



# Synthesis and characterization of dumbbell-like BTD-based derivatives to engineer organic building blocks in solid-state

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## ABSTRACT

Four BTB-derivatives **4**, **5**, **7** and **8** were synthesized and characterized by using solution NMR, FTIR and HRMS. In this study, BTB-central cores were supported on trityl type fragments in order to evaluate the influence of these groups prone to aggregation through interdigitation in the consolidation of ordered solids. Structural variation, between compounds **4–5** and **7–8**, was selected by introducing aromatic phenyl rings at positions C-4 and C-7 of the BTB central core in order to increase the stackable surface. Crystals of compounds **4** and **5** were obtained and solved in the  $C2/c$  and  $P2_1/c$  space groups, respectively. Both crystalline arrays are dominated by C–H $\cdots\pi$  and  $\pi$ -stacking interactions, desirable features for the bottom-up construction of highly polarizable organic crystals. The featured compounds with a dumbbell-like structure could be useful as scaffolds for self-assembled crystalline materials such as solid organic semiconductors.

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## 1. Introduction

Benzothiadiazole (BTB) derivatives have received much attention during the last decade due to their biological (antiviral, antibacterial, fungicide and controlling plant growth) [1] and remarkable photophysical properties (strong electron acceptor [2] and luminescent behavior [3]). BTB-containing derivatives have been used in combination with different  $\pi$ -extended compounds; in particular, 4,7- $\pi$ -extended-BTB derivatives are promising scaffolds due to their synthetic feasibility based on classical metal-mediated cross-coupling methodologies [4]. The characteristic photophysical properties of BTB-derivatives have allowed to

applied them as fluorescent probes for cellular imaging as organic polymeric dots [5], fluorescent two-photon absorption (TPA) dyes [6], electrogenerated chemiluminescence derivatives [7], organic optoelectronic materials [8], mesoporous COF's [9], and MOF's [10], also as electron-conducting pyrene-fused azaacenes [11].

In this sense, several organic chromophores supported on  $\pi$ -conjugated molecules have been used in various organic electronics [12–17]. However, only a few molecular building blocks have been explored in this area, among others we can find: quinoxalines, benzimidazoles, BTB-derivatives, and certain types of polymers [18–21]. These building blocks displayed some interesting capabilities such as high potential for reduction and electronic affinity (EA); the HOMO/LUMO energy levels of  $\pi$ -conjugated molecules depend on electron affinity and ionization potential (IP), which can be modulated by chemical functionalization. Among their most relevant characteristics we can find its reproducibility and synthetic versatility, facile processability and incorporation into thin-films, enhanced solubility as well as self-assembly in the solid-state.

In general, organic materials exhibit weak van der Waals interactions resulting in wide valence-conduction band gaps, strong

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