

# Preparation and Characterization of High Purity Cobalt (III) Tetrasulfonatophenyl Porphyrin Chloride

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## Introduction

Porphyrin aggregates are commonly found in nature where they are involved in oxygen transportation in the human body and light-harvesting in photosynthesis. Synthetic porphyrin aggregates are of interest because they have applications as catalysts for fuel cells, chemical nanosensors, and anti-cancer agents.

The objective of this project was to first synthesize, isolate, and characterize pure cobalt (III) meso-tetra(4-sulfonatophenyl) porphyrin chloride, CoTSPP, and then to study its aggregation by scanning probe microscopy (atomic force microscopy, AFM, and scanning tunneling microscopy, STM).

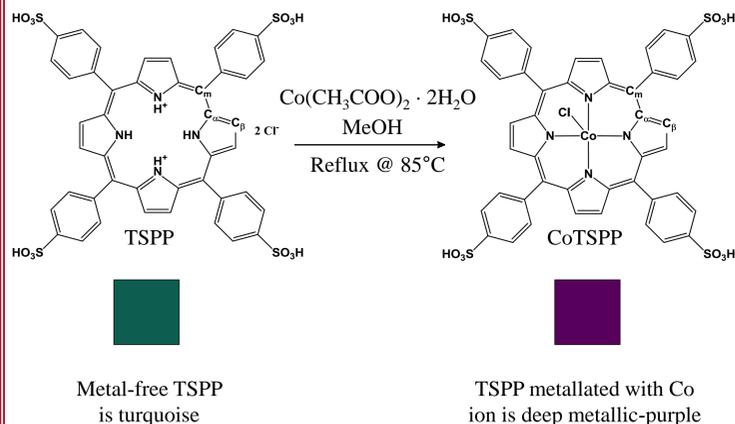
CoTSPP was successfully synthesized by using a modified literature method<sup>1</sup> involving the metallation of the free-base meso-tetra(4-sulfonatophenyl) porphyrin, TSPP. Purification of the final product was achieved by using column chromatography. Solution UV-vis spectrum of CoTSPP and its infrared spectrum in a KBr matrix compared favorably with the electronic and vibrational spectra of the compound previously reported. The aggregation studies of CoTSPP are currently on their way.

## Synthesis of CoTSPP

**Materials.**  $H_4[H_4TSPP]Cl_2$  (TSPP) was used as supplied by Porphyrin Products. Cobalt (II) acetate was purchased from Aldrich. All solvents used were reagent grade and the water was Millipore filtered.

**Synthesis 1.** In this synthesis a 1:1 ratio of TSPP to  $Co(CH_3COO)_2$  was employed. Accordingly, 201.6 mg of TSPP and 49.5 mg of cobalt (II) acetate were placed in a 100 mL round bottom flask and 30 mL of fresh methanol was added. The flask was outfitted with a reflux condenser and heating mantle. A few glass beads were added to the flask. The reaction mixture was refluxed for 2 hours at 85 °C. The product was concentrated using a rotary evaporator and precipitated with acetone as a reddish-orange solid. The final product was isolated using purification method number one described in the next section. The final yield of CoTSPP was 14.3 mg, 32.4%.

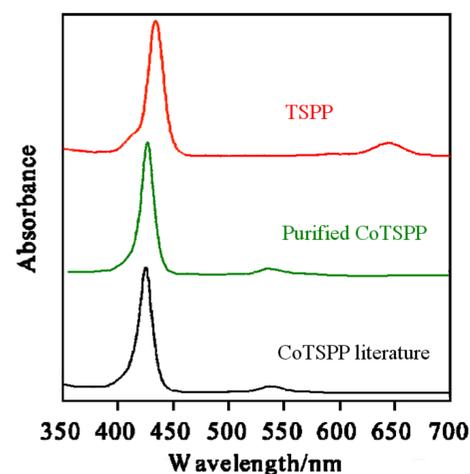
**Synthesis 2.** In this procedure a 1:10 ratio of TSPP to  $Co(CH_3COO)_2$  was used. The reaction proceeded according to the steps outlined in Synthesis 1. The final product was isolated using purification method number two described in the next section. The final yield of CoTSPP was 41.3 mg, 20.1%.



## Compound Purification

Two purification methods were employed in isolating pure CoTSPP. In the 1<sup>st</sup> purification procedure neutral alumina was used as the sorbent and water was used for eluting the sample. This column worked well for separating the impurities from the crude material but the desired compound adhered to the stationary phase. It was readily removed from the resin with 50/50 methanol/millipore water mixed with dilute HCl. CoTSPP was precipitated as a red-wine colored solid with acetone, filtered, washed with additional acetone, and dried.

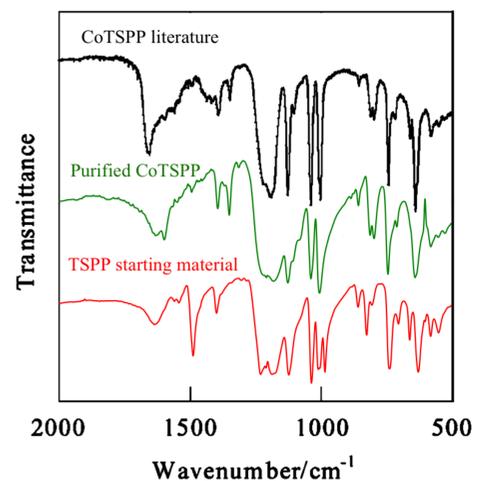
In the second purification method, a Dowex 50W-X8 cation exchange column was used as the stationary phase. Water was used as the eluting solvent. Two distinct red wine colored fractions were eluted. Both fractions were concentrated using a rotary evaporator and solid materials were precipitated with acetone. The precipitate obtained from the first eluted fraction was a deep metallic-purple solid that proved to be the desired product.



**Table 1:** UV-visible electronic transition in nm and assignments of TSPP and CoTSPP solution spectra in water.

TSPP	CoTSPP	Assignment
433.3 (s)	424.5 (s)	Soret band
545.2 (vw)	537.6 (w)	Q band
595.7 (vw)	---	Q band
646.2 (w)	---	Q band

**Figure 1:** Solution UV-visible spectra of the TSPP starting material, CoTSPP synthesized in work, and CoTSPP synthesized previously.<sup>2</sup> All solutions were 13  $\mu$  M in water. The spectra were acquired using a Perkin-Elmer 330 Spectrophotometer.



**Table 2:** IR vibrational band positions in  $cm^{-1}$  and assignments of TSPP and CoTSPP in a KBr matrix

TSPP	CoTSPP	Assignment
1635 (w)	---	---
1541 (vw)	1597 (m)	Phenyl <sup>1</sup>
1487 (s)	1493 (vw)	N-H stretch <sup>5</sup>
1397 (w)	1393 (w)	$\nu(C_2C_5)^2$
---	1349 (w)	$\nu(C_2-N)^2$
1229 (s)	---	---
1185 (s)	1180 (s)	-SO <sub>3</sub> <sup>-</sup>
1122 (s)	1125 (s)	-SO <sub>3</sub> <sup>-</sup>
1035 (s)	1037 (s)	Phenyl <sup>1</sup>
1009 (s)	1004 (s)	$\nu(C_2-N)\nu(C_2C_5)^2$
984 (s)	---	$\delta(C_2-H)^2$
857 (w)	856 (w)	---
825 (m)	---	---
---	811 (m)	Pyr def <sup>2</sup>
---	796 (m)	---
737 (s)	743 (s)	Ph in-plane def <sup>2</sup>
703 (w)	709 (vw)	Ph in-plane def <sup>2</sup>
660 (m)	---	N-H stretch <sup>5</sup>
---	639 (s)	Ph in-plane def <sup>2</sup>
627 (s)	---	NH-HCP <sup>3</sup>
580 (w)	579 (m)	---
550 (w)	---	$\gamma$ (pyr fold) <sup>2</sup>
---	489 (m)	---

**Figure 2:** IR spectra of the TSPP starting material, CoTSPP synthesized in work, and CoTSPP synthesized previously.<sup>2</sup> Spectra were acquired in a KBr matrix using a Perkin-Elmer 1700 FT-IR.

## Results and Conclusions

CoTSPP was successfully synthesized using TSPP and a ten-fold excess of cobalt acetate. The Dowex cation exchange resin proved to be superior for purifying the compound without demetallation of the porphyrin. The insertion of the cobalt ion into the free-base porphyrin results in a clear color change: the TSPP starting material is turquoise while the cobalt substituted porphyrin is deep metallic-purple.

The UV-vis (Figure 1 and Table 1) and IR (Figure 2 and Table 2) spectra of the synthesized material compared favorably with the same spectra of CoTSPP reported in the literature. The electronic spectrum of the CoTSPP shows a clear shift of the Soret band as well as the Q-band to shorter wavelengths relative to the Soret and Q bands in the spectrum of the unmetallated porphyrin, Figure 1. The infrared spectrum of CoTSPP exhibits no band at 1487  $cm^{-1}$  compared to the same spectral region of the free-base porphyrin, Table 2. This is due to the loss of the N-H vibrations upon metallation of TSPP.

## Future Work

200 mg quantity of CoTSPP will be synthesized next using a 1:10 ratio of the porphyrin to cobalt acetate. Purification method using the Dowex exchange resin will be employed. The purity of the compound will be ascertained with spectroscopic methods (UV-vis, IR, and x-ray photoelectron spectroscopy, XPS). Elemental analysis will also be performed on the CoTSPP product.

We will study aggregation of the pure CoTSPP under varying conditions of pH, concentration, and ionic strength utilizing UV-vis spectroscopy. The porphyrin aggregates will be deposited on a graphite substrate and imaged by atomic force and scanning tunneling microscopy (AFM and STM) to investigate their nanostructure.

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