SELF-ASSEMBLING CHLORINS AS A SIMPLE MODEL OF LIGHT-HARVESTING ANTENNA

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Introduction and Goal

The development of artificial photosynthetic systems has been widely explored as a solution to the consumption of fossil fuels and its corresponding problems, such as lack of sustainability, and extensive greenhouse gas emissions.[1] Ideal artificial photosynthetic systems include a light-harvesting antenna complex with strong electronic coupling and efficient energy transfer for an efficient collection of solar energy.[2]

The goal of this project is to develop a simple model for self-assembled photosynthetic light-harvesting antenna.

Molecular Design

To mimic natural photosynthetic antenna, the coordinated structure of bacteriochlorophyll c (Figure 1) was used as a model for the design of the target compound, zinc 13-pyridyl-18,18-dimethyl-10-tolyl chlorin (Figure 2).[3] With such a molecule, self assembly occurs when the hydroxyl of one molecule coordinates to the magnesium of a nearby neighbor through its lone pair, and simultaneously forms a hydrogen bond (acting as H-bond donor) to the carbonyl of a second neighbor. To simplify this system, and facilitate dimerization rather than larger assembly formation, we sought to utilize the lone pair of a nitrogen atom, in combination with zinc, as there are known reports of dimerization with zinc-metallated porphyrins.[2]

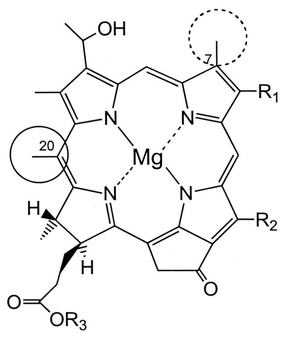


Figure 1. Bacteriochlorophyll c

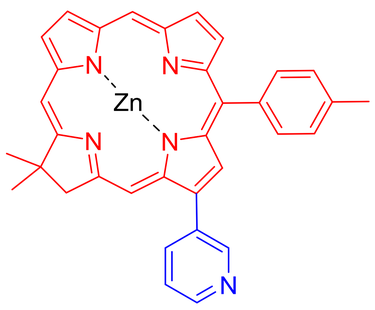
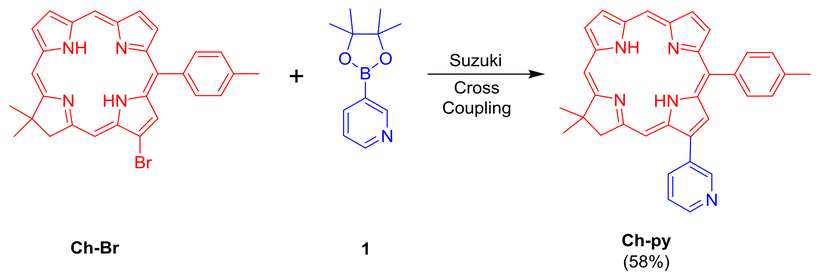


Figure 2. Zinc 13-pyridyl-18,18-dimethyl-10-tolyl chlorin

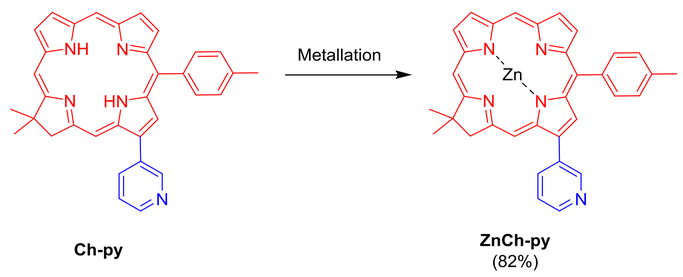
Synthesis

Naturally occurring hydroporphyrins are not amenable to extensive synthetic transformation, therefore, 13-bromo-10-tolyl chlorin (**Ch-Br**) was prepared *de novo* following well-established procedures.[4] Following preparation, Ch-Br was subjected to Suzuki coupling to form 13-pyridyl-10-tolyl chlorin (**Ch-py**) (Scheme 1). After purifying, zinc-chelated 13-pyridyl-10-tolyl chlorin (**ZnCh-py**) was produced via metalation (Scheme 2).



Ch-Br **1** **Ch-py** (58%)

Scheme 1. Synthesis of 13-pyridyl substituted chorin. **Ch-Br** (1.0 eq.), boronic pinacol ester (**1**, 3.0 eq.), sodium carbonate (10.0 eq), $Pd(PPh_3)_4$ (0.2 eq.), toluene/N,N-dimethyl formamide (2:1, 15 mL), 80°C, 19 hours.



Ch-py **ZnCh-py** (82%)

Scheme 2. Synthesis of zinc chelated 13-pyridyl chlorin. **Ch-py** (1.0 eq.), zinc acetate (5.0 eq.), chloroform/methanol (5:1, 1.2 mL), room temp., 6 hours.

Spectroscopic Characterization

Compound	Absorption Maxima (nm)			Emission Maxima (nm)
	B band	Q_x	Q_y	
Ch-py	408	503	640	641
ZnCh-py	412	-	617	621

Table 1. Absorption and Emission Maxima for Novel Chlorins. All data collected in toluene.

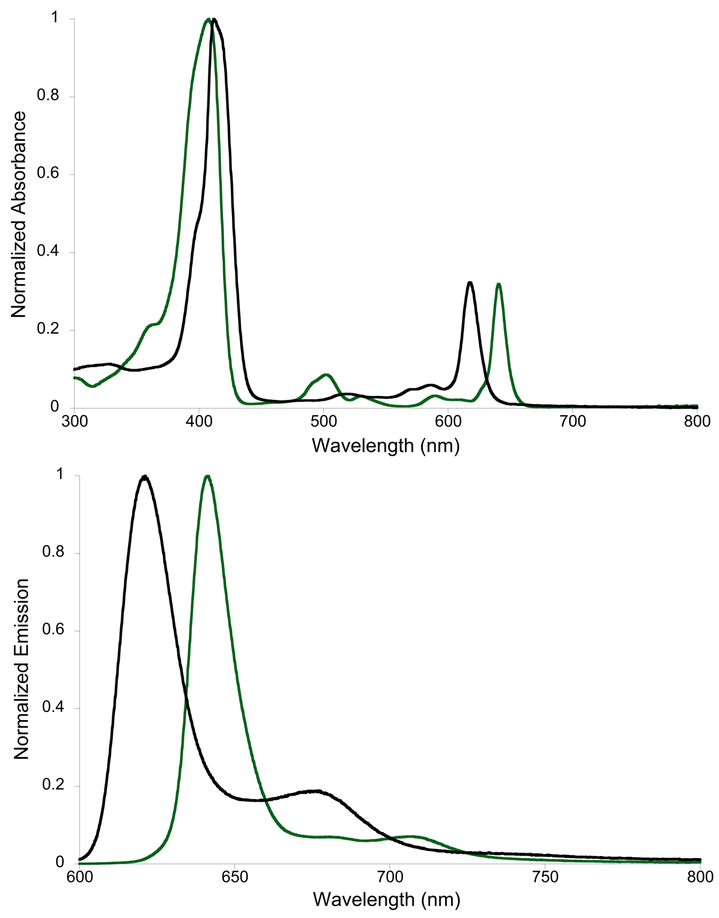


Figure 3. Normalized absorbance (top) and emission (bottom) spectra of **Ch-py** and **ZnCh-py** acquired in toluene.

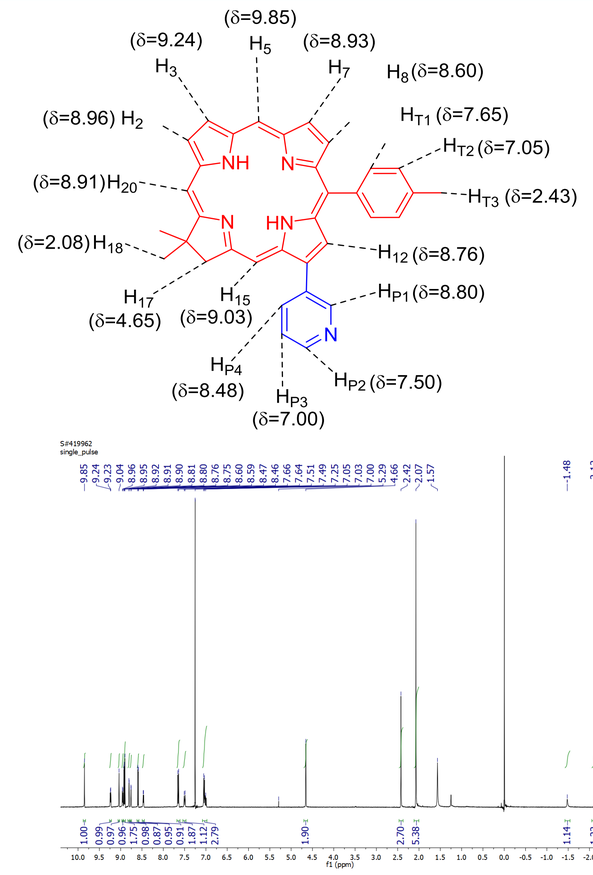


Figure 4. Ch-py proton chemical shifts with ^1H NMR spectra.

Conclusion & Future Works

Synthesis of target molecule with absorbance and emission characterization was successfully completed. However, further studies are required for ^1H NMR characterization of the target molecule. In addition, experimentation with self-assembly or dimerization (Figure 5) of the target molecule is needed to develop the model for a self-assembled light-harvesting antenna complex. Future studies are also recommended for synthesis and full spectroscopic characterization of imidazole substituted zinc chlorin derivatives (Figure 6).

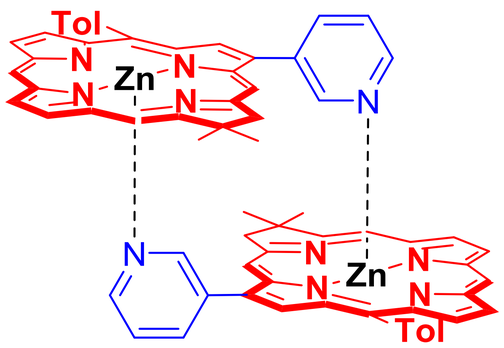


Figure 5. Dimerization of Zinc 13-pyridyl-18,18-dimethyl-10-tolyl chlorin

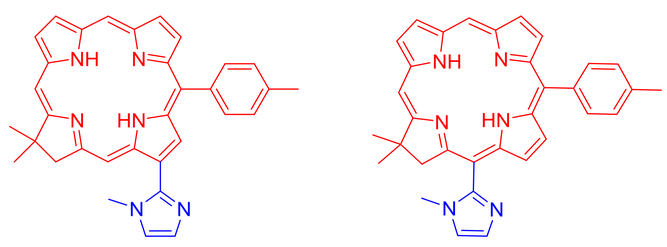


Figure 6. Potential target molecules (imidazole substituted zinc chlorin derivatives) for future studies.

Acknowledgements

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