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

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 metatlation (Scheme 2).

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption Maxima (nm)</th>
<th>Emission Maxima (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B band</td>
<td>Q1</td>
</tr>
<tr>
<td>Ch-py</td>
<td>408</td>
<td>503</td>
</tr>
<tr>
<td>ZnCh-py</td>
<td>412</td>
<td>-</td>
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Spectroscopic Characterization

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).

Conclusion & Future Works

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References