

Abstract

Tetraphenylporphyrin (TPP) is a macrocyclic molecule found in biological compounds. TPP's UV-Vis spectrum ranges from 380-500 nanometers. Metalloporphyrins (MeP) are considered “bioinspired oxidation catalysts” and are synthesized from TPP and metal anhydrous salts. Therefore, hypothesizing that the UV-Vis spectrum of the MeP will be altered by the type of benzaldehyde (electron-donating and electron-withdrawing groups attached to the benzene ring) which are added to the TPP ligand during the MeP synthesis reaction. In this project investigated solvent-free conditions, first with a silica gel support and then without it. The TPPs were produced in a Chemical Explorer Microwave (CEM) Reactor with a commercial 950W/1000W microwave oven. The conventional reflux method and an ultrasonic reactor were used to develop the MePs. TPPs were synthesized with substituted and unsubstituted benzaldehydes to investigate the effect of electron-donating and electron-withdrawing groups on the complex synthesis and the UV shift. The UV-Vis spectra for each MeP confirmed the formation of complexes with transition and p-block metals. The data displayed that the Tin MeP showed a red-shift UV-Vis spectrum (446 nm) compared to the initial TPP (417 nm). Complexation of Tin with the 4-chloroTPP displayed a maximum peak at 473 nm. This reaffirms that the electron-withdrawing benzaldehydes worked better than the electron-donating when added to the TPP. Thus, causing the UV-Vis spectra to have a red shift compared to the initial product.

Background

Tetraphenylporphyrin (TPP) is a macrocyclic molecule found in biological compounds, and is an essential cofactor for organismal carbohydrate and amino acid metabolism. Their distinctive ring structure is composed of conjugated double bonds which allow electrons to transfer charges and form complexes. The TPP UV-Vis spectrum frequently ranges from 380 to 500 nanometers, resembling solar radiation's biosphere emission spectrum. Thus, developing an instrument effective at converting radiation into chemical energy.

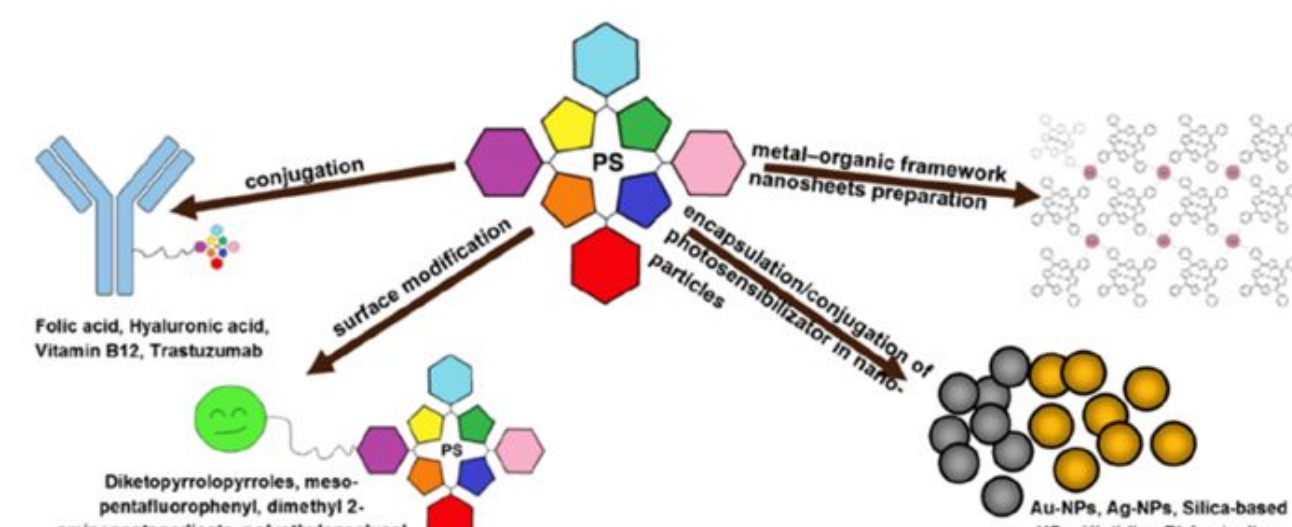


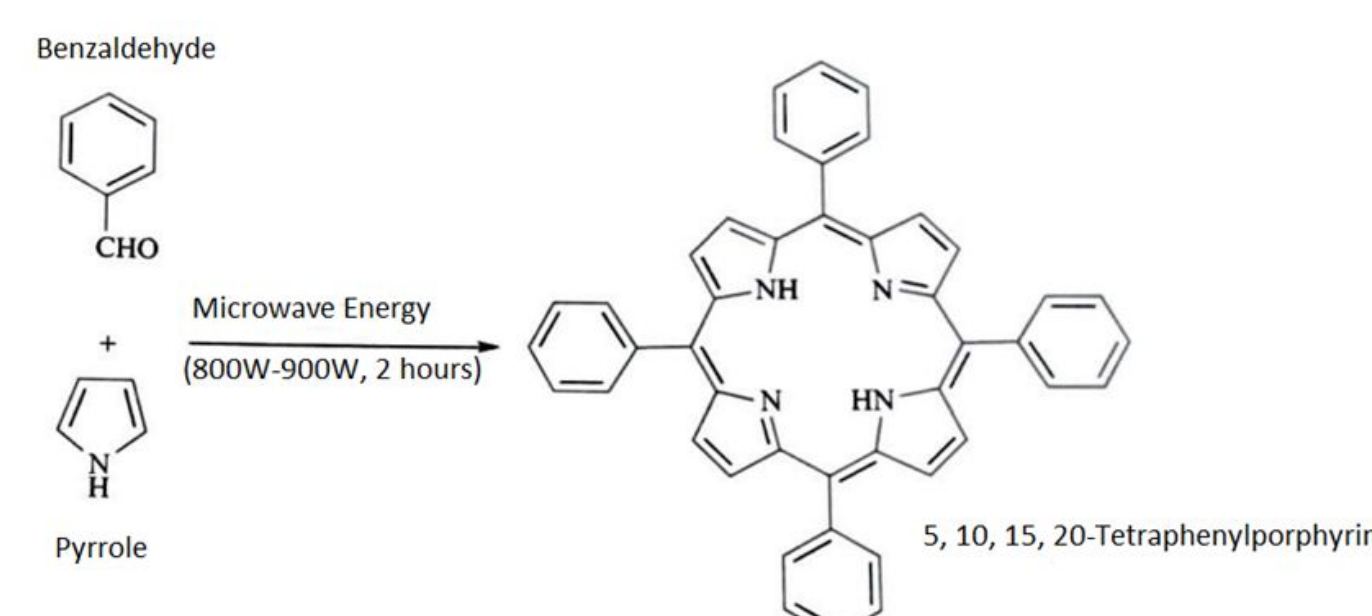
Figure 1. Applications of meso-tetraphenylporphyrins in biochemistry.¹

Metalloporphyrins (MeP) are considered “bioinspired oxidation catalysts” and are synthesized from TPP and metal anhydrous salts. MeP also serves as a contrast agent in diagnostic procedures like magnetic resonance imaging (MRI) by influencing the radiofrequency pulses detected by the MRI instrument.

Our hypothesis is that the UV-Vis spectrum of the MeP will be altered by the type of benzaldehyde (electron-donating and electron-withdrawing) added to the TPP ligand during the MeP synthesis reaction. The shift in the UV-Vis Spectrum may be a blue or a red shift.

Methods

The project investigated solvent-free conditions, first with a silica gel support and then without it. TPPs were synthesized, through 950-W microwave and Chemical Explorer Microwave (CEM) Reactor, with substituted and unsubstituted benzaldehydes to investigate the effect of electron-donating (4-methoxy and 4-methyl) and electron-withdrawing (2-chloro, 4-chloro, 4-bromo) groups on complex synthesis and UV shift. The maximum peaks of the TPP and Tin complexes were analyzed using the UV-1800 Shimadzu Spectrophotometer. To see where UV-Visible light will absorb at different wavelengths, such as the maximum peak of TPP at 417 nanometers.



Scheme 1. A simplified synthesis of 5, 10, 15, 20-Tetraphenylporphyrin.²

Results

The TPP ligand was complexed with several metal hydrates and anhydrous salts, including zinc chloride, nickel chloride, cupric chloride, ferric chloride, and Tin (II)/stannous chloride. The Stannous Chloride anhydrous salt was able to complex with the TPP ligand due to inserting the metal ions of 2+ charge with the two N-H protons of the meso-tetraphenylporphyrin. Also, the metal was stable enough to prevent the complex from photocatalytic degradation in visible light, as confirmed by the red shift shown on the UV-Vis spectra. As a result, the Stannous Chloride anhydrous salt complexed with the TPP ligand more effectively than the other metals (Figure 6).

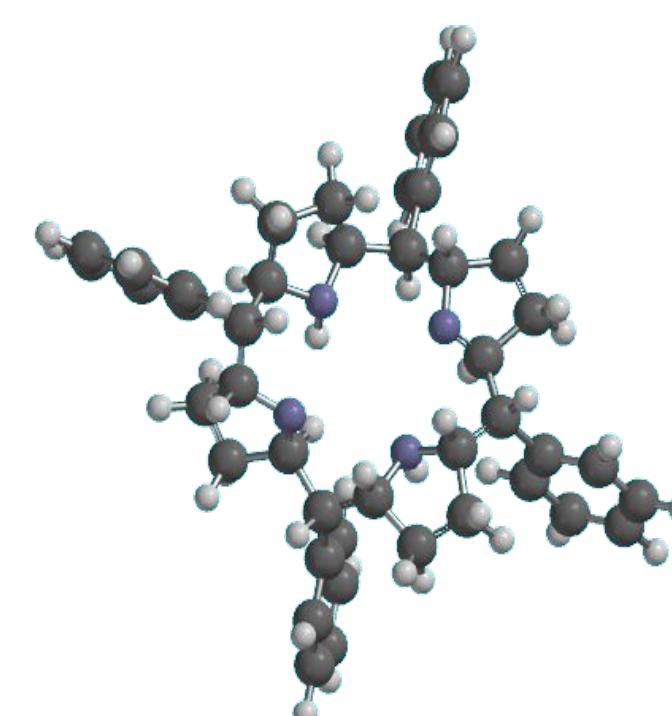


Figure 2. Spartan molecular modeling of 5, 10, 15, 20-tetraphenyl porphyrin (TPP).

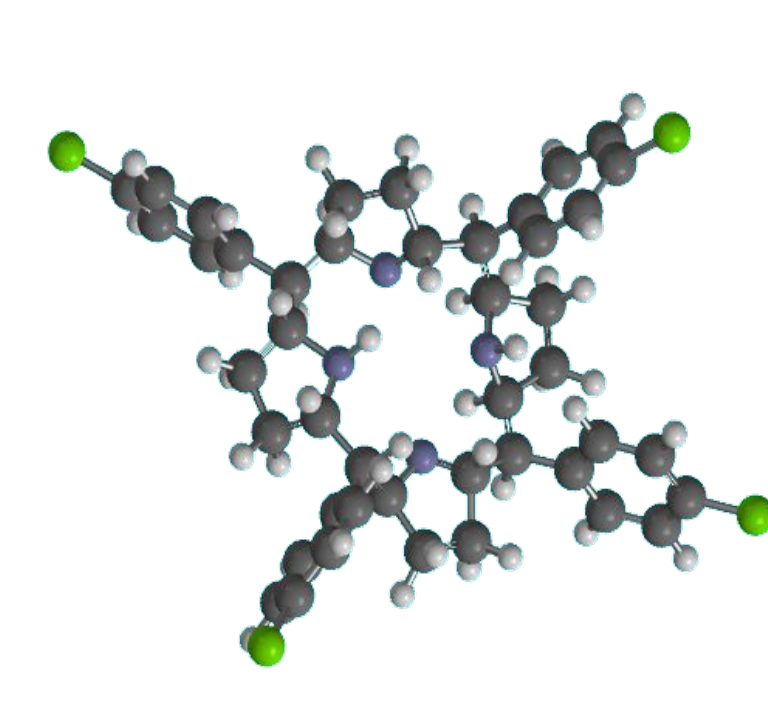


Figure 3. Spartan molecular modeling of 5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin or 4-chloro TPP.

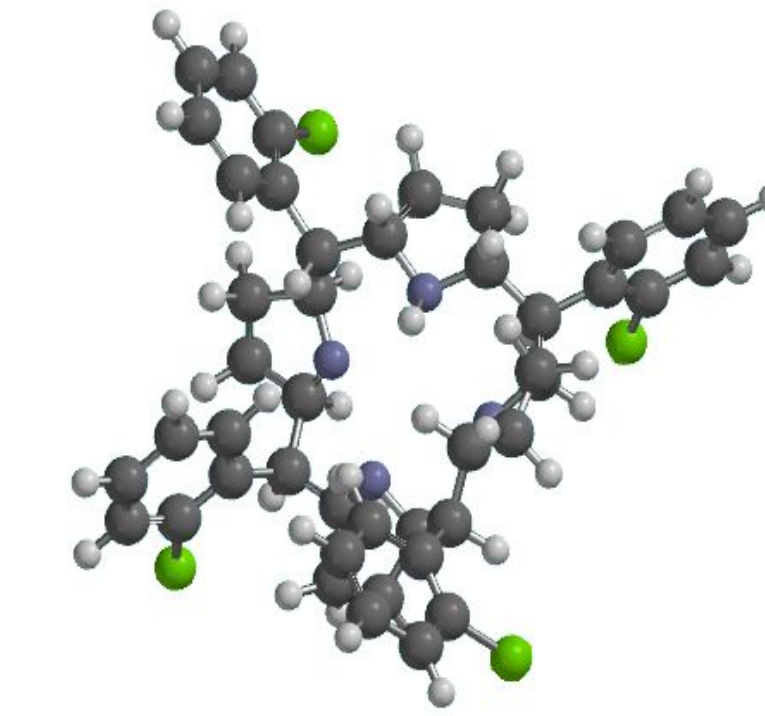


Figure 4. Spartan molecular modeling of 5,10,15,20-Tetrakis(2-chlorophenyl)porphyrin or 2-chloro TPP.

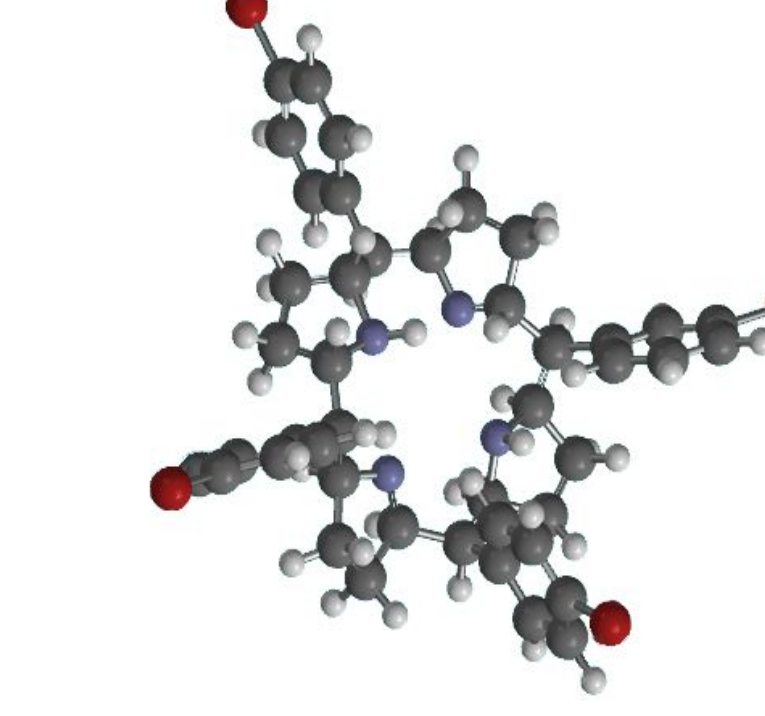


Figure 5. Spartan molecular modeling of 5,10,15,20-Tetrakis(4-bromophenyl)porphyrin or 4-bromo TPP.

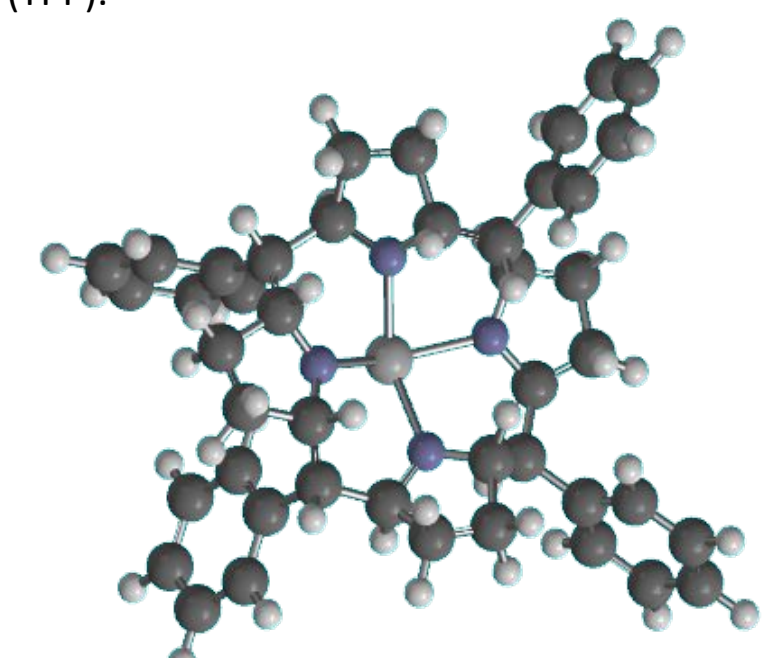


Figure 6. Spartan molecular modeling of Sn (II) and 5, 10, 15, 20-Tetraphenylporphyrin complex or TPP with Tin complex.

Figure 2 displays the molecular modeling of the 5, 10, 15, 20-tetraphenyl porphyrin (TPP). Figures 3 through 5 display the molecular modeling of the electron-withdrawing substituted tetraphenylporphyrins like 4-chloro TPP, 2-chloro TPP, and 4-bromo TPP. Figure 6 displays the metalloporphyrin that was synthesized in the experiments.

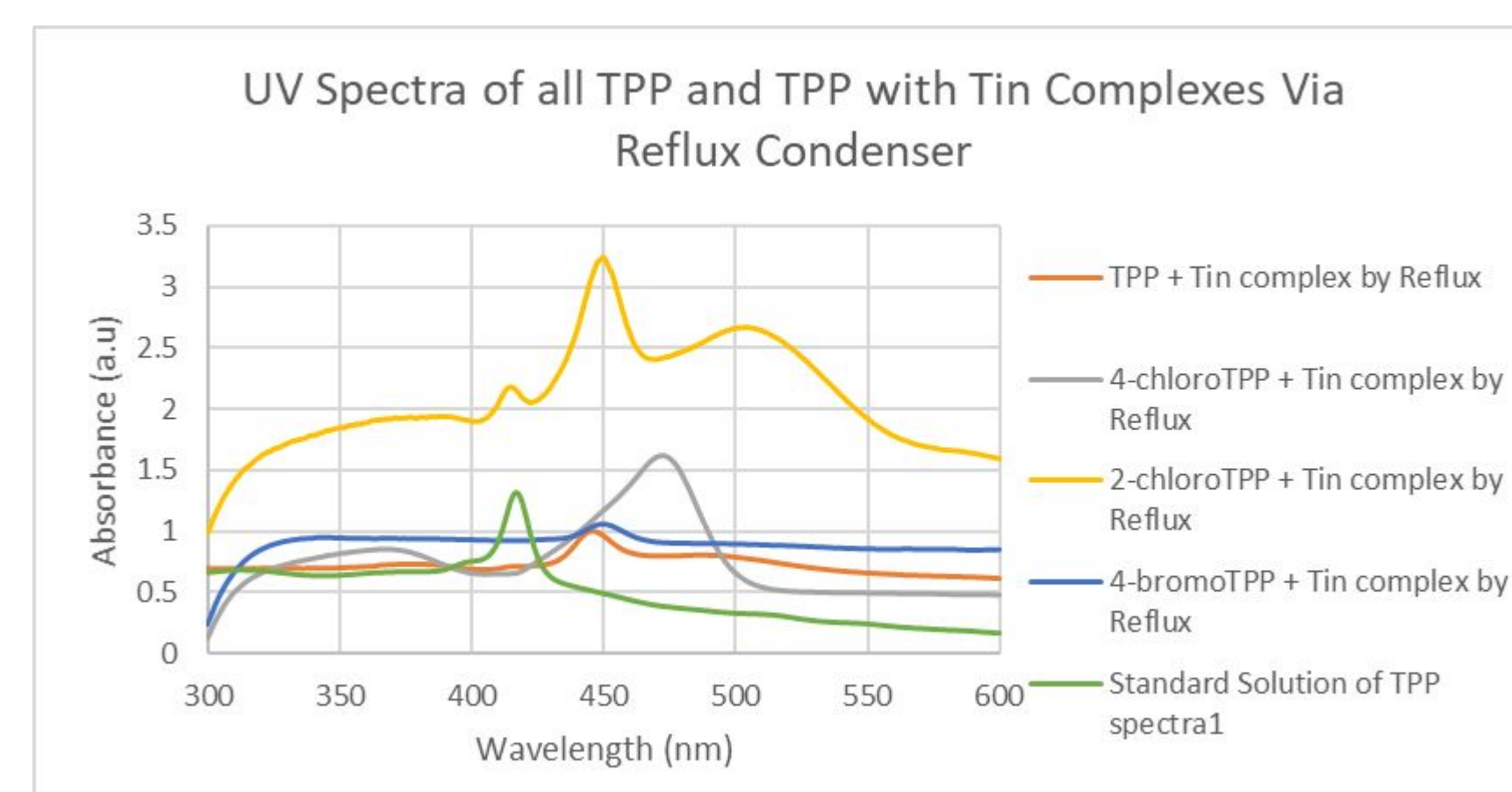


Figure 7. Steady State of UV-Vis Spectra of all tested electron-withdrawing TPP with Tin complexes by Reflux Condenser.

Figure 7 displays the UV-Vis spectra of all the TPP and electron-withdrawing substituted TPP complexed with the stannous chloride via reflux condenser.

Figure 8 displays an example of a metalloporphyrin crystal found as 2-chloroTPP + Tin complex by Reflux in Figure 7. This crystal is known as Sn (II) and 5,10,15,20-Tetrakis (2-chlorophenyl)porphyrin complex or the 2-chloro TPP with Tin complex.



Figure 8. 2-chloro TPP with Tin complex crystals through Reflux Condenser. The compound did not degrade which the complexation was a success.

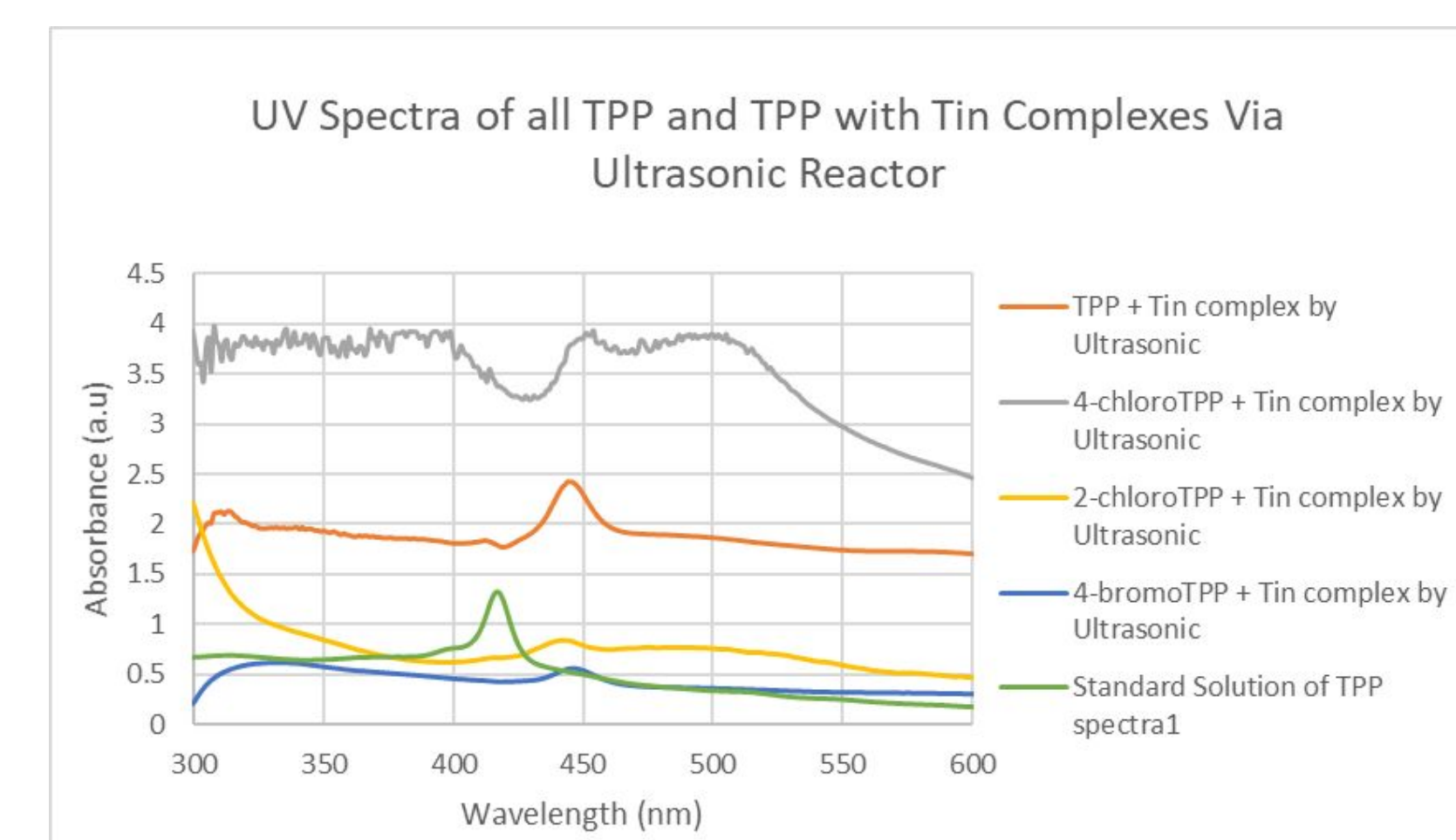


Figure 9. Steady State of UV-Vis Spectra of all tested electron-withdrawing TPP with Tin complexes by Ultrasonic Reactor.

Figure 9 displays the UV-Vis spectra of all the TPP and electron-withdrawing substituted TPP complexed with the stannous chloride via ultrasonic reactor.

Figure 10 displays an example of a metalloporphyrin crystal found as TPP + Tin complex by Ultrasonic in Figure 9. This crystal is known as Sn (II) and 5,10,15,20-Tetraphenylporphyrin complex or the TPP with Tin complex.



Figure 10. TPP with Tin complex crystals through Ultrasonic Reactor. The compound did not degrade which the complexation was a success.

Results continued

Table 1. Theoretical, Actual, and Percent Yields of all TPP products via Traditional Microwave, including crystalline solids.

Chemical	Theoretical Yield	Actual Yield	Percent Yield	Average Percent Yield	Crystal Images
5,10,15,20-Tetraphenylporphyrin 4 runs were done	5.562g	1.375g	24.72%	15.09%	
	5.544g	0.177g	3.19%		
	6.020g	1.620g	26.91%		
	6.506g	0.359g	5.52%		
5,10,15,20-Tetrakis (4-chlorophenyl)porphyrin	7.928g	1.146g	14.46%	14.46%	
5,10,15,20-Tetrakis (2-chlorophenyl)porphyrin	8.468g	0.727g	8.59%	8.59%	
5,10,15,20-Tetrakis (4-methoxyphenyl)porphyrin with catalyst 2 runs were done	7.864g	0.288g	3.66%	2.83%	
	7.886g	0.178g	2.26%		
	7.820g	0.266g	3.40%		
5,10,15,20-Tetrakis (4-methylphenyl)porphyrin	7.149g	0.203g	2.84%	2.84%	
5,10,15,20-Tetrakis (4-bromophenyl)porphyrin	10.164g	0.692g	6.81%	6.81%	

Societal Impact Statement

The porphyrin pathway is ubiquitous in the biological realm, serving throughout the plant and animal kingdoms as the assembly line for the most abundant pigments in nature. The ring-shaped porphyrin molecules bind an array of metal ions, with each combination associated with different biological functions. Chlorophylls bind magnesium to play a pivotal role in photosynthesis. Heme binds iron to coordinate molecular oxygen and carbon-dioxide transport, supports the electron-transport chains necessary for cellular respiration, and contributes to the catalytic activities of many enzymes. Also, porphyrins are at the heart of most of the reactions of bioremediation; therefore, it is essential to understand where they can be found, how they work, and which are the determinant enzymatic systems necessary for the biodegradation process to occur.

Conclusion

Models of all TPP derivatives and their metal complexes were constructed using Spartan '20 Molecular Modeling Software. In all cases, the beta-HOMO and the beta-LUMO energies were higher both for the TPPs and their corresponding metal complexes.

The TPPs were synthesized using both unsubstituted and substituted benzaldehydes. The TPP synthesis was more efficient when electron-withdrawing benzaldehydes were used, and the UV maximum of TPP-substituted benzaldehyde derivatives demonstrated a red shift.

References

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