

Synthesis and Photophysical Investigations of Polynuclear Rhenium

(I) Compounds with Bridging Imine Donors

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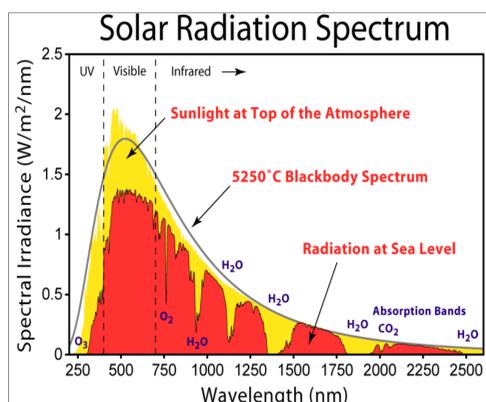
Abstract

Polynuclear molecular designs are attractive for light absorption over a broad spectral range, particularly when multiple chromophores may be incorporated into a single scaffold. The ability of Re(I) to accommodate a variety of ligands while maintaining efficient absorption and emission properties motivates its use in metallacycles and cages intended for light harvesting applications. Towards this end, a multidentate N-donor ligand with imine sites was selected for the formation of dinuclear complexes. The ligand is formed from ethylenediamine, 1,4-benzenedicarboxaldehyde, and 2,4,6-trimethylbenzaldehyde through a series of Schiff-base condensation reactions. Metalation is envisioned by treatment with $\text{Re}(\text{CO})_5\text{Br}$, resulting in the loss of two carbonyl ligands. Photophysical investigations will establish the extent of electronic communication between the metal centers and evaluate the emissive properties of the dinuclear complex.

Introduction

Natural photosystems harvest energy through highly organized assemblies of chromophores and catalysts. These assemblies can be used as models for the design of light-harvesting metal-organic frameworks (MOFs) for solar panels. Self-assembly strategies easily construct the complex systems of chromophores, charge separators, charge conduits, and redox centers.¹ The goal of this project is to design novel ligands and chromophoric polynuclear complexes for the light-harvesting aspect of a photosystem. For maximum efficiency, chromophore assemblies should be tuned to absorb over most or all of the solar flux (figure 1).

Figure 1:²



Rhenium was used as the metal center in this complex because of its efficient absorption and emission when coordinated to a variety of ligands, similar to ruthenium, a popular metal in MOFs.³ This quality promotes communication between metal centers, an important aspect when considering the charge transfer necessary in a complete photosystem.⁴

Methods

Figure 2: Ligand Synthesis

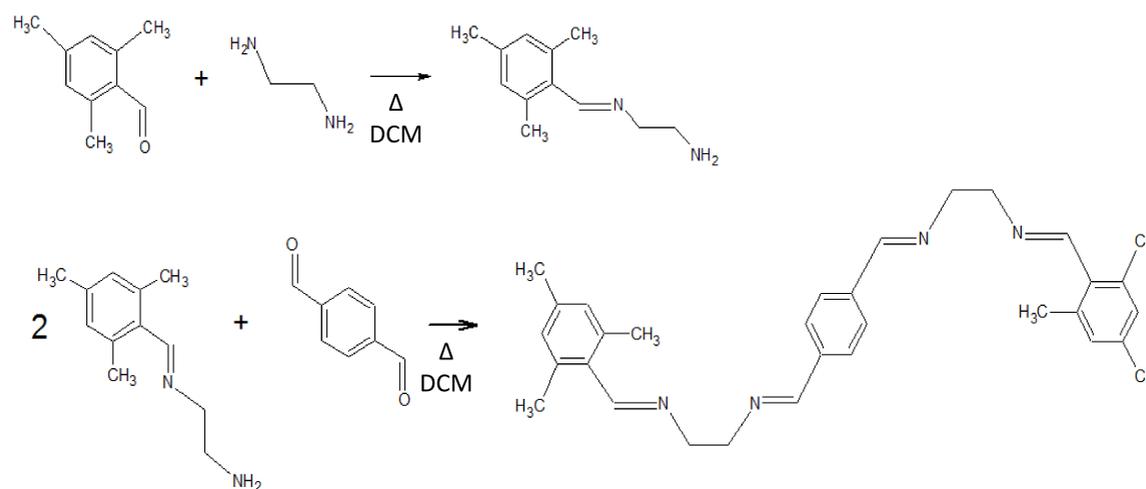
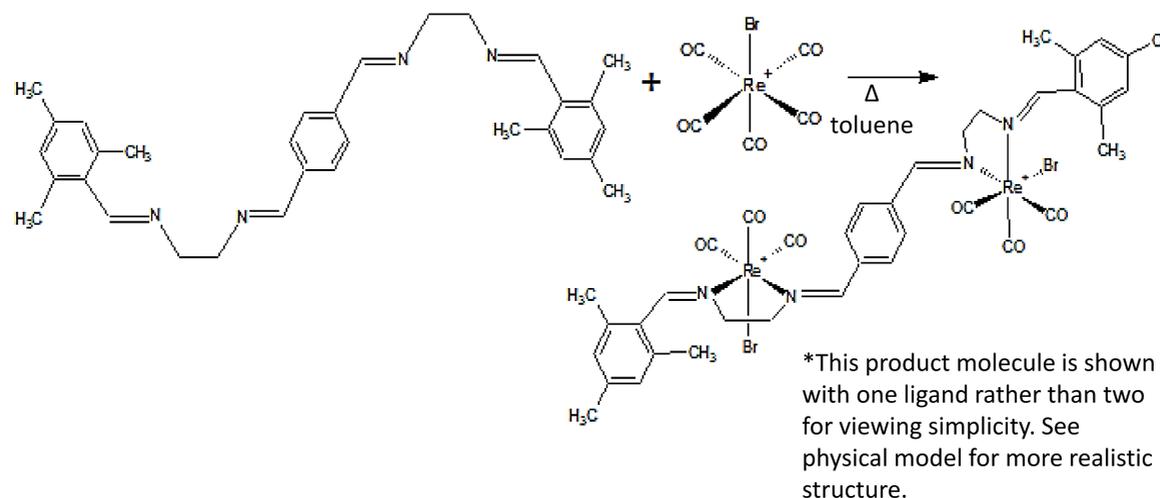


Figure 3: Rhenium Self-Assembly



Compounds purified by recrystallization and confirmed by ¹H NMR.

This synthesis was adapted from procedures in Kuhnert, et al⁵ and Potgieter, et al⁶.

Conclusion

The mesityl imine, the first product in the ligand synthesis was synthesized successfully based on ¹H NMR characterization. The product was a white to very pale yellow powder in a yield of approximately 60%. The novel tetraimine has not yet been successfully synthesized. Initial attempts at isolation furnish an insoluble light peach-yellow powder. The lack of solubility makes NMR characterization difficult, but given that the tetraimine is expected to be soluble in organic solvents, new synthetic conditions are being explored including more dilute reaction mixtures and shorter reaction times. Given the success of the first Schiff-base condensation, this step should work correctly as well.

The tetraimine, once synthesized, will be analyzed by UV-Vis and fluorescence spectrometers to obtain absorption and emission data and provided information about electronic structure. Self-assembly with bromopentacarbonylrhenium(I) will also be attempted with a goal of obtaining ¹H NMR, mass spectrometry, absorption, and emission spectra, along with a crystal structure. It would be desirable for the complex to absorb through the maximum emission shown in the solar radiation spectrum (figure 1²) as do similarly coordinated rhenium complexes (figure 5⁴).

Spectra

Figure 4: Predicted ¹H NMR of Novel Tetraimine Ligand from ChemBioDraw Ultra v.14.0.0.117

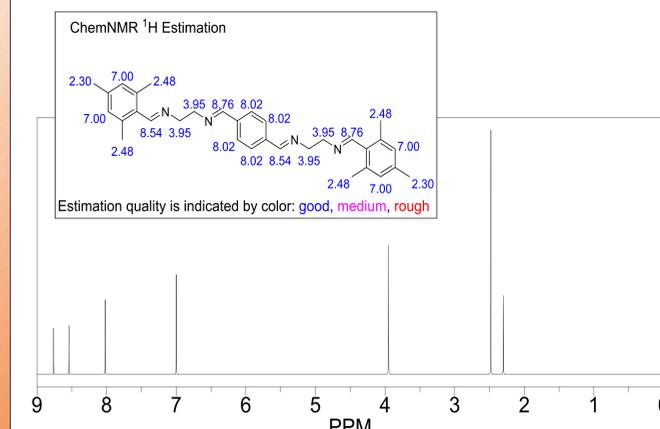


Figure 5: Exemplary Absorbance Spectrum of Imine-Coordinated Re and Ru⁴ Complexes

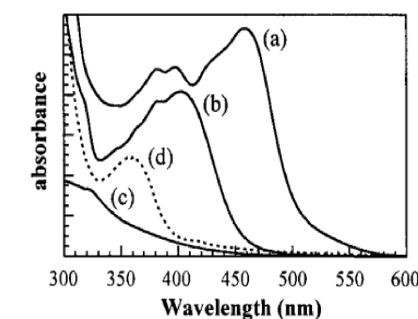
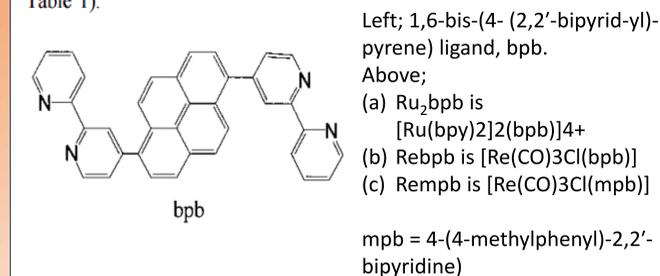


Figure 5. Electronic absorption spectra of (a) Ru_2bpb , (b) Rebpb , (c) Rempb , and (d) bpb in acetonitrile. Spectra have been scaled in order to simplify their comparison. (Extinction coefficients are reported in Table 1).



References

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