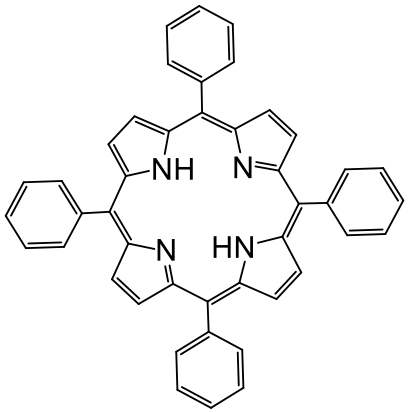
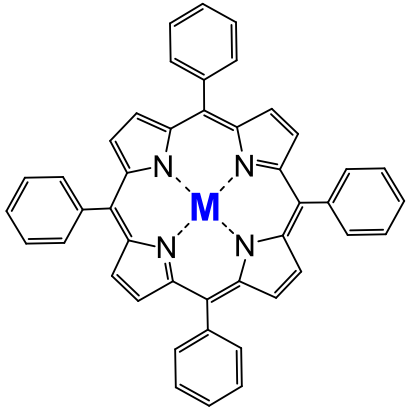
Synthesis of Tetraphenylporphyrin and its Copper(II) complexes

BACKGROUND KNOWLEDGE

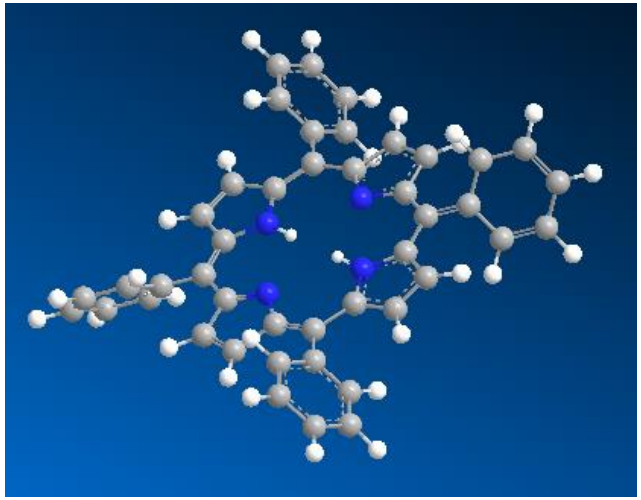
- Porphyrin systems contain 18 pi electrons, thus meeting the Hückel (4n+2) rule.
- ^{1}H NMR chemical shift data provide important physical evidence for delocalized electrons in aromatic systems.



$TPPH_2$



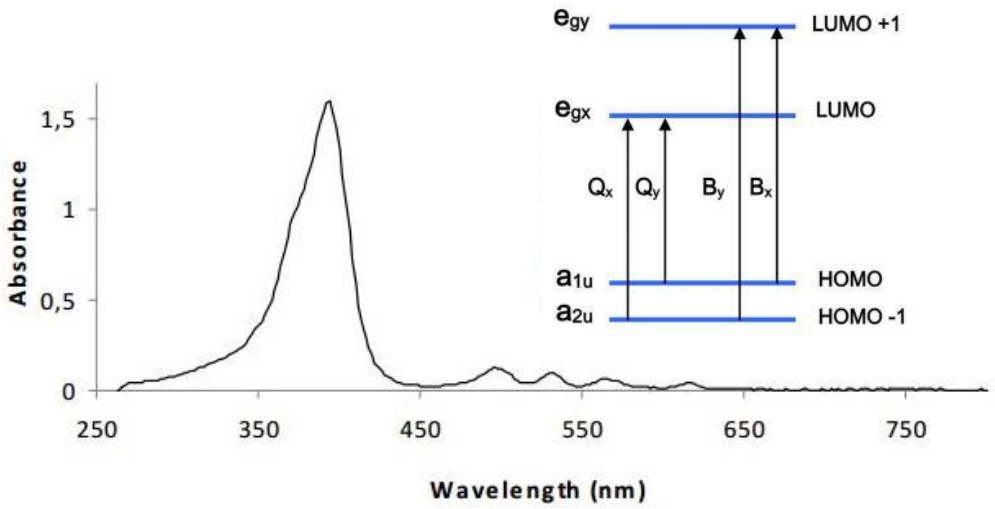
metallated tetraphenylporphyrin



3-D structure of $TPPH_2$

BACKGROUND KNOWLEDGE

- Hypsoporphyrins : metalloporphyrins (d^m, m = 6-9, having filled dπ orbitals.)
- Metal d π to porphyrin π * orbital interaction (metal to ligand π -backbonding).
- This results in an increased porphyrin π to π * energy separation causing the electronic absorptions to undergo hypsochromic (blue) shifts.



Tetraphenylporphyrin(TPPH2)

PROCESS OF EXPERIMENT 2

Synthesis : $TPPH_2$, CuTPP

↓

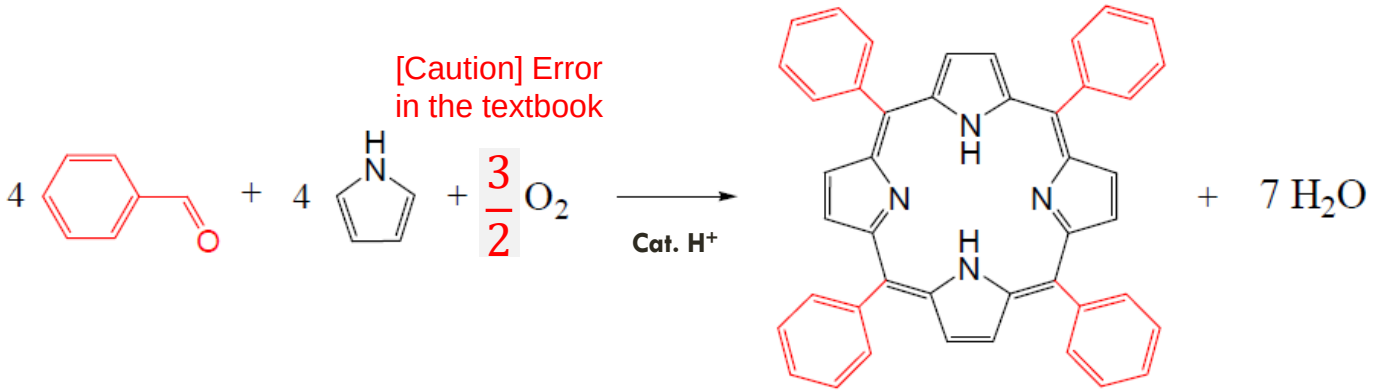
Purification : Recrystallization

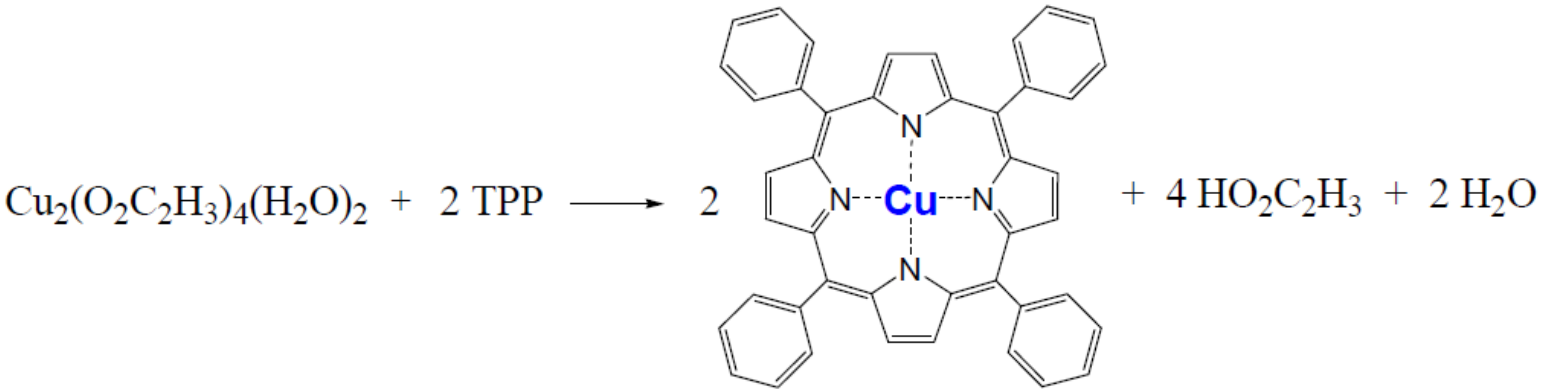
↓

Characterization : NMR, TLC, UV

SYNTHESIS OF TETRAPHENYLPORPHYRIN(TPP) COPPER(II) COMPLEX

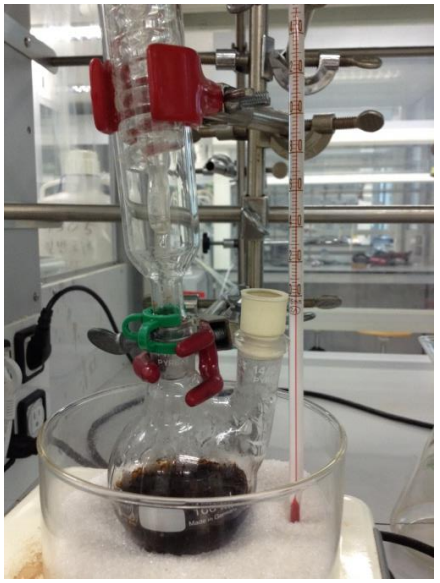
[Caution] Error in the textbook





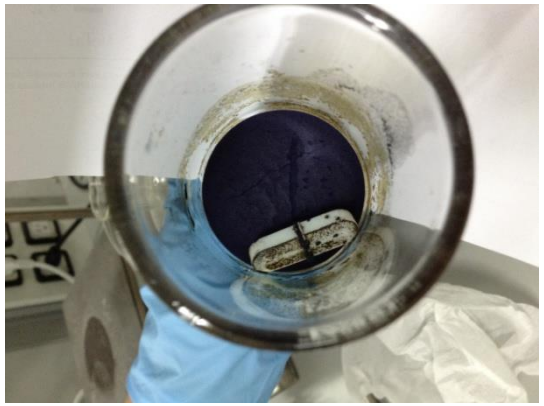
1. SYNTHESIS OF $TPPH_2$

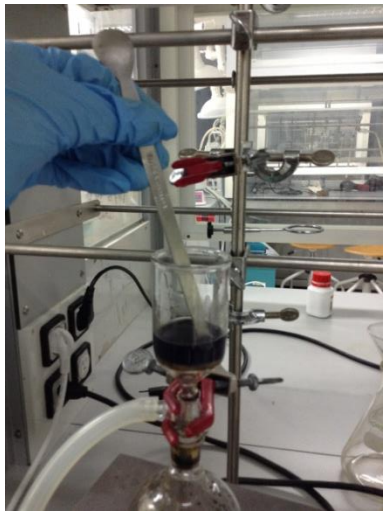
1. Place a 100mL round bottom flask, add boiling chips and fix the flask with a reflux condenser.
2. 2. Heat Propionic acid (20mL) briefly to reflux.
3. Temporarily remove the heat, add a solution of benzaldehyde (1.65mL, 15.75mmol) and pyrrole (1.00mL, 15.0 mmol) in 5 mL of propionic acid and heat again.



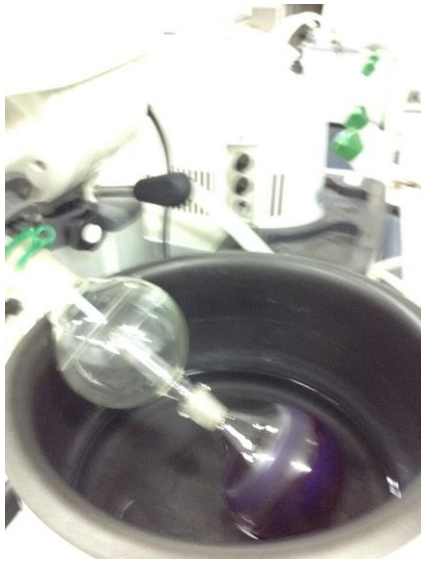
1. SYNTHESIS OF $TPPH_2$

4. After 30min of reflux, remove the flask from the heat and cool to room temperature.
5. Filtered the dark brown mixture and wash the crude product with ethanol (20mL X 3) to remove the tarry impurity.
   (***Caution!*** Filtering must be carried out inside the fume hood.)
6. Extract with hot CH_2Cl_2 (30mL + 20mL),
   (Note: Heat the CH_2Cl_2 in a hood using a large beaker and a hot plate.)





1. SYNTHESIS OF $TPPH_2$



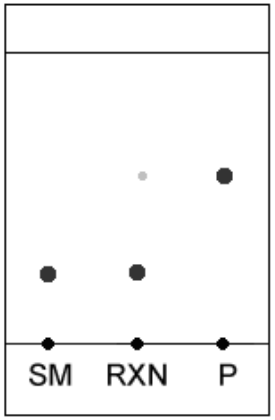
7. Transfer the filtrate to a 100mL round bottom flask, dilute with 30mL of methanol and condense to ~ 25mL on a rotary evaporator. Look for the presence of a crystalline product in the dark solution with a flashlight.

8. Filter the slurry using a medium 100mL glass frit, rinse with methanol and dry the product.

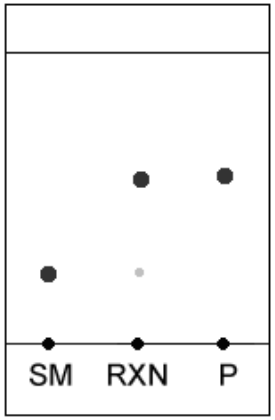
9. Record the yield, weigh some for transfer into a NMR tube, and bottle the rest. Label the bottle with the contents, your name, and the date.

1. SYNTHESIS OF $TPPH_2$

10. Determine the purity of the product by spotting a small amount of a concentrated toluene solution of your product on the analytical TLC plates provided by your TA. Use a small vial for dissolving your compound. Use a capillary tube for spotting it. TLC chambers (screw-capped jars) will also be available. Elute with toluene.



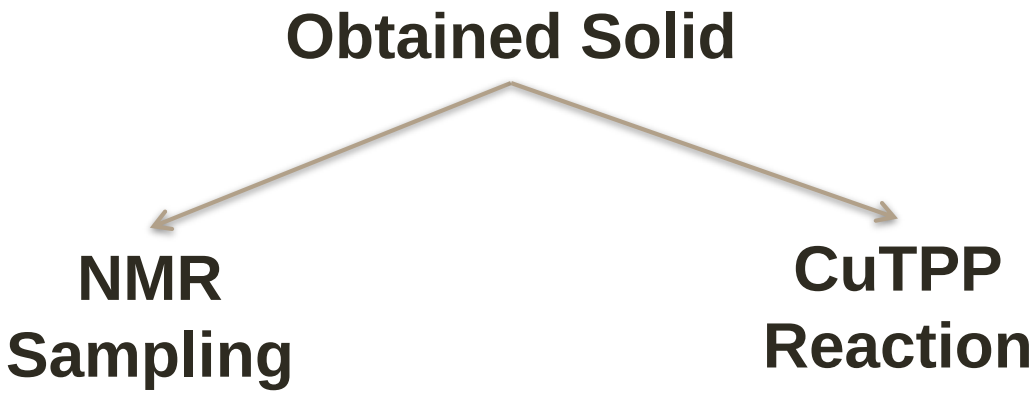
reaction just started;
little product has formed



reaction is done;
S.M. has been consumed

Observe the emission using **356 nm** UV radiation

1. SYNTHESIS OF $TPPH_2$



11. Submit your product sample for the ^1H NMR spectroscopic measurement. NMR spectrum will be measured using a Bruker AM-300 spectrometer. (By TA)

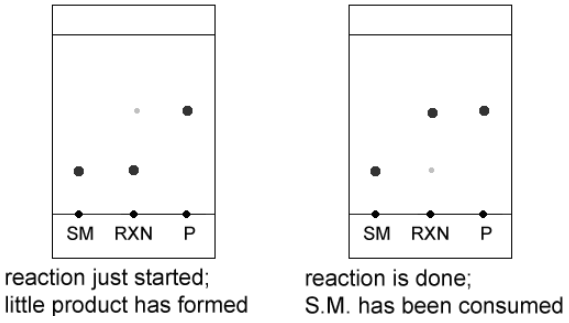
2. SYNTHESIS OF CUTPP

1. Bring 75mL dimethyl formamide (DMF) to a gentle reflux in a 100mL round bottom flask equipped with a reflux condenser and stir magnetically.

2. Add $TPPH_2$ (100-200mg) and allow to dissolve (several minutes), then add 1.2 equivalent of cupric acetate, $Cu(OAc)_2$-H_2O. Allow the reaction to proceed for 30min.

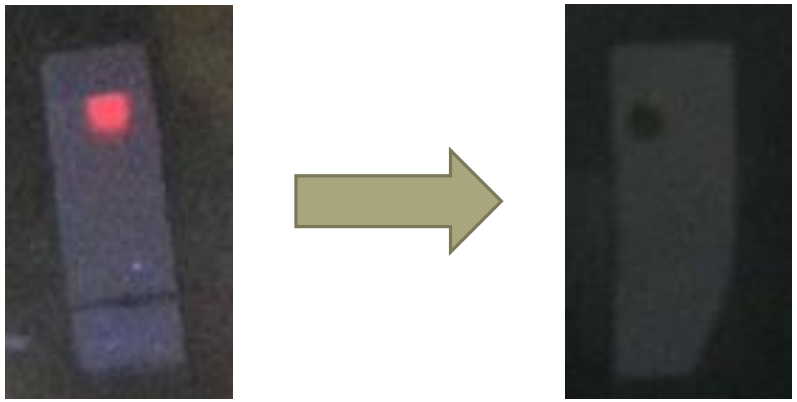
2. SYNTHESIS OF CUTPP

3. Spot some of the solution on a TLC plate using a Pasteur pipette, and examine the plate under a UV light (356nm). No fluorescence means that conversion to the copper complex is complete. If the conversion is not complete, add an additional small amount of cupric acetate.



reaction just started; little product has formed

reaction is done; S.M. has been consumed



$TPPH_2$ CuTPP

2. SYNTHESIS OF CUTPP

4. Allow the reaction mixture to cool in an ice water bath for 10-15min.
5. After the reaction mixture has cooled, add 75mL of distilled water to precipitate the porphyrinic material. Cool the solution again.
6. Filter the solution through 5 cm of alumina on the 100mL glass frit. Wash the solid with distilled water and small amount of cold methanol.

2. SYNTHESIS OF CUTPP

7. Filter the insoluble solid on the alumina was extracted with CH_2Cl_2.

8. Dry all the solvents using rotary evaporator. Weigh the solid and record its weight.

9. Submit your product to TA. TA will obtain the visible spectrum of a very dilute toluene solution of the purified CuTPP product (the molar absorption coefficient in benzene is reported to be 20,600 A.U. at 538nm).