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Ethan Spielvogel
Binghamton University--SUNY

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Quantum Yields of Photoredox Catalyzed α-Arylation of Amines

Ethan Spielvogel, Bernard Stevenson, Emily Loiaconi, John Swierk*

Department of Chemistry, Binghamton University, Vestal NY

Abstract

Photoredox Catalysis is a powerful tool for the formation of chemically challenging bonds that normally require high temperatures, high pressures, and harsh chemicals to synthesize. Despite widespread method development for use in pharmaceuticals and organic synthesis, a detailed mechanistic understanding of photoredox catalysis is needed. A major obstacle to understanding the chemistry of photoredox catalysis is the lack of data on reaction quantum yields. In this study we analyze the quantum yields of an alpha arylation reaction of amines catalyzed by an Iridium polypyridyl photosensitizer. We will present our investigations into the quantum yields of this reaction with an emphasis on the effects of wavelength, light intensity, and reaction time. Additionally, we conducted Stern Volmer quenching studies to compare rates of quenching among various coupling partners to understand the correlation between rate of quenching and product yield.

Introduction

- Photoredox catalysis provides a tool for energetically challenging bond formations
- Replaces the use of high temperatures, high pressures and harsh chemicals with visible light
- Single electron chemistry and overall redox neutral transformations[1]
- Unique catalysts of Iridium and Ruthenium with visible light charge transfer absorptions, and high luminescence quantum yields[2,4]
- **Atomic level mechanistic understanding of photoredox catalyzed reactions remains largely a mystery**

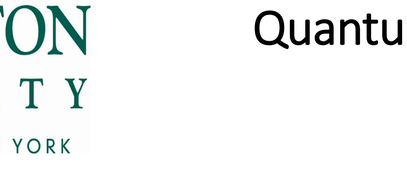
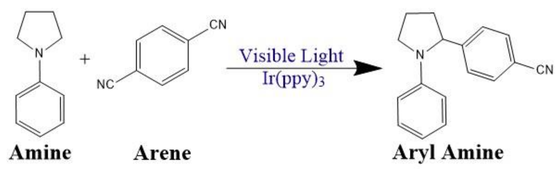


Figure 1. Properties of Tris[2-phenylpyridinato-C2,N]iridium(III) as a photoredox catalyst

Reaction Scheme



Proposed Mechanism[3]

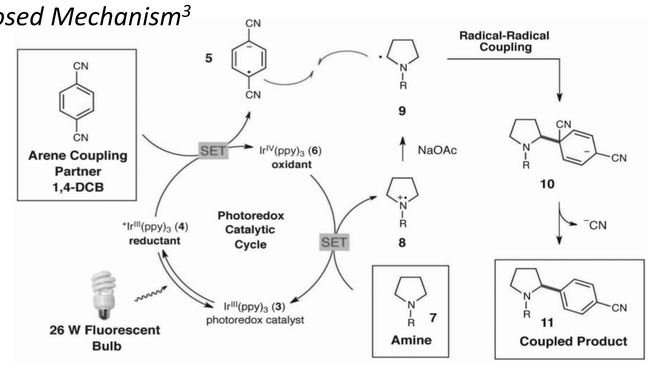


Figure 2. Overall reaction and MacMillan 2011 proposed photoredox mechanism[3]

Methodology

Aims:

1. **Understand how wavelength, light intensity, and illumination time effect quantum efficiency and product distribution**
2. **Elucidate relationship between rate of quenching and product yield**

Quantum Yields

- Quantum yields were collected for reactions with varying wavelength, illumination time, and light intensity
- Products and side products characterized using GCMS
- Product yields determined using quantitative NMR

Stern Volmer

- Rates of quenching determined for coupling partners with varying product yields
- Rates of quenching compared among coupling partners
- Utilized absorption and fluorescence spectroscopy

Results

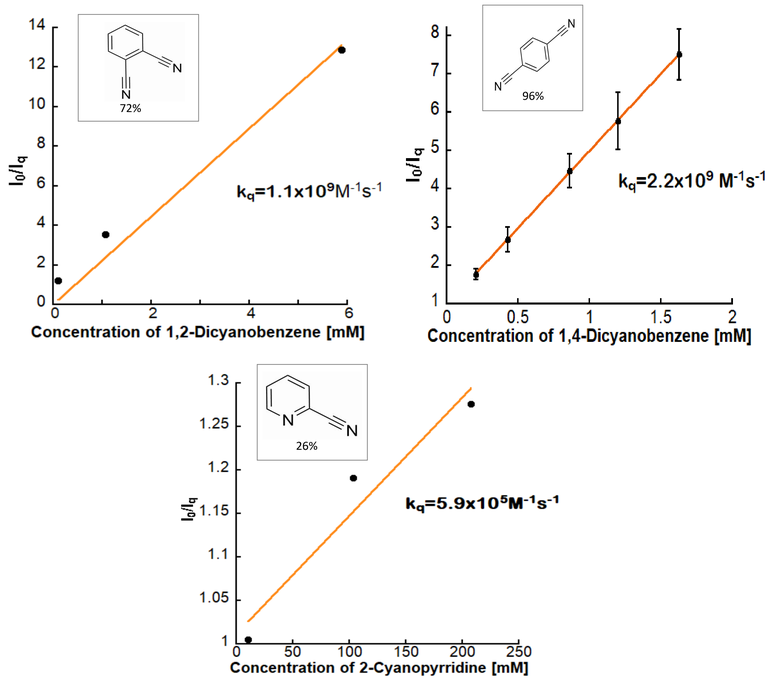


Figure 3. Stern Volmer emission quenching plot with structure and corresponding reported product yield[3] of various coupling partners

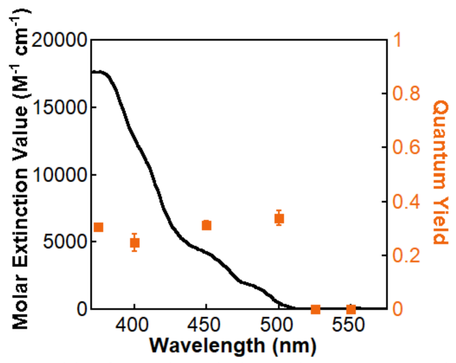


Figure 4. Quantum yields of wavelength dependent reactions plotted with molar extinction values of $Ir(ppy)_3$.

Results

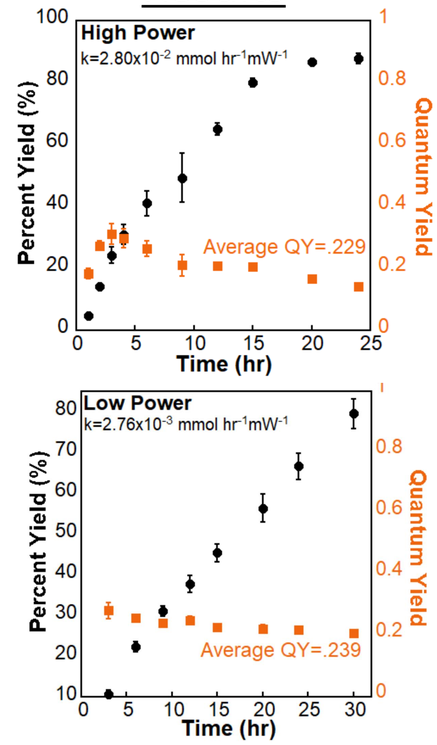


Figure 5. Quantum and product yields of power dependent C-H arylation reactions at 415nm along with average quantum yield and photon normalized reaction rate..

Discussion

- Lower yielding coupling partners had significantly slower rate of quenching
- Rate of quenching plays a role in low reaction yield and this exact role needs to be further explored
- No significant difference in quantum yields and reaction rates across differing light intensity
- Hypothesized presence of initial induction period where no product formed followed by period of rapid product formation
- Product yield tapered off at around 86%

Acknowledgements

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