Synthesis, Photophysical Properties Investigations of *o*-Hydroxy Benzimidazole and Their Applications as Down-Conversion in the Perovskite Solar Cells

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Abstract

Fluorescent molecules exhibiting excited-state intramolecular proton transfer (ESIPT) have attracted significant interest due to their large Stokes shifts and unique photophysical properties. However, tuning these fluorophores for optimal fluorescent emission remains a challenge. In this study, *o*-hydroxyphenyl benzimidazole (*o*-HPB) derivatives featuring various electron-withdrawing and electron-donating groups were synthesized via the oxidative condensation of *o*-phenylenediamine and salicylaldehyde derivatives. Their photophysical properties were systematically investigated, revealing structure-dependent emission behaviors in the range of 440–510 nm. Among the synthesized derivatives *o*-HPBOMe was preliminarily applied in down-conversion films, demonstrating an enhancement in power conversion efficiency (PCE) in perovskite solar cells. The results shed light on the structure fluorescence relationship, providing valuable insights for designing fluorophores for energy-related applications.

Introduction

- **Down-conversion materials** such as **quantum dots**, **inorganic materials**, and **organic materials** have improved the photoluminescence (PCE) of photovoltaic cells (PSCs).
- Organic materials such as **ESIPT fluorescence molecules** from organic materials offer several benefits, including enhanced photochemical properties, large stokes shifts that reduce self-absorption, and versatile applications in bioimaging and sensing, which make them valuable for various fields, including optoelectronics and laser dyes.

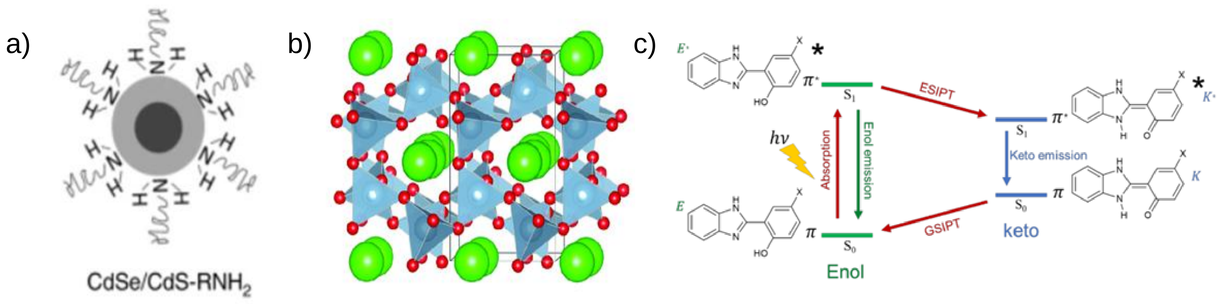


Figure 1. Examples of down-conversion materials: a) CdSe quantum dots, b) $SrAl_2O_4$ doped with Eu, and c) organic materials, *o*-hydroxyphenyl benzimidazole (*o*-HPB) that exhibit ESIPT fluorescence properties.

Research Objectives

- To synthesize *o*-HPB derivatives via oxidative condensation of *o*-phenylenediamine and salicylaldehyde derivatives.
- To investigate the substituent effects on the photophysical properties, e.g., UV-vis absorption and fluorescence emission of *o*-HPB derivatives in tetrahydrofuran.
- To evaluate the application of *o*-HPB derivatives in down-conversion films for enhancing power conversion efficiency (PCE) in perovskite solar cells.

Research Methodology

1. Synthesis, Characterizations and Photophysical Properties Investigations

• organic synthesis • purifications by column chromatography • ^{1}H NMR
• UV-vis absorption • Fluorescence emission • Structure-properties relationship

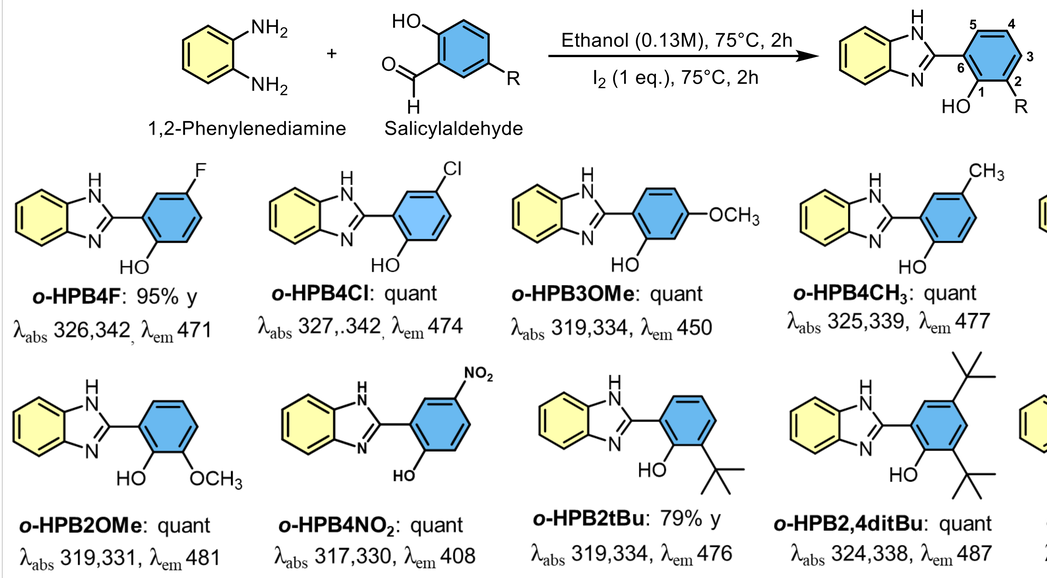
2. Applications as Down-conversion Materials in the Perovskite Solar Cells

• down-conversion film fabrications • external quantum efficiency (EQE) and short-circuit current density (J_{sc}) measurement

Results and Discussion

1. Synthesis, Characterizations and Photophysical Properties Investigations

- *o*-Hydroxyphenyl benzimidazole (*o*-HPB) can be synthesized from 1,2-phenylenediamine and salicylaldehyde derivatives.
- This method could readily provide the desired products typically in a good yield in which the structures were characterized by ^{1}H-NMR techniques.



Scheme 1. Synthesis, absorption and emission wavelengths (λ_{abs}, λ_{em} in nm) of *o*-HPB derivatives.

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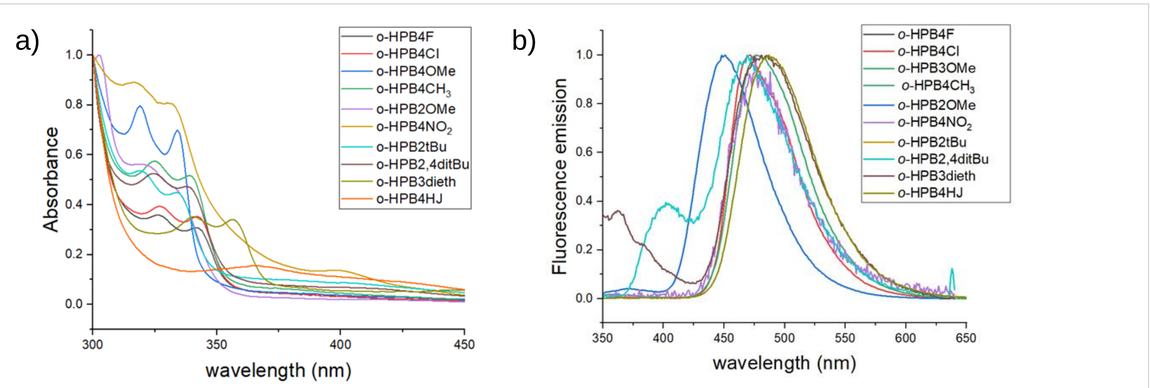

Figure 2. a) UV-Vis absorption and b) Fluorescence emission spectra of *o*-HPB derivatives.

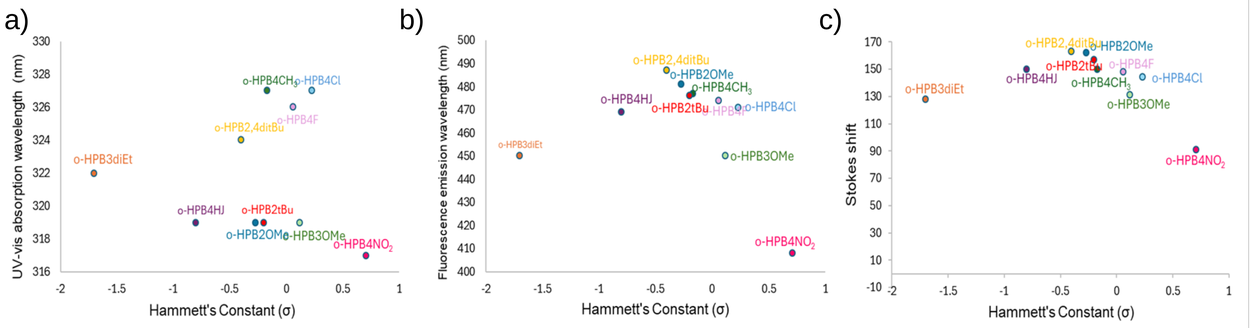

Figure 3. Relationship between Hammett's constant and a) UV-vis absorption wavelength (λ_{abs}) , b) Fluorescence emission wavelength (λ_{em}), and c) Stoke's shift (calculated from $\lambda_{em} - \lambda_{abs}$).

- The UV-vis absorption and fluorescence emission of o-HPB derivatives in THF were measured, revealing structure-dependent emission behaviors in the 440–510 nm range.
- To establish the structure-property relationship, Hammett's constant for each substituent was correlated with photophysical properties, revealing that while UV-vis absorption was not strongly influenced, fluorescence emission and Stokes shift exhibited a curved trend, suggesting a nonlinear relationship.

2. Applications as Down-Conversion in the Perovskite Solar Cells

Table 1. %EQE and J_{sc} performance comparison with and without *o*-HPB film.

Samples	External Quantum Efficiency, EQE (%)		Short-Circuit Current Density, J_{sc} (mA/cm²)	
	Without o-HPB	With o-HPB	Without o-HPB	With o-HPB
***o*-HPB4F**	30.70	28.82	6.76	6.21
***o*-HPB3OMe**	36.22	45.02	7.94	9.51
***o*-HPB2tBu**	41.74	31.17	9.29	9.58

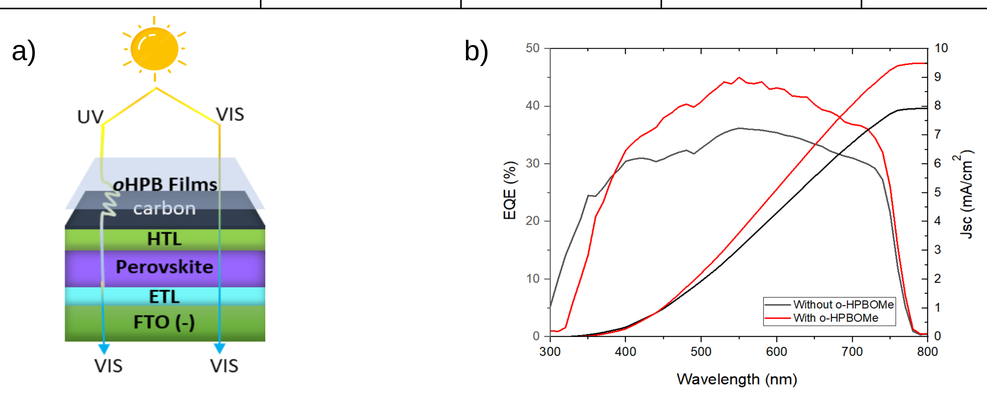

Figure 4. a) Perovskite solar cell device and b) %EQE and J_{sc} performance spectrum comparison with and without *o*-HPB3OMe film.

- *o*-HPB4F, *o*-HPB3OMe and *o*-HPB2tBu were fabricated as polyvinyl alcohol (PVA) films, but only *o*-HPB3OMe shows improvement of both external quantum efficiency (EQE) and short-circuit current density (J_{SC}).

Conclusion

- *o*-Hydroxyphenyl benzimidazole (o-HPB) derivatives were successfully synthesized and characterized, exhibiting structure-dependent fluorescence emission.
- While UV-Vis absorption showed minimal correlation with Hammett's constant, fluorescence emission and Stoke's shift followed a nonlinear trend.
- Among the PVA films fabricated, *o*-HPB3OMe demonstrated enhanced external quantum efficiency (EQE) and short-circuit current density (J_{SC}), highlighting its potential for optoelectronic applications.

References

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