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Synthesis and Characterization of Bay-Annulated Indigo Derivatives as Ligands for Photoactive Metal Complexes

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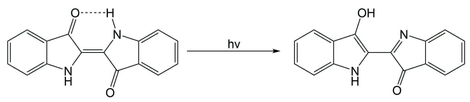
Abstract

New small molecule chromophores zinc-bis-7-phenyl-BAI and zinc-bis-7-thiophenyl-BAI were synthesized. These chromophores are designed to have longer excited state lifetimes compared to indigo. Characterization was performed by analyzing their UV-VIS absorbance spectra. Red-shifting was observed as well which allows an increase in the absorbance of lower energy photons which make up a large portion of the sun's radiation. Due to this the photoactive metal complexes formed can be considered for use in organic photovoltaics.

Introduction



Scheme 1. Light activated proton transfer in indigo

Indigo-based chromophores are of interest for organic photovoltaics due to their light absorption properties and tunability. Synthetic modifications to indigo can alter its excited state lifetime, absorption, and frontier orbital energy levels. Although indigo has a short-lived excited state due to intramolecular proton transfer shown in Scheme 1, the excited state lifetime can be extended through annulation at the bay position. The benefit of a longer excited state lifetime is that it aids in redirecting the energy that is absorbed. Another effect of this is the shrinking of the HOMO-LUMO gap which causes the indigo derivative to absorb lower energy photons that make up a large portion of the sun's radiation spectrum as shown in Figure 1.

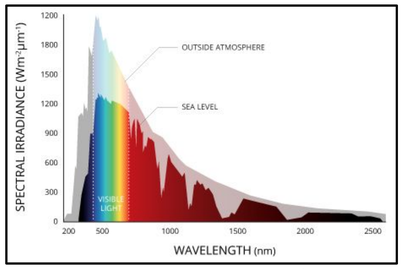
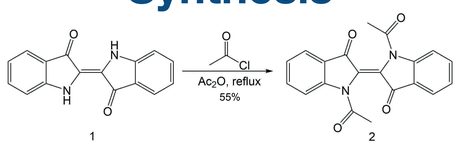


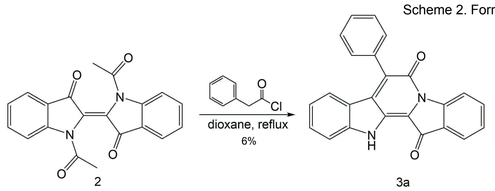
Figure 1. Solar radiation spectrum[1]

Synthesis



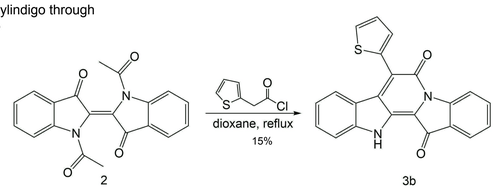
1 2

Scheme 2. Formation of N,N'-diacetylindigo through acetylation of Indigo



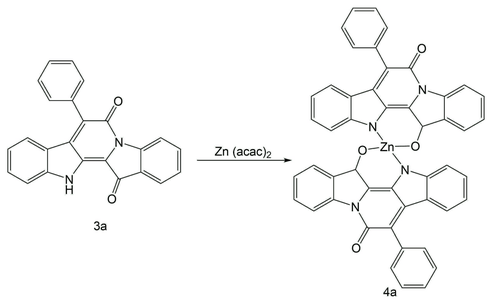
2 3a

Scheme 3a. Formation of 7-Phenyl BAI



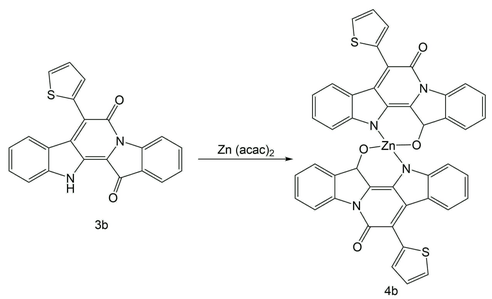
2 3b

Scheme 3b. Formation of 7-Thiophenyl BAI



3a 4a

Scheme 4a. Formation of Zinc-bis-7-Phenyl BAI



3b 4b

Scheme 4b. Formation of Zinc-bis-7-Thiophenyl BAI

Synthetic modifications performed on indigo include acetylation using acetyl chloride shown in Scheme 2 followed by annulation at the bay position with phenyl and thiophenyl groups as shown in Scheme 3a and 3b respectively.[2] Only one bay position was annulated, leaving the second position open to coordinate the ligand to zinc to form the metal complexes shown in Scheme 4a and 4b.

Spectral Data

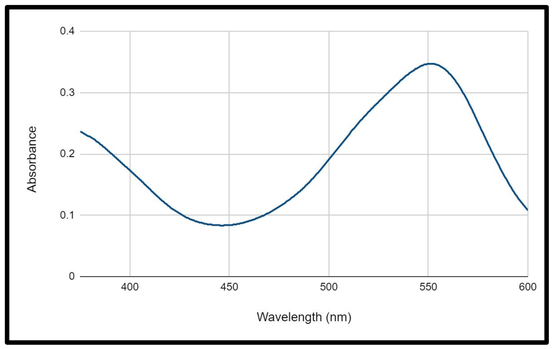


Figure 3. UV-VIS of 7-Phenyl-BAI

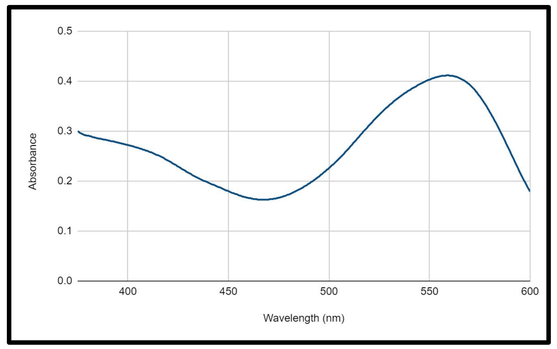


Figure 4. UV-VIS of 7-Thiophenyl-BAI

	7-Phenyl-BAI	Zinc-bis-7-Phenyl-BAI	7-Thiophenyl-BAI	Zinc-bis-7-Thiophenyl-BAI
λ_{Max}	551.5 nm	610.0 nm	559.0 nm	662.0 nm

7-Thiophenyl-BAI is more red-shifted than 7-Phenyl-BAI because thiophene is a stronger electron-donating group which raises the HOMO effectively shrinking the HOMO-LUMO gap. A clear red-shifting of absorption can be seen in the formation of the metal complexes as shown by the increase in λ_{Max}. The free ligands exhibit π - π* transitions whereas the complexes formed exhibit π - π* transitions along with lower energy ligand-to-ligand charge transfer (LLCT). The LLCT absorption is due to the presence of two identical ligands in different redox states.[3] Because the transfer takes place between two orbitals that are far apart the result is an extended excited state lifetime.

Future Work

Future research is planned to include further characterization through cyclic voltammetry as well as through molecular modeling to determine the HOMO and LUMO energy and structure of the complexes. In addition new complexes are planned to be synthesized by varying the aromatic group on the bay position of the ligand along with forming complexes with other first row transition metals.

Conclusions

Zinc-bis-7-phenyl-BAI and zinc-bis-7-thiophenyl-BAI were successfully synthesized from indigo and characterized using UV-VIS. Characterization through UV-VIS was performed by looking at π - π* transitions and LLCT and comparing λ_{Max} to see red shifts. Other forms of characterization are planned for the future to further confirm the synthesis of the products.

Acknowledgements

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References

1. Fondriest Environmental, Inc. "Solar Radiation and Photosynthetically Active Radiation." Fundamentals of Environmental Measurements. 21 Mar. 2014. Web.
2. Matthew A. Kolaczkowski, Bo He, and Yi Liu Organic Letters (2016) Stepwise Bay Annulation of Indigo for the Synthesis of Desymmetrized Electron Acceptors and Donor–Acceptor Constructs, 18 (20), 5224-5227, DOI: 10.1021/acs.orglett.6b02504
3. Arnd Vogler & Horst Kunkely (1990) Optical Ligand to Ligand Charge Transfer of Metal Complexes Including Ligand-Based Mixed-Valence Systems, Comments on Inorganic Chemistry, 9:3-4, 201-220, DOI: 10.1080/02603599008035810