Fluoro-2,6-Dimethyphenyl Mono-Hydroxychlorin and Porphyrin Congeners

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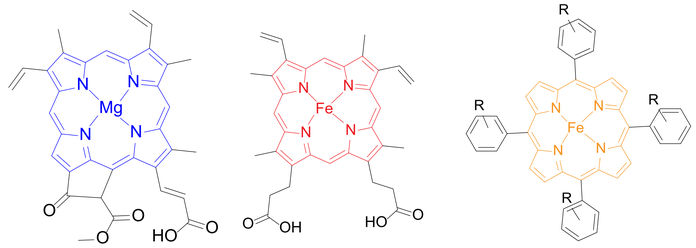
Introduction

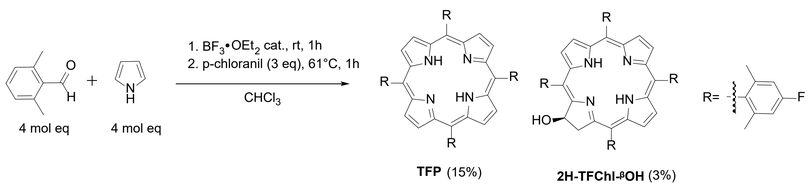
Porphyrins are an Essential Class of Molecules

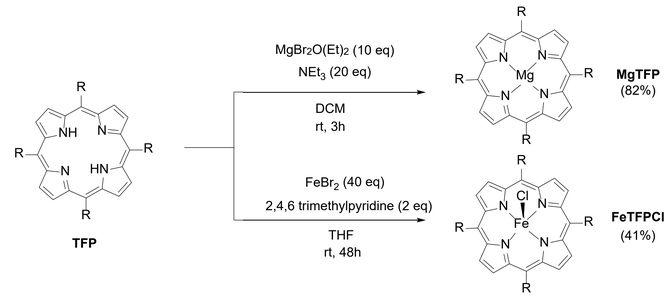


Chlorophyll C | *Fe(II)-protoporphyrin IX (Heme)* | *Small Molecule Catalyst (E.g., CO_2, O_2)*[1]

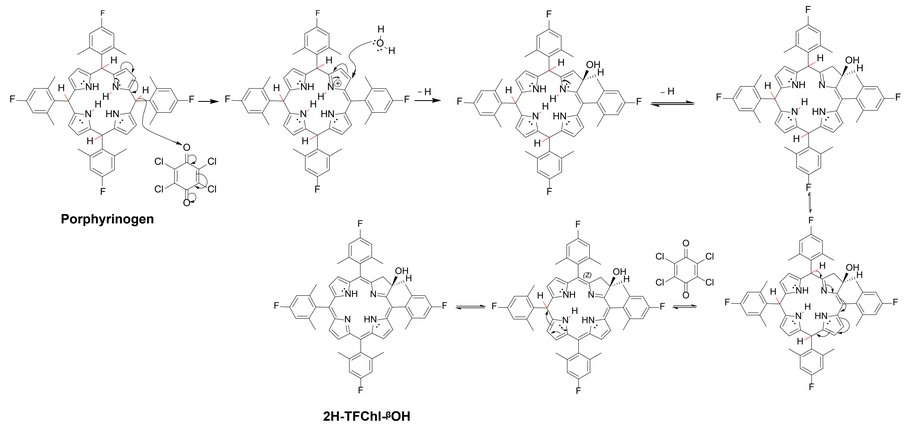
- **Porphyrins are integral to both plant and animal life**
- **Porphyrins have numerous applications in catalysis and solar cells[1,2]**
- **To gain more understanding and leverage porphyrins in catalysis, energy creation and other disciplines, we must continue to characterize these molecules**

Synthesis

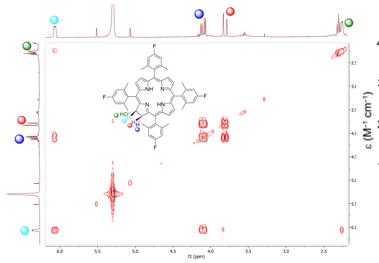




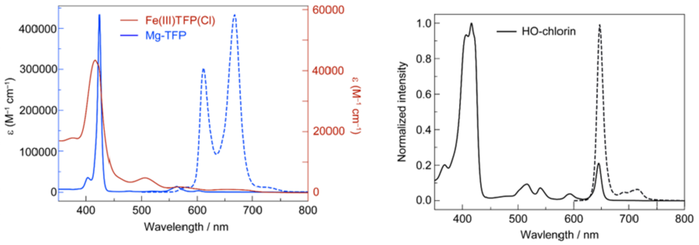
Possible* 2H-TFChl-βOH *Mechanism:



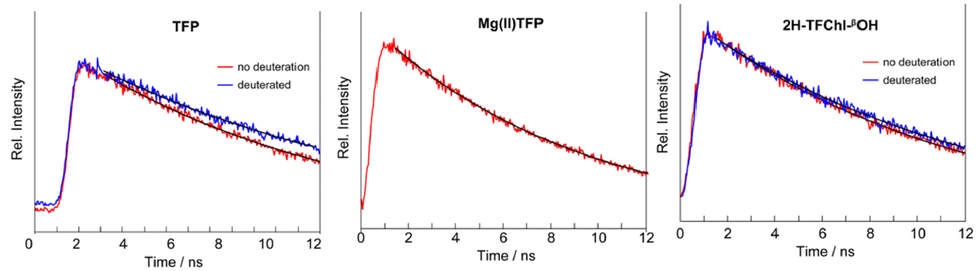
Characterization of Mono-Hydroxychlorin



^{1}H-^{1}H COESY of 2H-TFChl-βOH

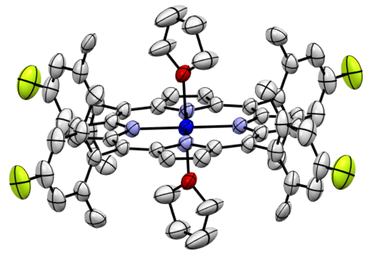


Electronic Spectra of Mg(II)TFP, Fe(III)TFP(Cl) and 2H-TFChl-βOH

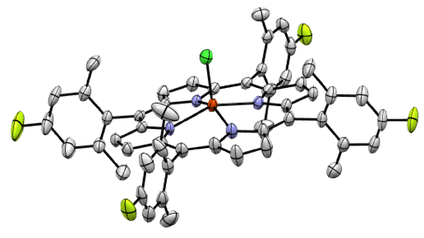


Time-Resolved Emission Decay Traces of TFP, Mg(II)TFP and 2H-TFChl-βOH

Characterization of Mg(II)TFP and Fe(III)TFP(Cl)



Mg(II)TFP Crystal Structure



Fe(III)TFP(Cl) Crystal Structure

Observed Mass	820.30	852.25
19F NMR	-117.16 ppm, triplet	-113.89 ppm, singlet
Spin State	-	High
Geometry	Octahedral	Square pyramidal
Absorption	Soret Band: 404 Q Bands: 426, 564, 603	Soret Band: 417 Q Bands: 506, 585
Emission	Excitation: 573 nm Emission: 621-678 nm	Excitation: 508 nm Emission: 550-800 nm
Mössbauer	-	Delta isomer shift: 0.35 mm/s Quadrupole splitting: 0.77 mm/s
EPR	-	G=4,6

***Structures also validated through ^{1}H and ^{13}C NMR, CV and IR**

Discussion & Future Steps

- In this study, Mg(II)TFP and Fe(III)TFP(Cl) were synthesized in excellent yield and were stable as long as kept away from strong acid
- Mg(II)TFP and Fe(III)TFP(Cl) were extensively characterized and crystal structures were obtained for each compound.
- Mono-hydroxychlorin, a relatively rare compound, was also synthesized in the TFP-forming reaction, avoiding the use of harsh reagents such as OsO_4 while still achieving similar known yields
- Mono-hydroxychlorin showed similar excited state electronic effects to the parent porphyrin, suggesting mono-hydroxychlorins could exhibit similar physicochemical activity
- This work warrants further study on whether mono-hydroxychlorins can be leveraged in catalysis in a similar manner to known chlorin compounds
- Porphyrins with unique metal centers should be studied to determine any electronic deviations from Mg(II)TFP and Fe(III)TFP(Cl)

References

1. **Dalton Trans.**, 2019, **48** ,5869-5878
2. **J. Mater. Chem. A**, 2023, **11**, 12659-12680

Brown et al. (in press) Fluoro-2-6-dimethylphenyl mono-hydroxychlorin and porphyrin congeners, *J. Porph. Phthalocyanines* (2023)

Acknowledgments

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