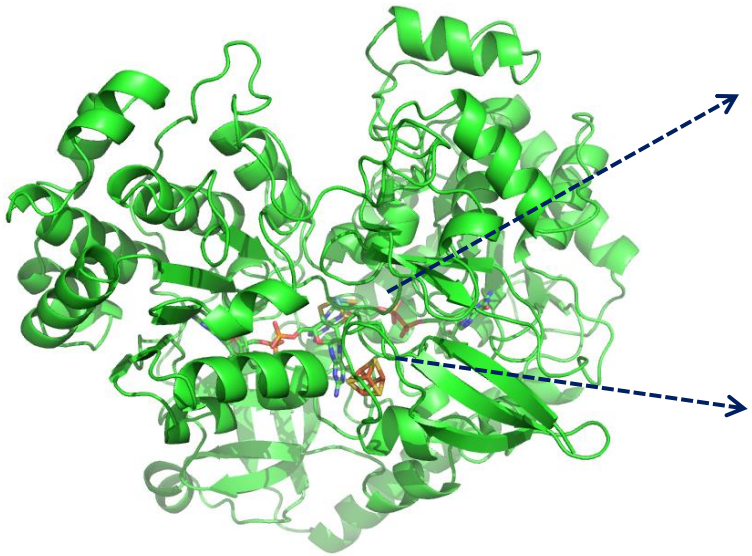
Dithiolene Containing Peptides: Synthesis and Characterization of their Molybdenum Complexes

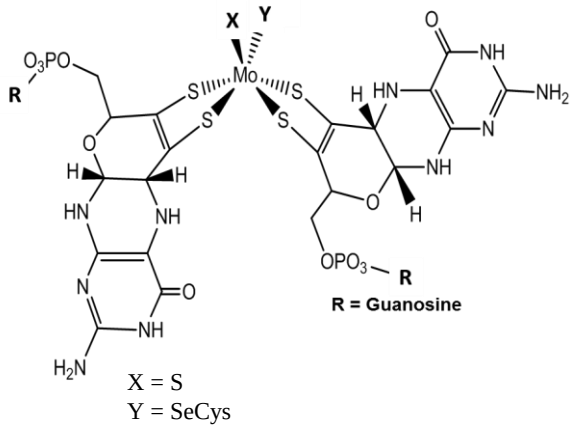
Soniya AHAMMAD , Emmanuel OHEIX , Renaud HARDRE , Bruno GUIGLIARELLI , Maylis ORIO , Olga IRANZO

Aix Marseille Univ, CNRS, Cent Marseille, iSm2, 13013 Marseille, France, Aix Marseille Univ, CNRS, BIP, Marseille, France

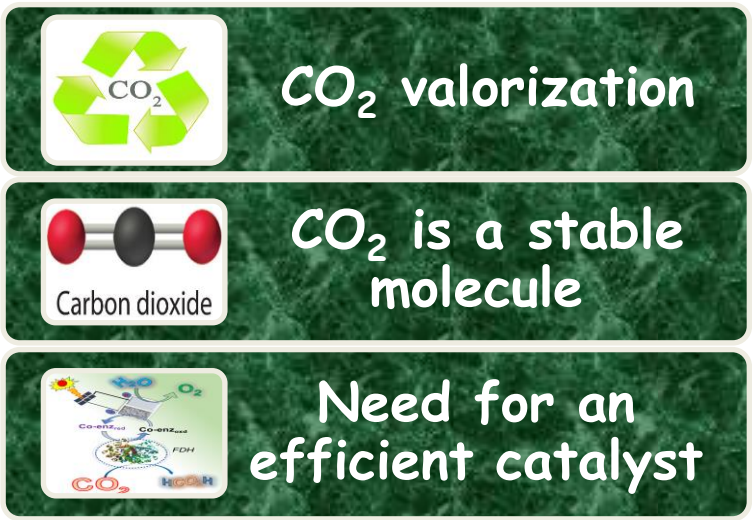
* soniyaahammad.3010@gmail.com



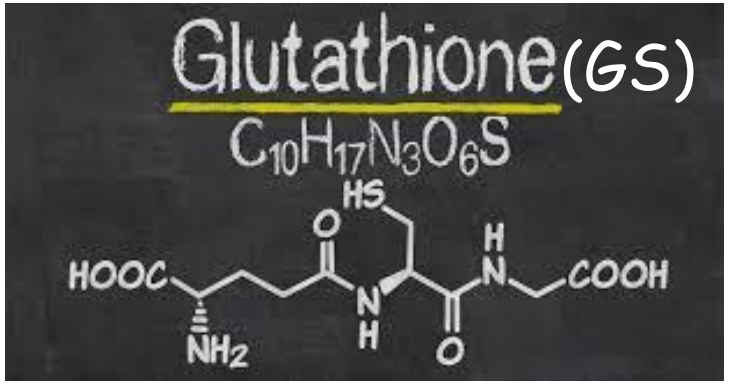
FDH, *E. coli*, PDB



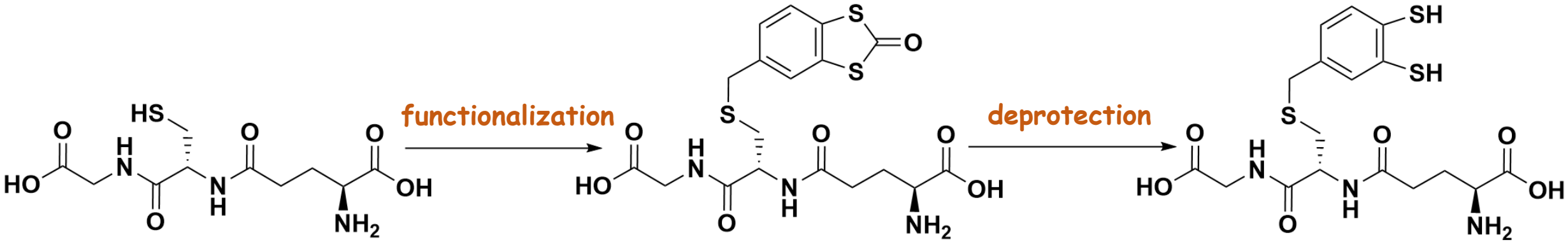
$$HCOOH \rightleftharpoons CO_2 + 2e^- + 2H^+$$



Synthesis of Dithiolene Containing Peptides



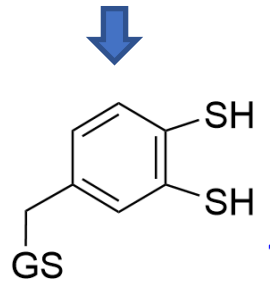
Functionalization of Glutathione



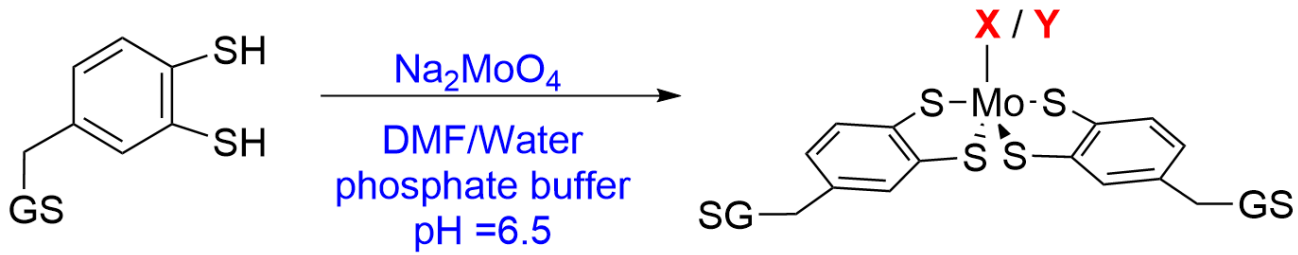
GStdt

Purified by HPLC-preparative

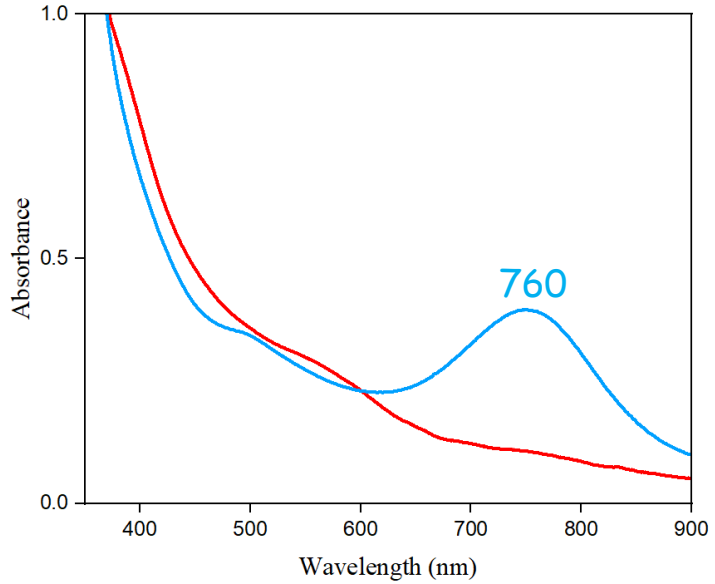
Characterized by NMR, mass spectrometry, HPLC-analytical



Synthesis and Characterization of Mo Complex of Functionalized Glutathione



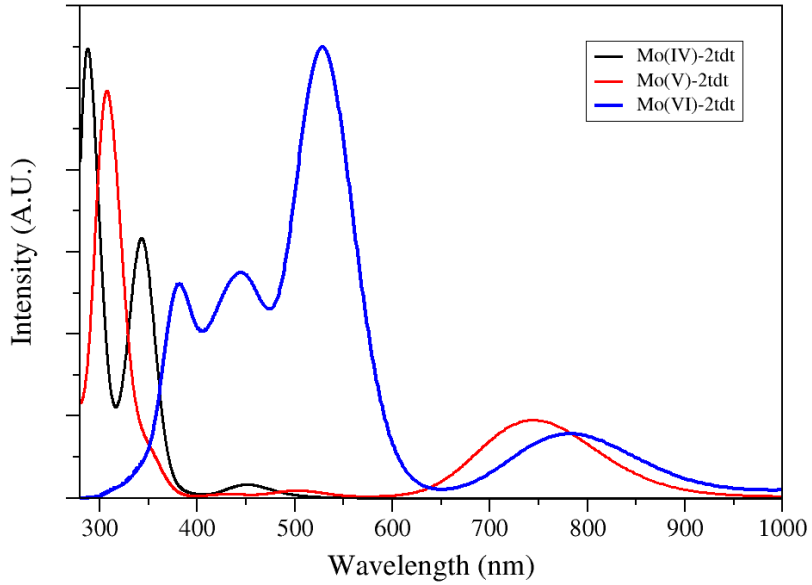
UV of Mo-GStdt obtained after experiment

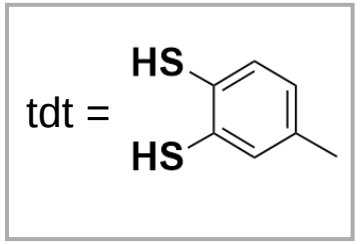


Before addition of Na_2MoO_4

After addition of Na_2MoO_4

DFT-predicted UV-vis spectra of Mo-GStdt models

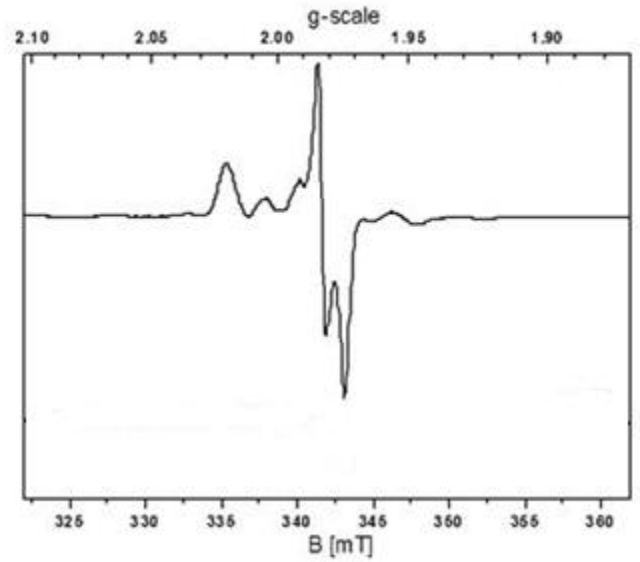




ORCA

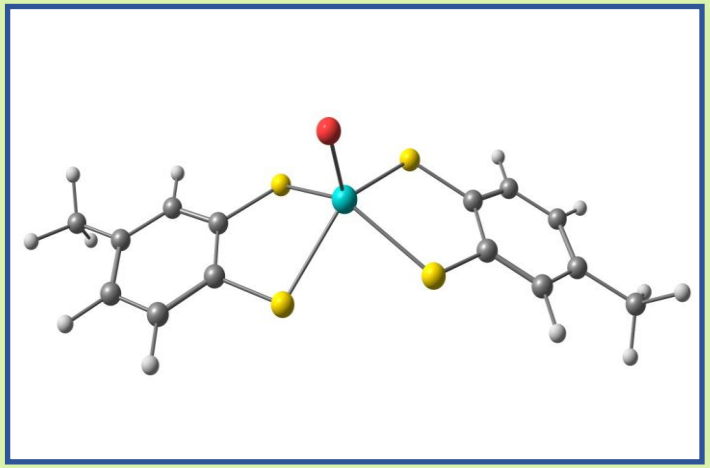
B3LYP
TZV-ZORA

Characterization of Mo Complex of Functionalized Glutathione



EPR spectra for Mo-GStdt recorded in DMF:water

Theoretically proposed structure for Mo complex



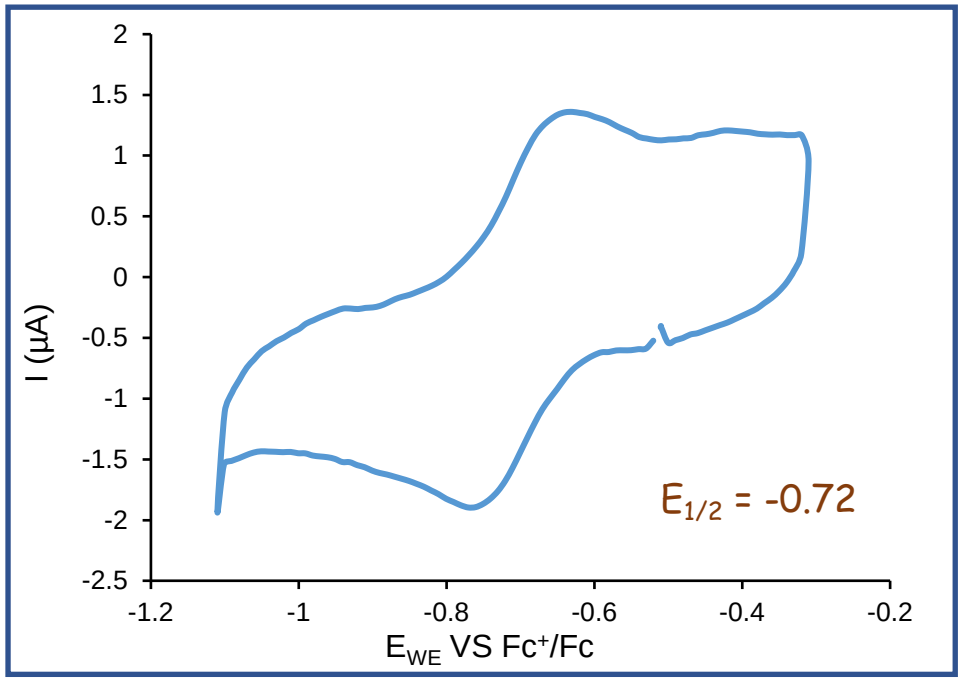
DFT structure of the $Mo^{V}O(tdt)_2$ complex

B3LYP
def2-TZVP ZORA

	g_{min}	g_{mid}	g_{max}	$g_{max}-g_{mid}$	g_{iso}
Expt.	1.974	1.982	2.020	0.046	1.992
Calc.	1.977	1.988	2.024	0.047	1.997

Characterization of Mo Complex of Functionalized Glutathione

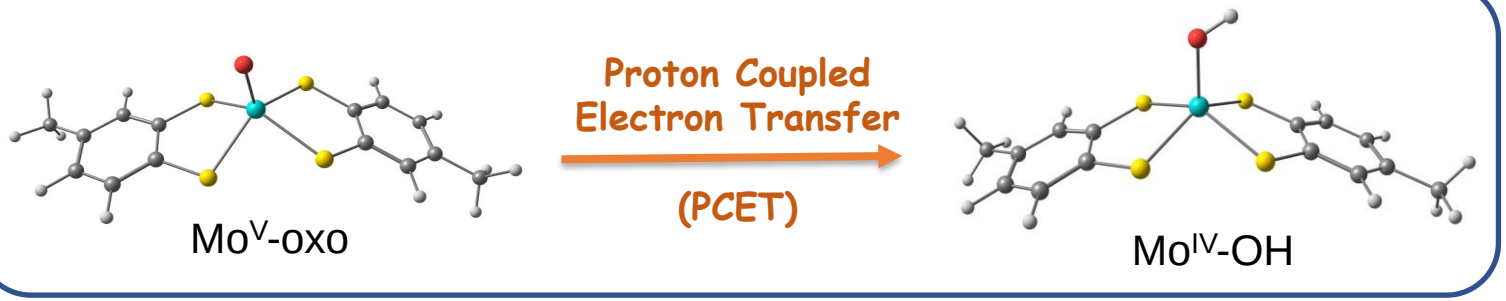
CV of $Mo^{V}O(GStdt)_2$



Cyclic voltammograms of 1 mM $Mo^{V}O$(**GStdt**)$_2$ stationary glassy carbon electrode in NBu_4NPF_6, phosphate buffer, DMF/water. Scan rates 100 mV/s.

Theoretically Proposed Mo-complex redox process

BP86
TZV-ZORA



Expt = -0.72 eV
Theoretical = -0.99 eV

Conclusion

- A dithiolene containing peptide was prepared
- Metal coordination was performed and the resulting Mo complex was characterized
- UV-Vis and EPR studies: $Mo^{V}O(GStdt)_2$
- CV : Redox Cycling between Mo(V) and Mo(IV)

Perspectives

- Fully characterize the system
- Evaluate complex capability to mediate CO_2 reduction

Acknowledgements

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