



# Synthesis of Highly Emissive 4,7-Distyrylbenzo[c][1,2,5]thiadiazole Fluorophores by Hand-grinding in a Solvent-free Horner-Wadsworth-Emmons (HWE) Reaction

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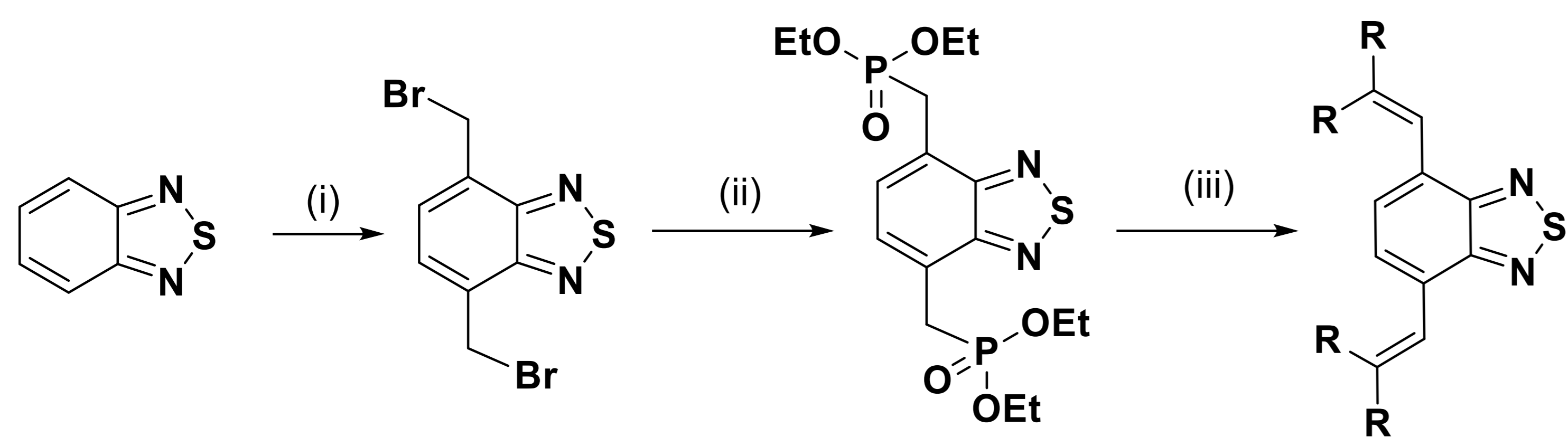


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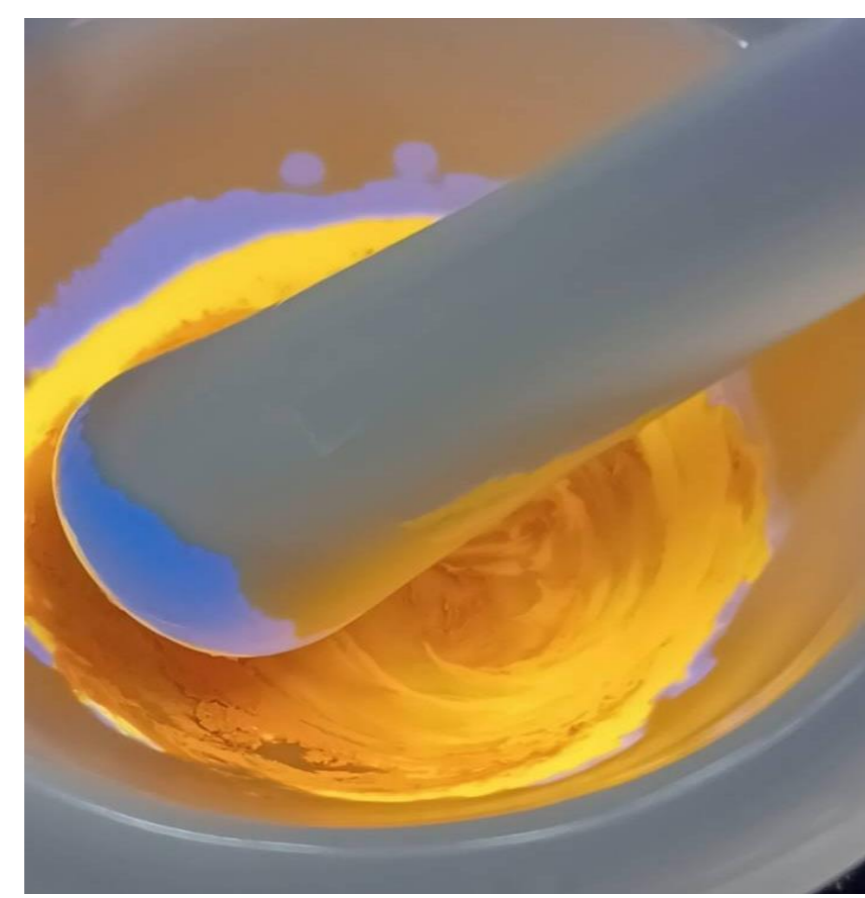
## Abstract

We report for the first time the synthesis of highly emissive benzo[c][1,2,5]thiadiazole (BTD) derivatives based on 4,7-distyrylbenzo[c][1,2,5]thiadiazole (**DS-BTD**) using a solvent-free Horner–Wadsworth–Emmons (HWE) reaction. The reaction was carried out by hand grinding tetraethyl(benzo[c][1,2,5]thiadiazole-4,7-diylbis(methylene))bis(phosphonate) with various carbonyl compounds in the presence of potassium tert-butoxide, yielding the target products in excellent isolated yields. Remarkably, the reaction time was  $\leq 1$  minute—significantly shorter than any previously reported solvent-free mechanochemical synthesis or solvent-assisted HWE reaction. The photophysical properties of six synthesized luminophores (**E1–E6**) were thoroughly investigated. Their emission maxima were observed at 533, 551, 620, 545, 568, and 558 nm, respectively. This work represents the first green and efficient hand-milled solvent-free HWE reaction, offering a rapid and sustainable route for the development of **DS-BTD**-based emissive materials for organic light-emitting diodes (OLEDs).

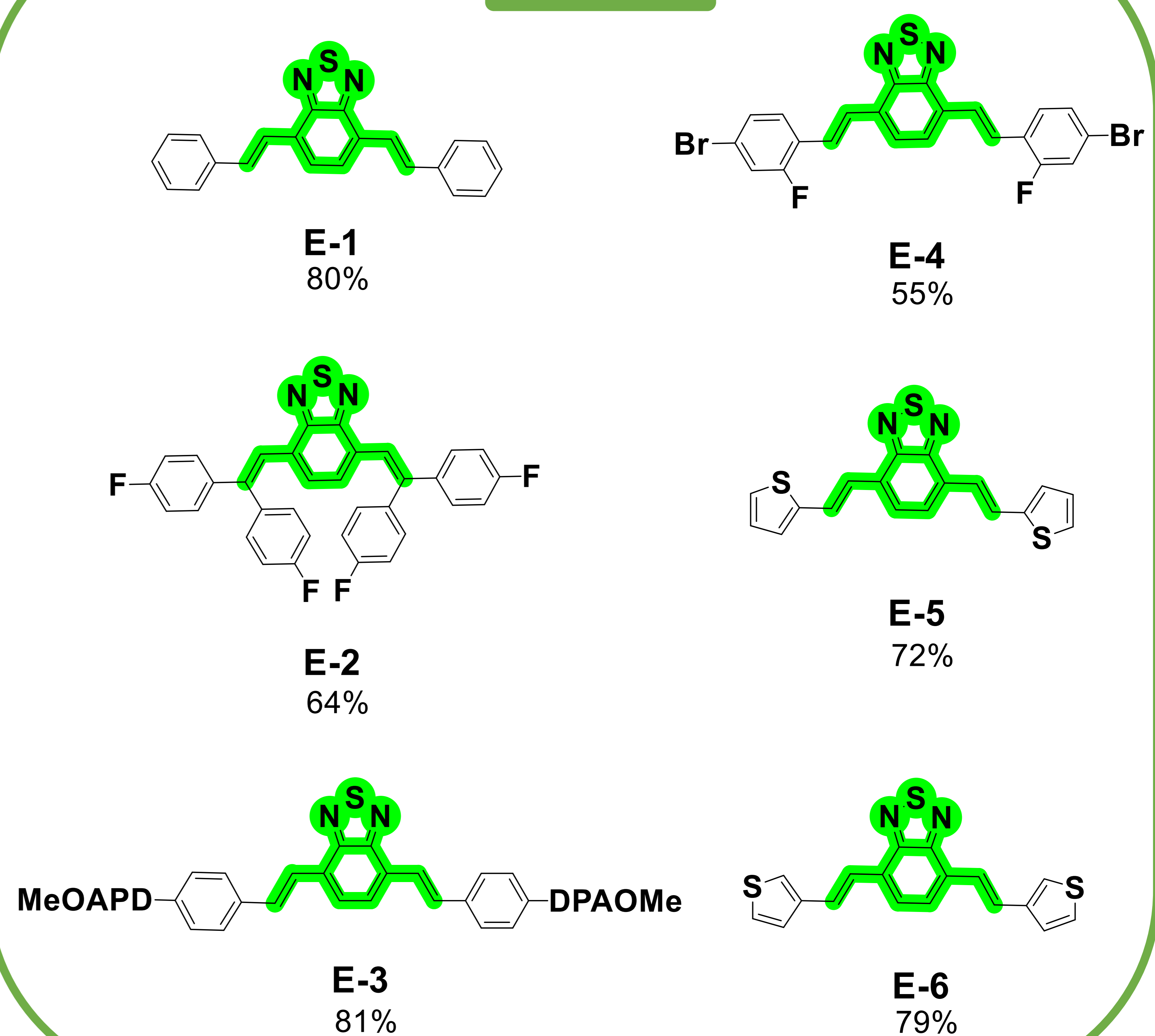
## Synthesis



(i) Trioxane (5 eq), Tetradecyltrimethylammonium bromide (10 mol%),  $\text{HBr}_{(\text{aq})}$ ,  $\text{H}_2\text{SO}_4$ , reflux, 16h. (ii) Triethylphosphine (15 eq), 150 °C, 24h. (iii) aldehyde (2.2 eq),  $\text{KO}^t\text{Bu}$  (10 eq), Grinding, RT, 1 min.

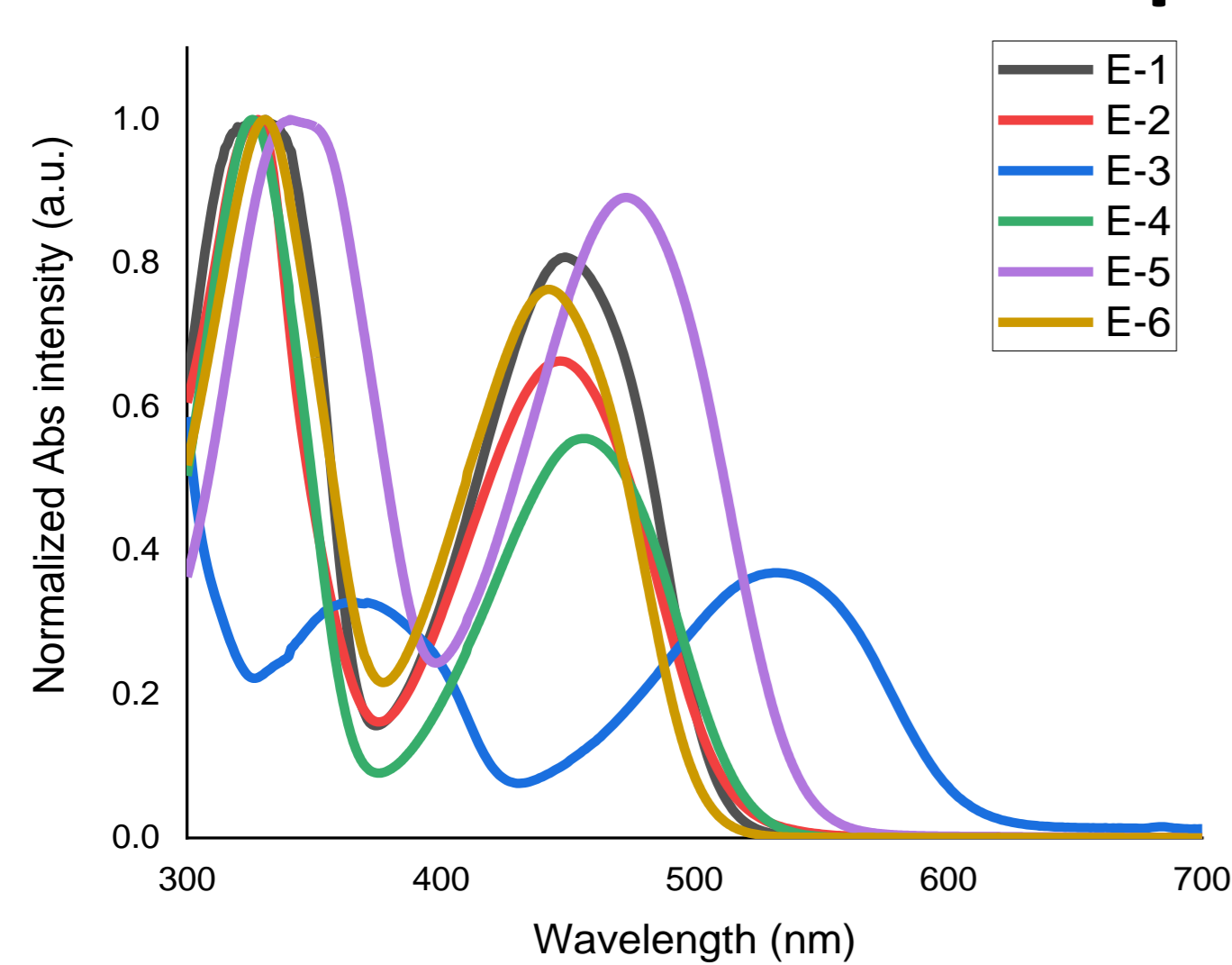


## Structure

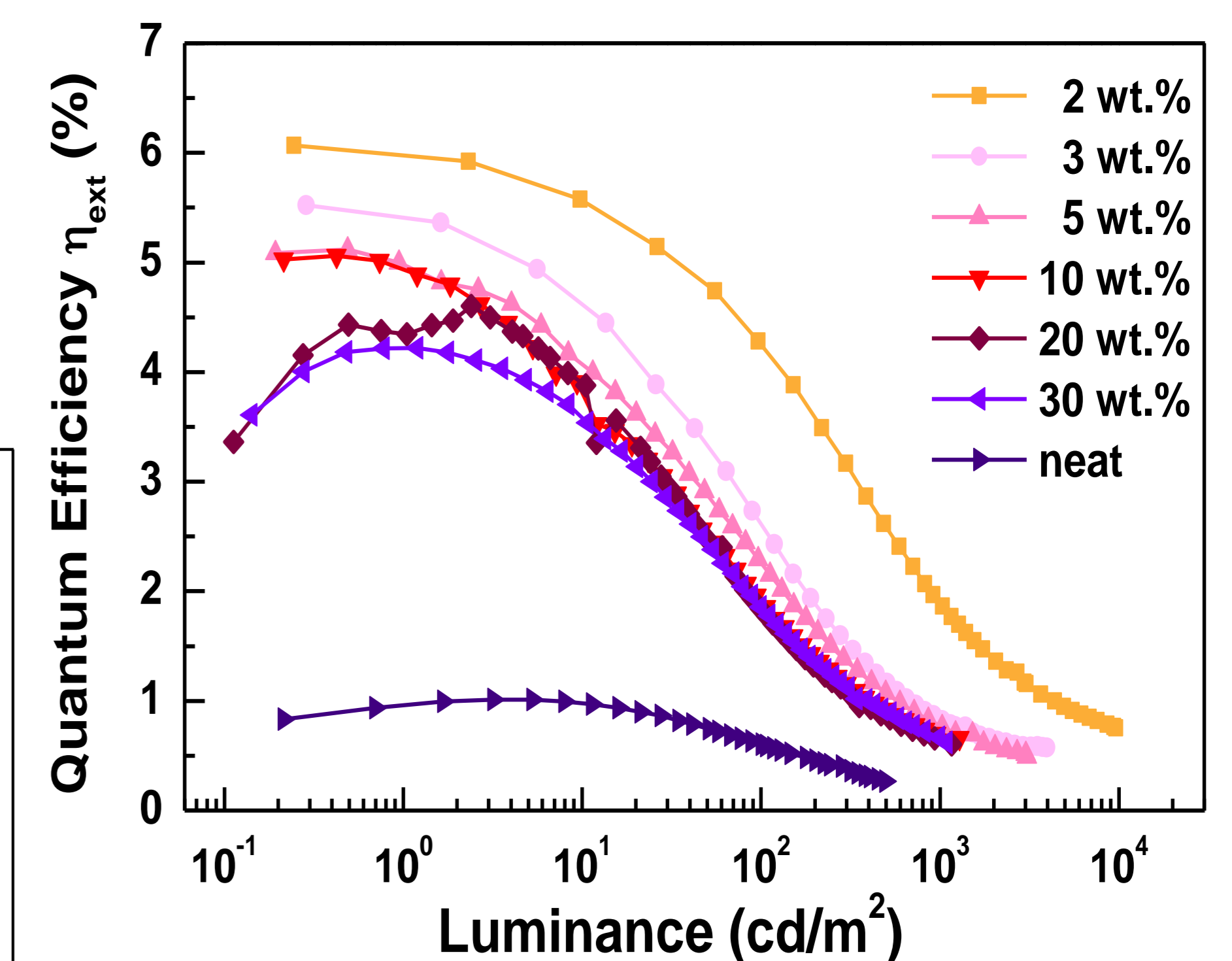
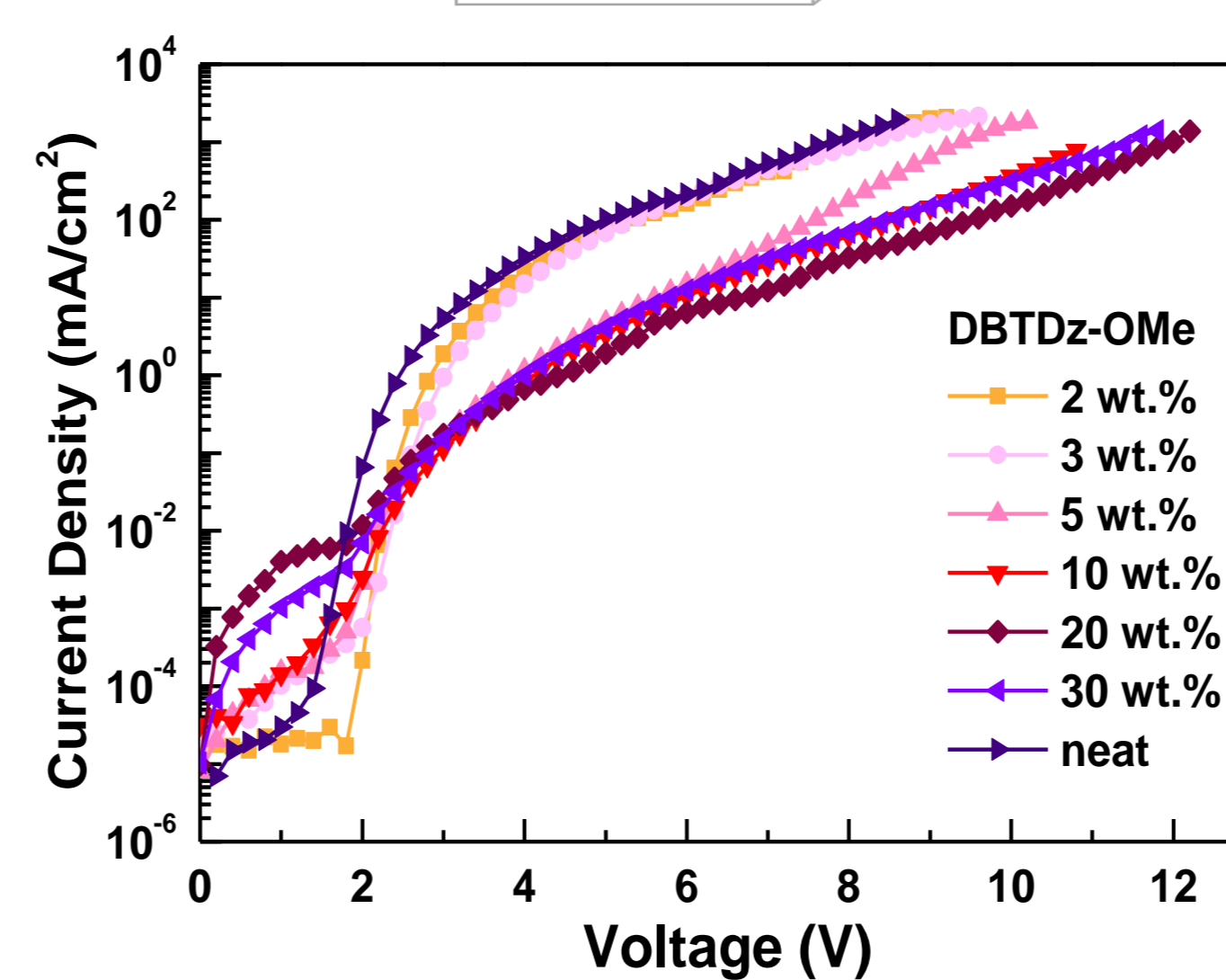
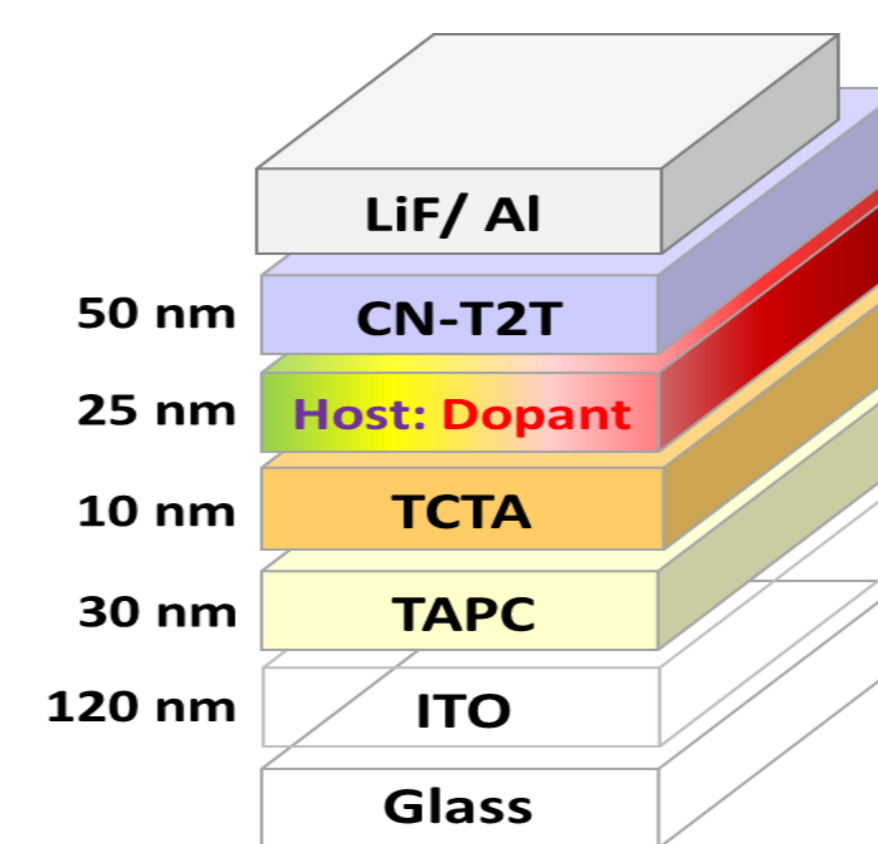
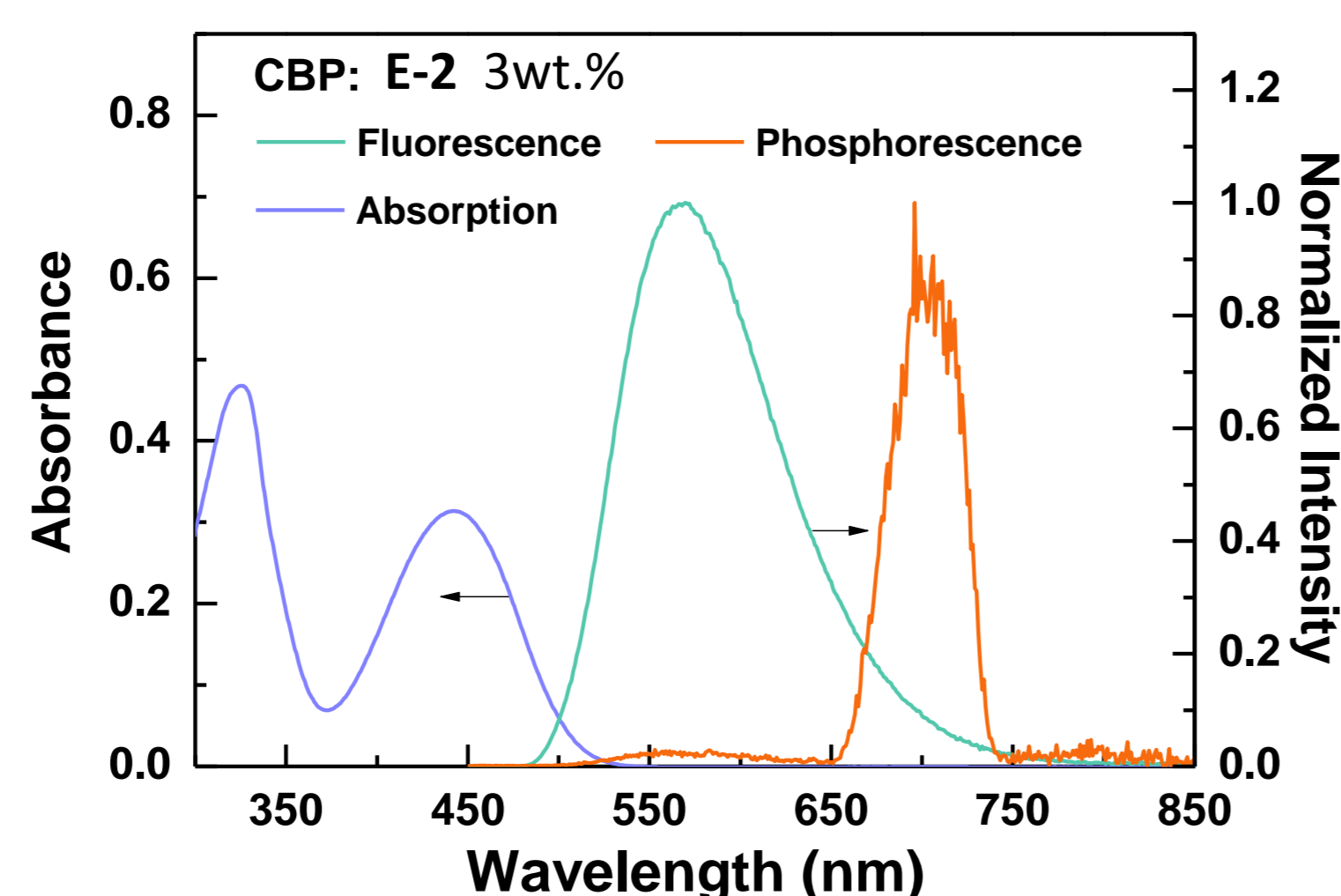
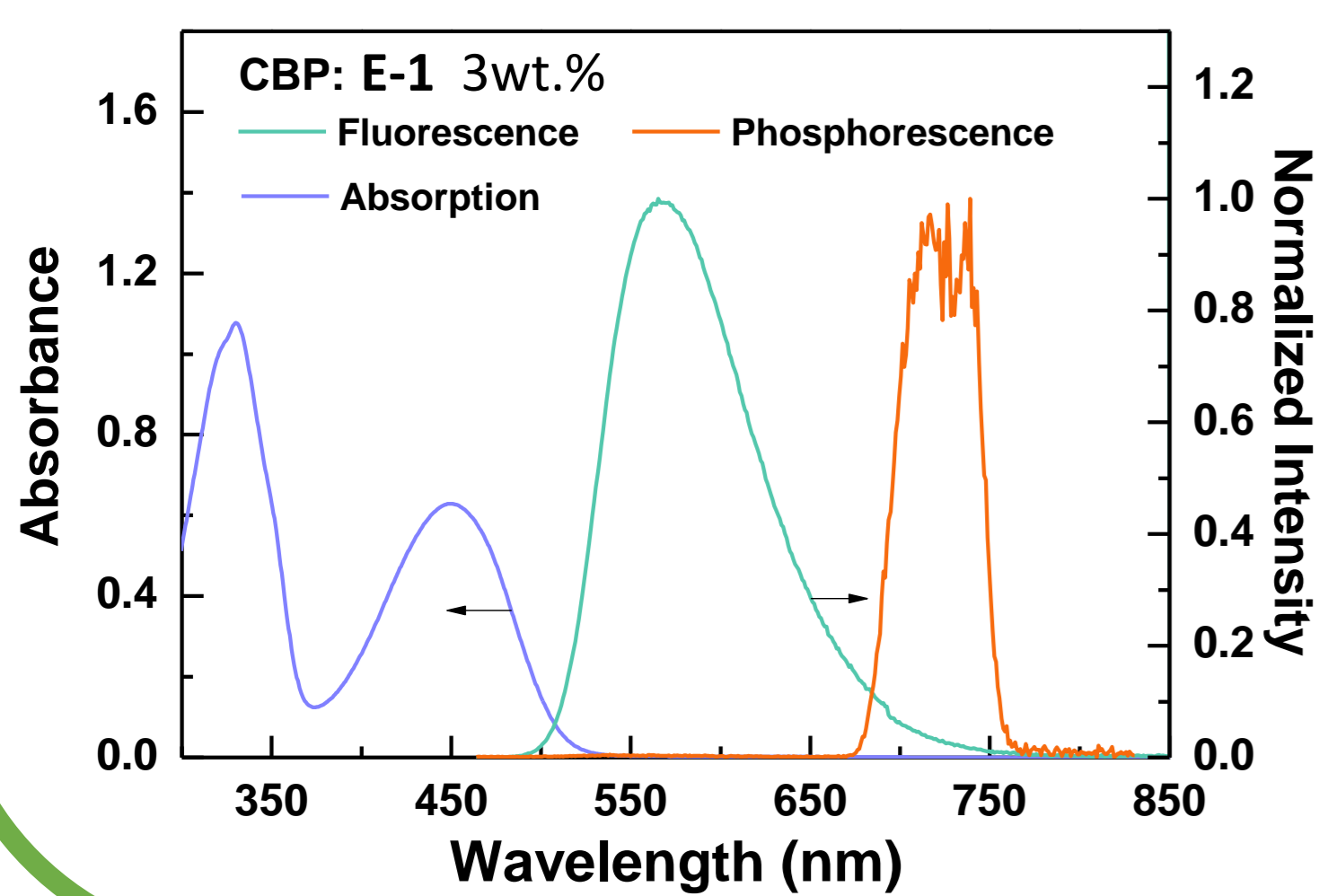
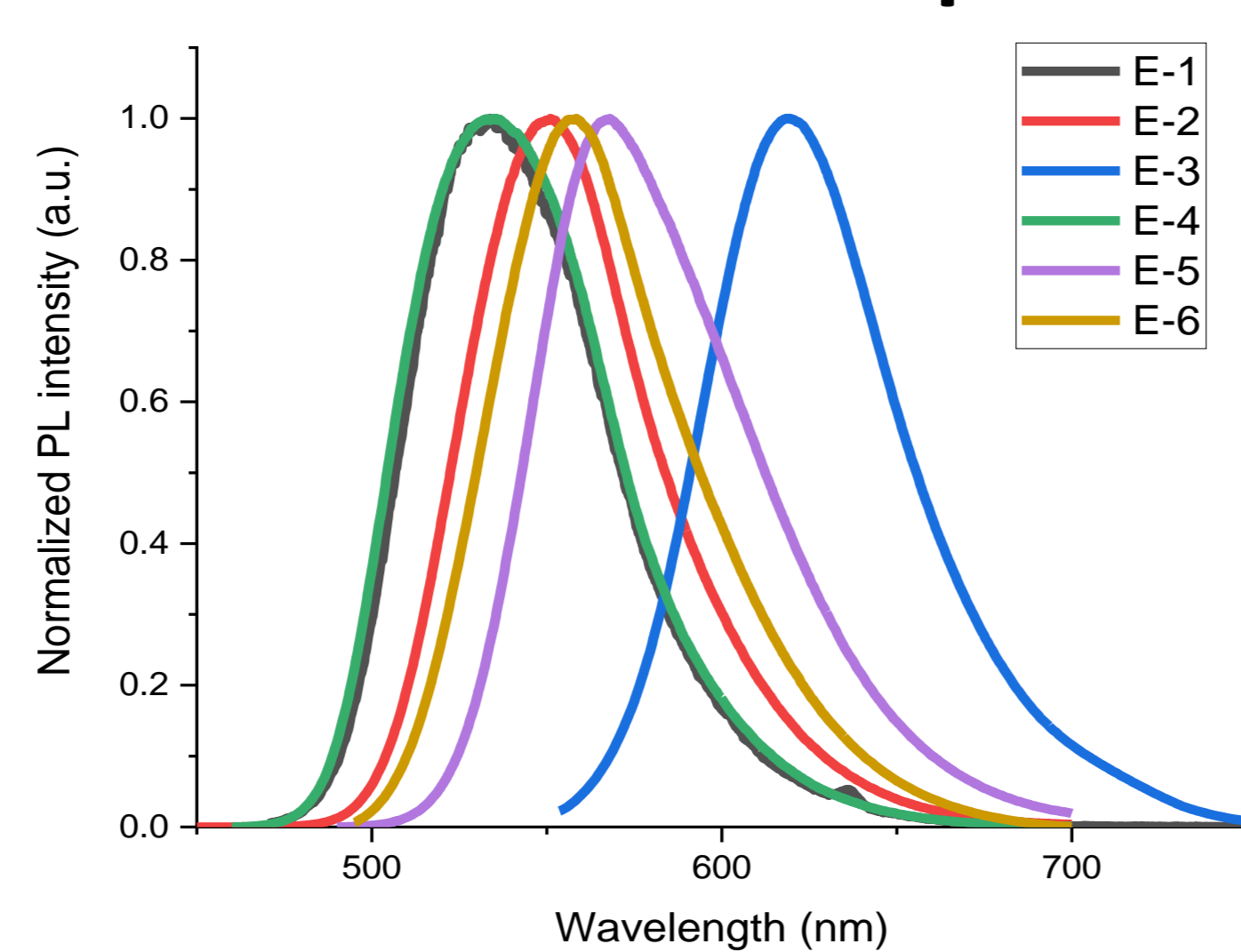


## Photophysical properties & OLED device performances

### Normalized UV-Vis absorption



### Normalized PL spectrum



## Conclusions

We have successfully developed an eco-friendly approach for synthesizing a range of 4,7-Distyrylbenzo[c][1,2,5]thiadiazole (**DS-BTD**) fluorescent emitters using a solvent-free Horner–Wadsworth–Emmons (HWE) reaction. By simply grinding tetraethyl(benzo[c][1,2,5]thiadiazole-4,7-diylbis(methylene))bis(phosphonate) with a carbonyl compound in the presence of potassium tert-butoxide, we achieved high isolated yields. Furthermore, we explored the photophysical properties of six fluorescent emitters (**E1–E6**), which exhibited emission maxima at 533, 551, 620, 545, 568, and 558 nm. This pioneering, sustainable hand-grinding HWE method paves the way for designing and synthesizing **DS-BTD**-based emitters in a greener, more efficient manner.

