

## Overview

The overarching purpose of this research is to develop earth abundant sensitizers for photocatalytic carbon dioxide reduction. Photocatalytic carbon dioxide is a way in which waste carbon dioxide can be catalytically transformed into new sources of fuel, making the use of petroleum fuels more renewable. This research is focused on zinc dipyrromethene (dipyrrin) complexes. Dipyrrin ligands have similar light absorbing properties as porphyrins but are synthetically more accessible. The zinc metal center acts as a template, holding two dipyrrin ligands orthogonal to each other in a pseudo-tetrahedral geometry. This allows for intramolecular electron transfer between the two dipyrrin ligands to form a charge separated (CS) state. This CS state can potentially quench the initially excited singlet state and is theorized to facilitate intersystem crossing (ISC) to the long-lived triplet state. The first objective of this research is to synthesize a series of zinc dipyrrin complexes and determine how efficiently they form long-lived triplet states in both polar and non-polar solvent environments. The second objective of this research is to use these zinc dipyrrin complexes to sensitize photocatalytic carbon dioxide reduction, using a known carbon dioxide reduction catalyst.

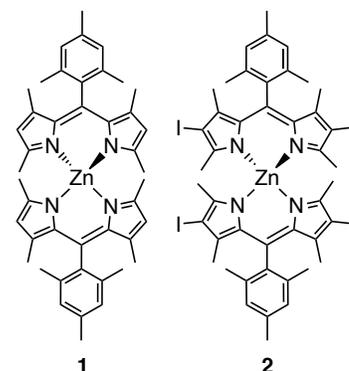


Figure 1. Zinc dipyrrin complexes studied

## Research Progress

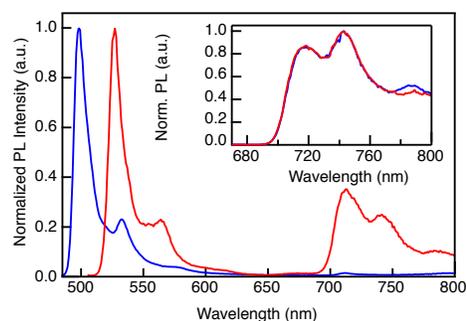


Figure 2. Normalized low temperature emission spectra of **1** (blue) and **2** (red) recorded at 77 K in frozen 2-methyltetrahydrofuran solution. Inset shows normalized phosphorescence spectra collected with a 650 nm long pass filter.

in both complexes has a node through the center of the dipyrrin ring and the substituents at the 2 and 8 positions (H or I), which explains the fact that triplet states of both complexes phosphoresce at the same energy.

Triplet quantum yields were determined by nanosecond transient absorption in two steps. First the extinction coefficients of the long-lived triplet states were determined by energy transfer to perylene, a triplet acceptor with a known extinction coefficient. Transient absorption spectra (Figure 4) of **1** or **2** and perylene in deaerated solvent at early times show the show the dipyrin triplet state, with a strong bleach around 500 nm and positive absorptions to the blue and red of the bleach. At later time, the dipyrin triplet signals decay and are replaced by the characteristic perylene triplet spectrum, indicating that energy transfer rather than electron transfer has occurred between the zinc dipyrrin complex and perylene. Single wavelength kinetic decay traces at 490 nm, 600 nm, and 700 nm were used to quantify the maximum triplet state absorbance of the perylene, **1** and **2** respectively. The second step to determine the triplet quantum yields of **1** and **2** is relative actinometry experiments, using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  as the standard. Deaerated samples of **1**, **2**, and  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  were independently measured and the single wavelength kinetic decay traces were

In our first year of funding we have synthesized and purified two zinc dipyrrin complexes, shown in Figure 1. The yields of these complexes ranged from around 50% for **1** to 8% for **2**. Steady state absorption spectra of **1** and **2** show intense visible absorptions ( $\epsilon = 1.6\text{-}1.7 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ ) due to a ligand localized  $\pi \rightarrow \pi^*$  transition. At room temperature, steady state emission spectra of **1** and **2** reveal only fluorescence from the initially excited singlet ligand localized state ( $S_1$ ). The addition of the electron withdrawing iodine atoms in **2** red-shifts both the absorption and emission bands by around  $1000 \text{ cm}^{-1}$ . Moving from the less polar toluene to the more polar THF has little effect on the absorption or fluorescence energies, but does lead to a significant decrease in fluorescence quantum yield, 12.9% to 2.6% in **1** and 2.0% to 0.14% in **2** due to the stabilization of the CS state in the more polar environment. When frozen at 77 K, both fluorescence and phosphorescence are observed in the emission spectra of **1** and **2**, as seen in Figure 2. Curiously, while the fluorescence of **2** is red shifted compared to **1** due to the electron withdrawing I atoms, the phosphorescence of **1** and **2** occurs at nearly identical energies. Computational studies of **1** and **2** revealed that the spin density in the lowest energy triplet state

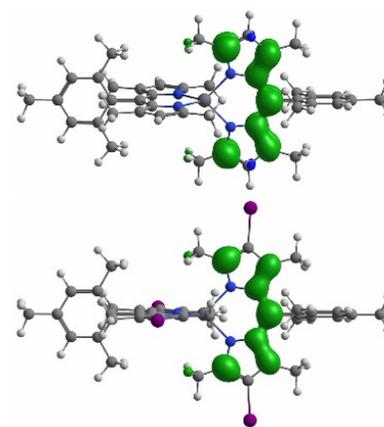


Figure 3. Spin density in the lowest energy triplet state of **1** (top) and **2** (bottom) calculated in a toluene continuum.

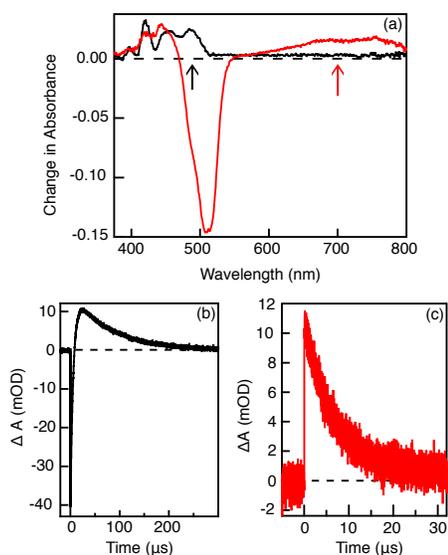


Figure 3. Transient absorption measurements of **2** and perylene ( $6.0 \times 10^{-5}$  M) in deaerated toluene. (a) Transient absorption spectra collected 100 ns (red) and 50  $\mu$ s (black) after 510 nm excitation. Arrows indicate probe wavelengths for kinetic traces. (b) Kinetic decay trace probed at 490 nm. (c) Kinetic decay trace probed at 700 nm.

used to determine the triplet state concentrations and quantum yields for **1** and **2**. The results can be seen in Table 1. The triplet extinction coefficients of **1** and **2** are insensitive to solvent polarity, with magnitude of **2** about 50% larger than **1**. In complex **1**, without the heavy I atoms, the triplet yield increases significantly when the solvent polarity increases, mirroring the decreased fluorescence quantum yield (and increased CS state formation). However, in complex **2** the triplet quantum yield of around 60% is insensitive to solvent polarity, despite the increased CS state formation in the more polar THF. To investigate this further in the next year of funding we will synthesize and investigate additional zinc dipyrin dyes and well as their corresponding boron difluoride complexes, where CS state formation is not possible.

Table 1. Triplet excited state properties of **1** and **2** in deaerated solutions

Complex	Solvent	$\epsilon^T$ ( $M^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>	$\Phi_T$ (%) <sup>b</sup>
<b>1</b>	Toluene	4100	16
	THF	4900	27
<b>2</b>	Toluene	6900	63
	THF	6800	62

<sup>a</sup> Error  $\pm$  20% <sup>b</sup> Error  $\pm$  15%

For our second objective, cyclic voltammetry of **1** and **2**, coupled with the phosphorescence energies determined from the 77 K emission spectra have allowed us to determine both the ground and excited state redox potentials of **1** and **2**. With this information we have selected a low overpotential, commercially available carbon dioxide reduction catalyst, 5,10,15,20-Tetrakis(pentafluorophenyl)-21*H*,23*H*-porphyrin iron(III) chloride and sacrificial electron donor, benzyl mercaptan that are energetically compatible with both **1** and **2**. In preparation for photocatalysis experiments we are optimizing our photoreactor setup and calibrating our GC for CO detection. In the next year of funding we will perform photocatalytic carbon dioxide reduction sensitized by **1** and **2** and look for correlations between triplet yield and CO yield, turnover frequency, or turnover number.

## Research Impact

In the first year of this project, three undergraduate students were supported, two during the academic year and one over the summer. Two of these students worked on the synthesis and photophysical characterization of the zinc dipyrins and one worked on the photocatalysis objective, building a photoreactor and optimizing the GC detection of carbon monoxide. This student also wrote his ETSU honors thesis on this work. All of these students graduated in Spring 2019 and are now employed as a lab technician, enrolled in pharmacy school, and enrolled in medical school. Three graduate students have also worked on this project during the first year. One student during the academic year only, one during both the academic year and summer, and one new student began work on the project during the summer. Two of these students worked on the synthesis of substituted pyrroles and zinc dipyrin complexes and one student focused on the photocatalysis and CO detection aspect of the project. During the first year of the grant the PI was invited to present this work at the Inter-American Photochemical Society annual winter meeting in January 2019. In the coming year the PI has been invited to present this work at NC Photochem, a regional photochemistry conference, in Oct 2019 and the spring 2020 national ACS meeting. The first publication based on this work is currently under review at the Journal of Physical Chemistry A.