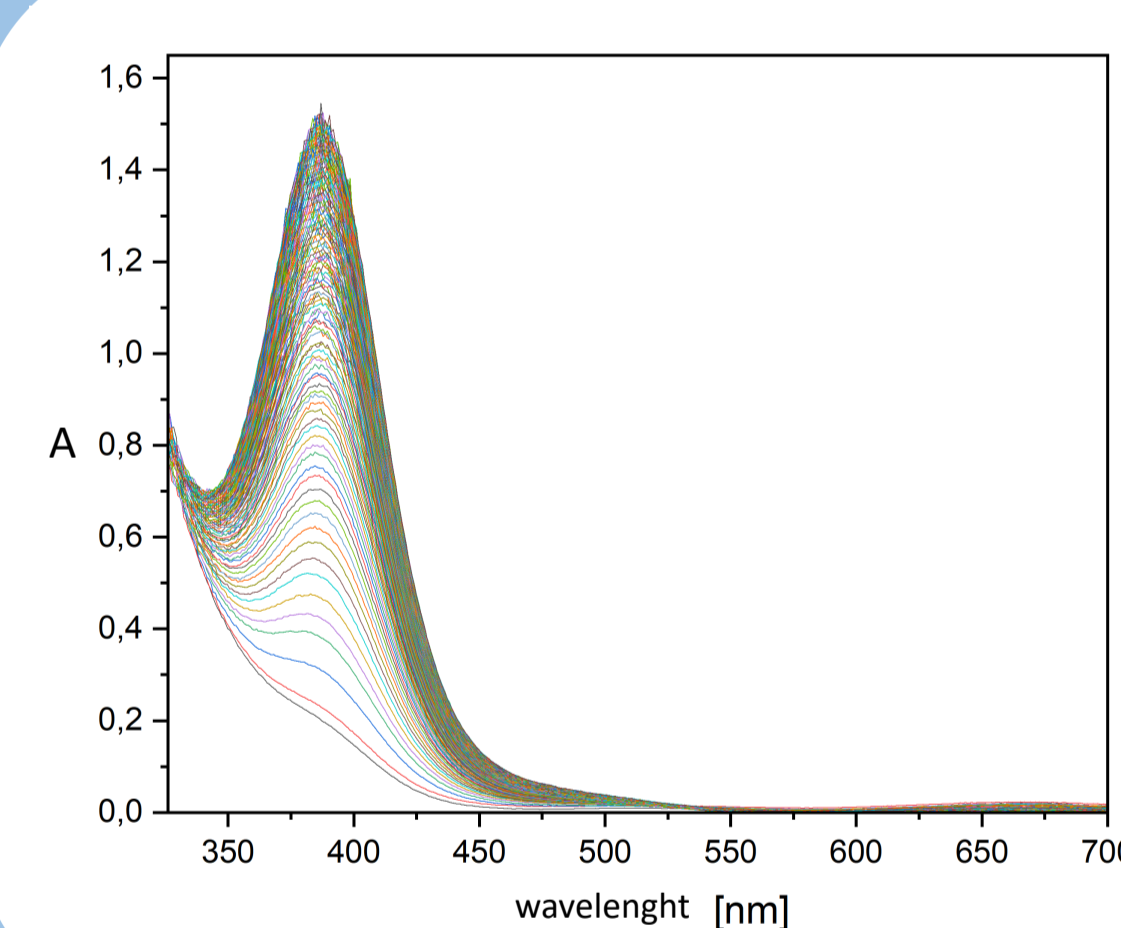
## Oxygen activation:



- All complexes were able to activate O<sub>2</sub>
- Color change from blue to green not reversible!

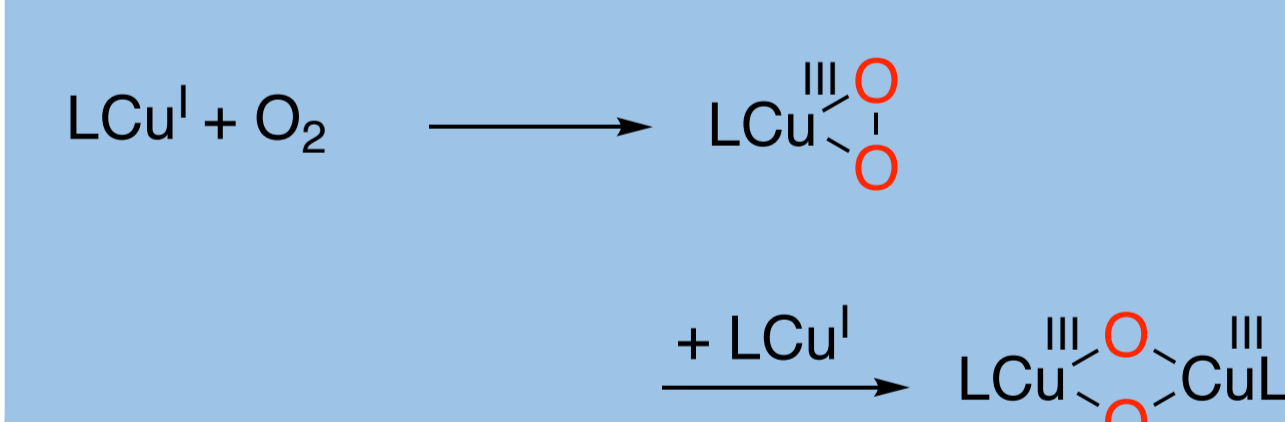


## UV/Vis



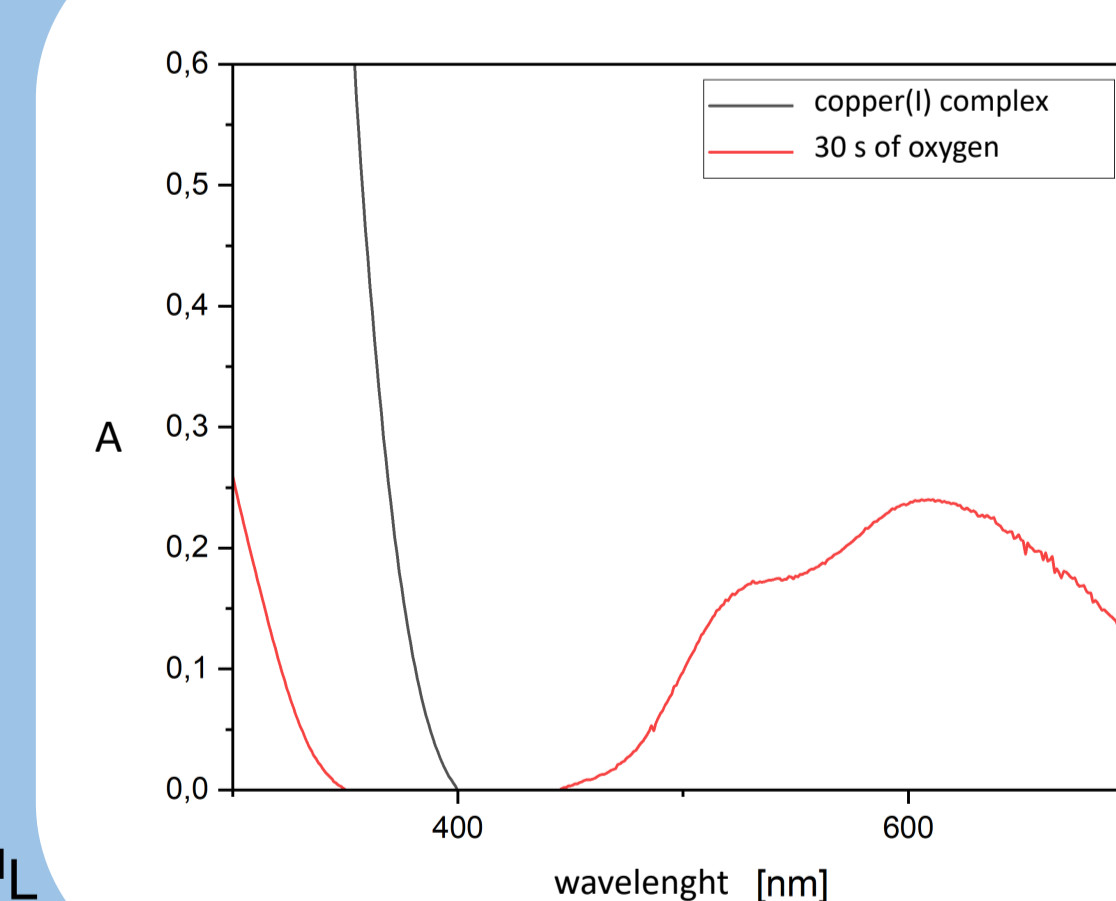
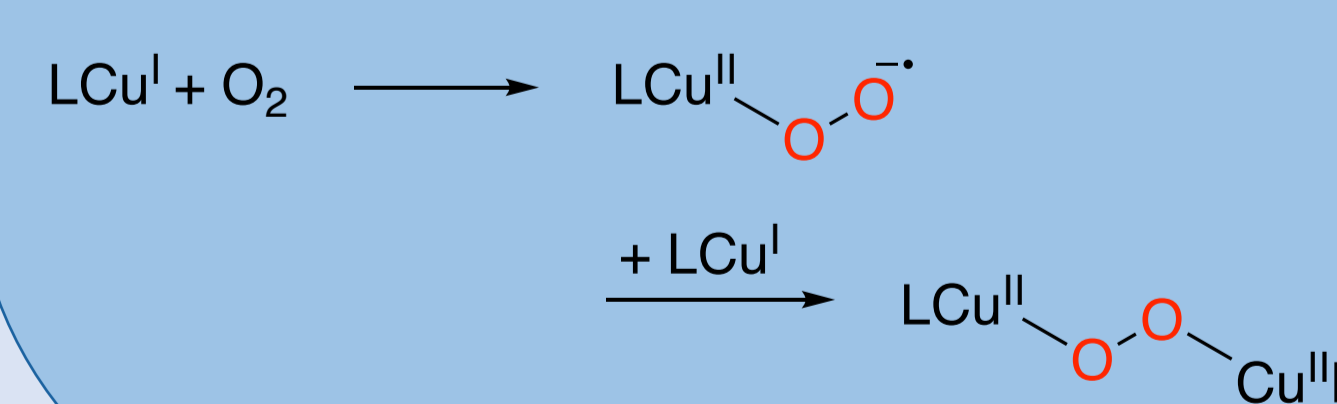
Ligands L2, L7 + O<sub>2</sub>:

- band at 389 nm
- bis (μ-oxo)dicopper(III) complex



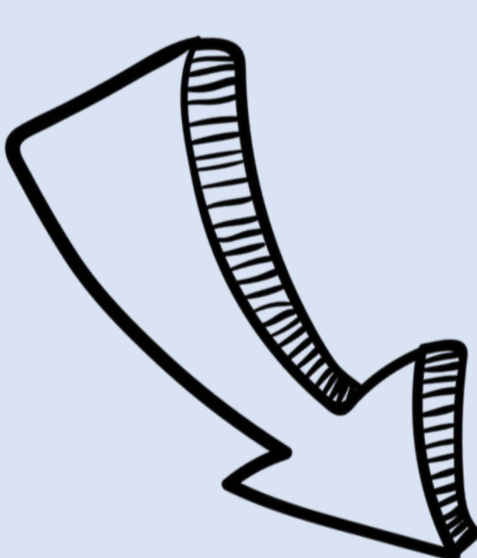
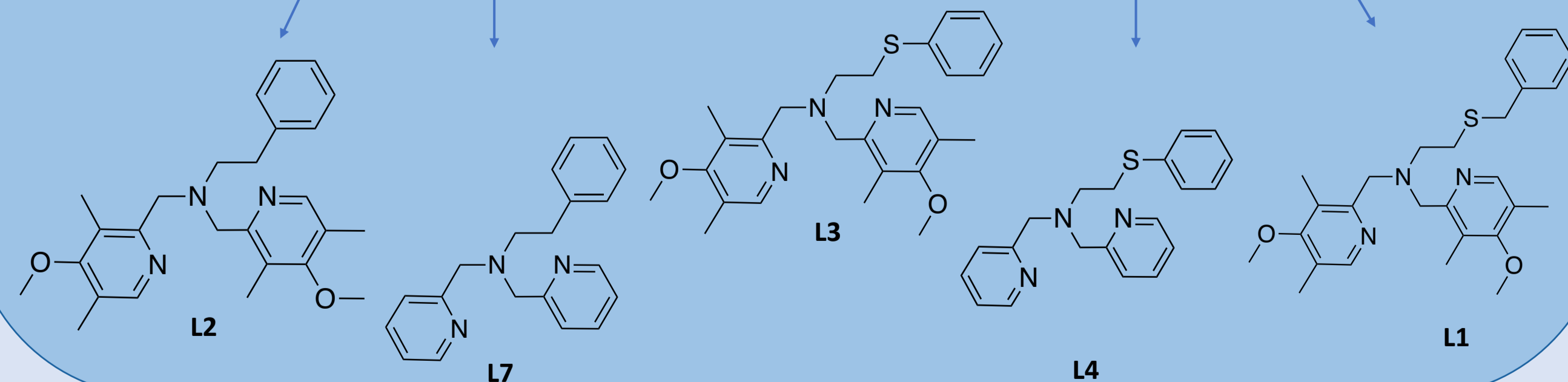
Ligands L1, L4 + O<sub>2</sub>:

- band at 525 nm and 600 nm ←
- trans-1,2 peroxodicopper(II) complex ←

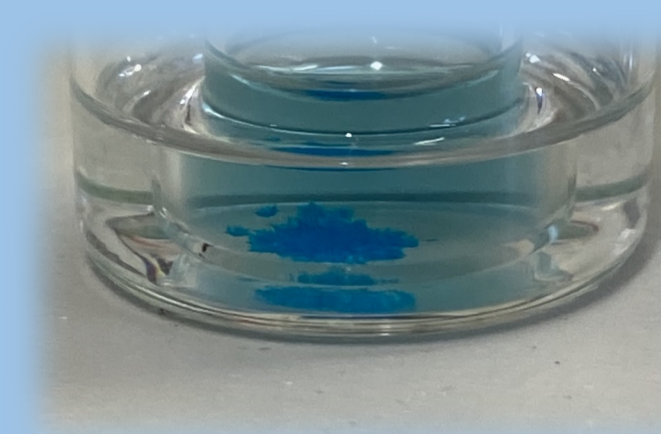


## Summary

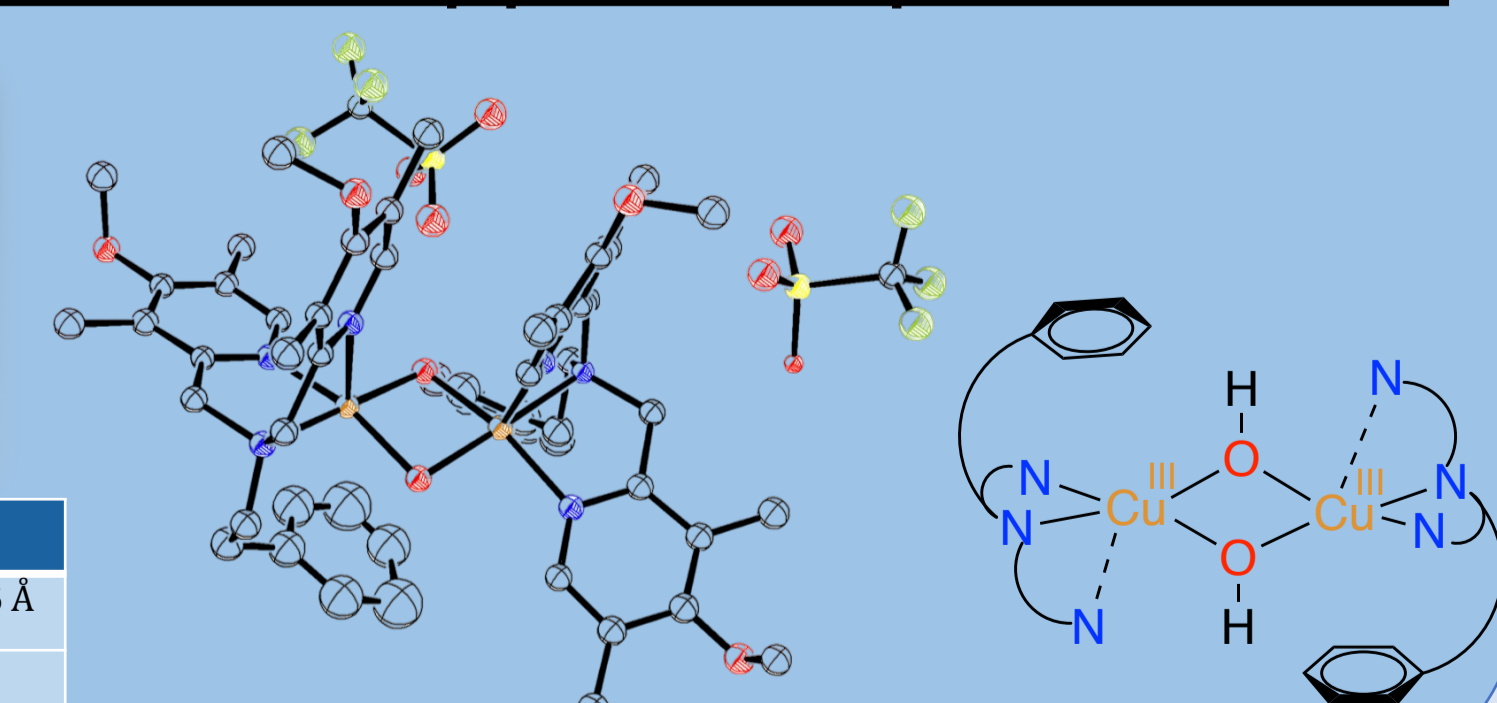
The tripodal ligands (L2, L7) form bis (μ-oxo)dicopper complexes as predicted from literature<sup>[4]</sup>. Two of the tetrapodal ligand system (L1, L4) show trans-1,2 peroxodicopper complexes. The ligand L3 (tetrapodal ligand) is able to form both copper complexes.



## Crystal structure of a copper complex with L2



	crystal	hydroxo <sup>[6]</sup>	oxo <sup>[6-7]</sup>
Cu-O	1.939 Å	1.942 Å	1.79 – 1.86 Å
Angle	82.7°	81.7°	80.2°



## References:

- [1] E. Roduner, W. Kaim, B. Sarkar, V. B. Urlacher, J. Pleiss, R. Gläser, W.-D. Einicke, G. A. Sprenger, U. Beifuß, E. Klemm, C. Liebner, H. Hieronymus, S.-F. Hsu, B. Plietker, S. Laschat, *ChemCatChem* **2013**, *5*, 82–112. [2] M. Rolff, F. Tuczek, *Angew. Chem. Int. Ed.* **2008**, *47*, 2344–2347. [3] C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem.* **2006**, *118*, 3951–3954. [4] V. Gómez-Vidales, I. Castillo, *Euro. J. Inorg. Chem.* **2022**, 2022, e202100728. [5] S. Kim, J. W. Ginsbach, A. I. Billah, M. A. Siegler, C. D. Moore, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2014**, *136*, 8063–80. [6] H. Hayashi, S. Fujinami, S. Nagatomo, S. Ogo, M. Suzuki, A. Uehara, Y. Watanabe, T. Kitagawa, *J. Am. Chem. Soc.* **2000**, *122*, 2124–2125. [7] L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013–1046.

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