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Progress Towards Synthesis and Characterization of Bay-Annulated Indigo Chromophores

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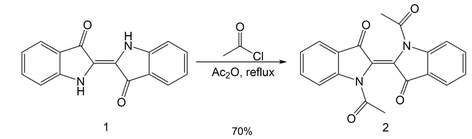
Abstract

Through acetylation, N,N'-diacetylindigo was synthesized from indigo. N,N'-diacetylindigo and 2-thiopheneacetyl chloride were combined in an attempt to synthesize 7-thiophenyl bay-annulated indigo (BAI). After ^{1}H NMR characterization, it was found that the product was not 7-thiophenyl BAI. A previously synthesized sample of 7-phenyl BAI was purified. UV-VIS absorbance, fluorescence, IR, and ^{1}H NMR were used to characterize the compounds.

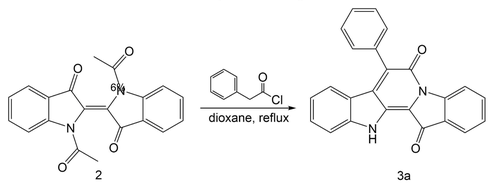
Introduction

Indigo is a widely used and readily available dye. Indigo can be reacted into chromophores that limit the typical hydrogen bonding structure of indigo. Hydrogen bonding allows an unwanted proton transfer excited state to occur, which rapidly decays through a nonradiative pathway. The short-lived excited state makes indigo a poor choice of chromophore for photovoltaic applications, however, the molecule can be substituted to improve the excited state lifetime. The substituted group can be used to tune the photophysical properties. The substitution made for these chromophores extends the pi-conjugation of the system and a smaller HOMO-LUMO gap. Indigo itself is not very soluble in common organic solvents. Through acetylation of indigo, N,N'-diacetylindigo can be synthesized and is a much more soluble compound. From the diacetylated product, selective bay-annulation can derivatize one side of the molecule. The side across from the bay-annulation is deacetylated and can be later bound as a ligand to a metal complex.

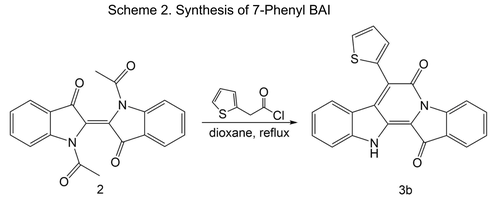
Synthesis



Scheme 1. Synthesis of N,N'-diacetylindigo through acetylation of Indigo



Scheme 2. Synthesis of 7-Phenyl BAI



Scheme 3. Synthesis of 7-Thiophenyl BAI

Acetylation of indigo with acetyl chloride and acetic anhydride allows for the synthesis of N,N'-diacetylindigo as seen in Scheme 1. Annulation of N,N'-diacetylindigo can be done in different ways. Schemes 2 and 3 represent annulation at the bay position. Scheme 2 is the formation of 7-phenyl BAI, and Scheme 3 is the synthesis of 7-thiophenyl BAI. Both annulations leave behind asymmetric molecules, which are best for use as a ligand to create a metal complex.

Photophysical Data

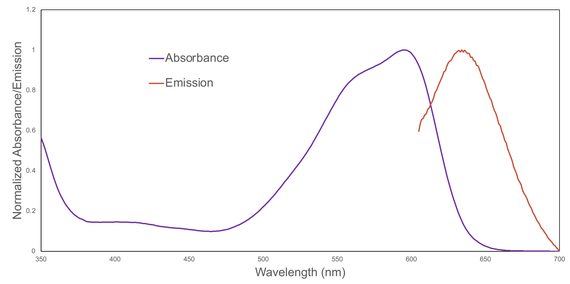


Figure 1: UV-VIS of isolated Scheme 3 product

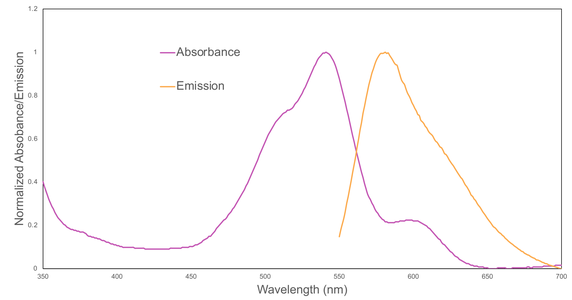
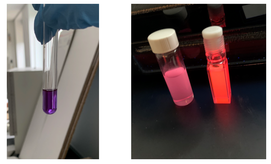
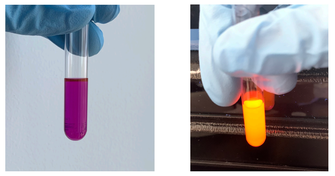


Figure 2: UV-VIS of 7-phenyl BAI



Product in solution appears purple (left). Solution under UV light appears bright pink (right).

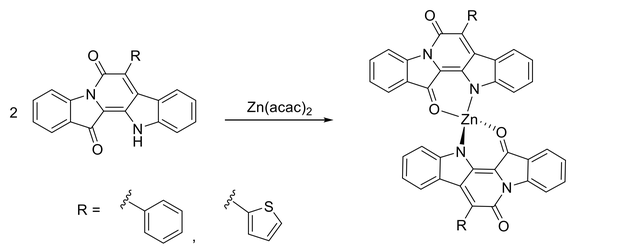
The maximum wavelengths of the Figure 1 graph are 594 nm and 634 nm for the absorption and emission respectively. As seen below Figure 1, the product appears purple in solution in normal light and emits a bright pink. The emission data was unexpected. The molecule was not presumed to be emissive.
The max wavelengths of Figure 2 are 304 nm and 581 nm for the absorption and emission. 7-phenyl BAI appears pink to the eye and emits bright orange when under UV light. As with the Figure 1 emission data, this result was unexpected.



7-phenyl BAI appears pink in solution (left). The same solution under UV appears bright orange (right).

Future Work

Future research will most likely include the synthesis of new chromophores to use as a ligand for a metal complex. The goal of creating a metal complex with these indigo derivative chromophores is to lower the energy of the ligand-to-ligand charge transfer. Additionally, further characterization of the compounds synthesized can be done to determine their structure.



Scheme 4. Synthesis of a bis-metal complex coordinated to the metal center across from the site of bay-annulation

Conclusion

UV-VIS, IR, and ^{1}H NMR were used in attempt to characterize the product from Scheme 3b as well as 7-phenyl BAI. The ^{1}H NMR of the Scheme 3b product was compared to the literature of 7-thiophenyl BAI to determine that the product was not actually 7-thiophenyl BAI. Both molecules currently being characterized are emissive. They were not originally expected to emit. Further characterization of the molecules is planned.

Acknowledgements

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References

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