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

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Abstract

Four BTD-derivatives **4**, **5**, **7** and **8** were synthesized and characterized by using solution NMR, FTIR and HRMS. In this study, BTD-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 BTD central core in order to increase the stackable surface. Crystals of compounds **4** and **5** were obtained and solved in the C2/c and P2₁/c space groups, respectively. Both crystalline arrays are dominated by C-H···π and π-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.

Keywords

BTD Derivatives; organic semiconductors; SXRD; molecular crystals; solid-state selfassembly

1. Introduction

Benzothiadiazole (BTD) 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]). BTD-containing derivatives have been used in combination with different π extended compounds; in particular, 4,7- π -extended-BTD derivatives are promising scaffolds due to their synthetic feasibility based on classical metal-mediated cross-coupling methodologies [4]. The characteristic photophysical properties of BTD-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 π -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 found: quinoxalines, benzimidazoles, BTD-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 π -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 thinfilms, 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 interactions between charge carriers and the lattice due to low dielectric constants, high susceptibility to defects formation, and a strong dependence on processes taking place at the interface with dielectrics. In order to manipulate the self-assembly of organic molecules, and to modulate the photophysical properties of molecular materials in different phases of condensed matter, it is necessary to understand the molecular structure as well as intra- and intermolecular interactions that govern their solid-state organization (single crystals, polycrystalline solids, amorphous solids or thin films).

In recent years, dumbbell-like molecules have been used in the design, synthesis and dynamic characterization of amphidynamic crystals; built with molecular components which create an ordered rigid framework in combination with structural elements that are able to experience fast internal rotational motion [22]; however, a common feature in this systems is the appearance of interdigitation between molecular components *via* C-H··· π and π -stacking interactions [23], an interesting structural characteristic that that may be applied in the development of organic semiconductors. Herein, we explore the self-assembly of BTD derivatives with dumbbell-like molecular architectures, following interdigitation strategy for the bottom-up construction of organized solids. The absorption profiles of these in solution are relatively insensitive to the nature of the flanking groups and the electronic excitations (TDDFT).

2. Materials and methods

2.1 Materials

Starting materials were purchased from commercial suppliers and used as received. Reagent-grade solvents were fractional distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium-benzophenone in a continuous still under nitrogen atmosphere. Sonogashira cross-coupling reactions were carried out under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC-sheets ALUGRAM XtraSIL G/UV silica gel 60 with fluorescent indicator. Column chromatography was performed using silica gel (230-400 mesh) as stationary phase.

Melting points were measured in a Barnstead Electrothermal 9300 apparatus and are uncorrected. IR experiments were registered in a PerkinElmer Spectrum 400 spectrometer; the signals are reported in wavenumber v (cm⁻¹). NMR experiments were recorded in CDCl₃ in a Varian MR-400 instrument. All the chemical shifts are reported in ppm with respect to TMS using residual solvent as reference. The coupling constants are reported in Hz. Signals multiplicities are reported as: single (s), doublet (d), doublet-doublet (dd), triplet (t) and multiplet (m). High resolution mass spectra were obtained with an Agilent G1969A spectrometer. Absorption studies were performed on a UV/VIS Lambda 35 Perkin Elmer spectrophotometer. The spectroscopic data of BTD-derivatives were determined on solutions prepared by dissolving crystalline compounds in CHCl₃ and toluene. Stock solutions (1 x 10^{-4} M) were prepared and diluted to appropriate concentrations for determination of absorbance.

2.2. Synthetic procedures

General synthetic procedure for Sonogashira cross-coupling reactions.

A solution of BTD core (1 mmol), trityl type derivative (2 mmol), $Pd(PPh_3)_2Cl_2$ (6 % mmol), CuI (10 % mmol), Et₃N (1.5 mL) in THF (50 mL) was stirred and refluxed for 3 or 4.5 h under nitrogen atmosphere. After this time, the reaction mixture was cooled down to room temperature, quenched with NH₄Cl saturated and extracted with methylene chloride (3 x 30 mL), the combined organic portions were dried over anhydrous Na₂SO₄ and evaporated to dryness under vacuum. The crude products were purified by column chromatography with silica gel as stationary phase and hexanes:ethyl acetate as eluent.

4,7-bis(3,3,3-triphenylprop-1-yn-1-yl)benzo[c][1,2,5]thiadiazole (4).

White crystalline solid (0.50 g, 75 %). Melting point: 251 – 252 °C. FTIR-ATR (v, cm⁻¹): 3050, 3014, 2188, 1588, 1486, 1442, 1336, 1176, 1044, 1030, 880, 840, 756, 694, 634, 540. ¹H NMR [400 MHz, CDCl₃] (δ, ppm): 7.69 (s, 1H, H-3), 7.49-7.45 (m, H*m*, 6H), 7.39-7.34 (m, H*o*, 6H), 7.33-7.26 (m, H*p*, 3H). ¹³C NMR [100 MHz, CDCl₃] (δ, ppm): 155.1 (C-1), 145.1 (C*i*), 132.1 (C-3), 129.4 (C*m*), 128.3 (C*o*), 127.1 (C*p*), 117.5 (C-2), 103.8 (C-5), 81.6 (C-4), 58.6 (C-6). HRMS (ESI-TOF): Calculated for C₄₈H₃₃N₂S, 669.2358. Found, 669.2356 [M⁺+H⁺].

4,7-bis((triphenylsilyl)ethynyl)benzo[c][1,2,5]thiadiazole (5).

Yellow crystalline solid (0.56 g, 80 %). Melting point: 204 – 205 °C. FTIR-ATR (v, cm⁻¹): 2948, 2922, 2846, 2134, 2048, 1718, 1480, 1422, 1266, 1182, 1106, 1074, 958, 690, 494. ¹H NMR [400 MHz, CDCl₃] (δ, ppm): 7.84-7.80 (m, H-3, Ho, 7H), 7.51-7.42 (m, Hm, Hp,

9H). ¹³C NMR [100 MHz, CDCl₃] (δ, ppm): 154.7 (C-1), 135.9 (Co), 133.3 (C-3), 133.1 (Ci), 130.3 (Cp), 128.3 (Cm), 117.6 (C-2), 104.4 (C-5), 98.9 (C-4). HRMS (ESI-TOF): Calculated for C₄₆H₃₂N₂SSi₂, 701.1897. Found, 701.1900 [M⁺+H⁺].

4,7-bis(4-(3,3,3-triphenylprop-1-yn-1-yl)phenyl)benzo[c][1,2,5]thiadiazole (7).

Yellow crystalline solid (0.51 g, 63 %). Melting point: 270 – 272 °C. FTIR-ATR (v, cm⁻¹): 3044, 3006, 2270, 2232, 1588, 1482, 1442, 1172, 1064, 1002, 880, 846, 802, 752, 694, 636, 520. ¹H NMR [400 MHz, CDCl₃] (δ, ppm): 7.87 (d, *J* = 8.6 Hz, H-6, 2H), 7.79 (s, H-3, 1H), 7.70 (d, *J* = 8.6 Hz, H-5, 2H), 7.36-7.21 (m, H*o*, *m*, *p*, 15H). ¹³C NMR [100 MHz, CDCl₃] (δ, ppm): 154.0 (C-1), 144.6 (C*i*), 136.2 (C-4), 132.7 (C-3), 132.0 (C-5), 130.9 (C-6), 129.4 (C*m*), 128.3 (C*o*), 128.1 (C-7), 127.3 (C*p*), 123.0 (C-2), 103.4 (C-9), 84.4 (C-8), 56.4 (C-10).

4,7-bis(4-((triphenylsilyl)ethynyl)phenyl)benzo[c][1,2,5]thiadiazole (8).

Yellow crystalline solid (0.58 g, 68 %). Melting point: 258 – 259 °C. FTIR-ATR (v, cm⁻¹): 3052, 2998, 2062, 1576, 1546, 1464, 1424, 1278, 1108, 1002, 878, 802, 688, 600, 500. ¹H NMR [400 MHz, CDCl₃] (δ, ppm): 7.88 (d, *J* = 8.5 Hz, H-6, 2H), 7.80 (s, H-3, 1H), 7.71 (d, *J* = 8.5 Hz, H-5, 2H), 7.67 (dd, *J* = 7.9, 1.4 Hz, Ho, 6H), 7.50-7.38 (m, Hm, Hp, 9H). ³C NMR [100 MHz, CDCl₃] (δ, ppm): 153.8 (C-1), 136.1 (C-4), 135.6 (Co), 132.5 (C-3), 132.2 (C*i*), 131.9 (C-5), 130.8 (C-6), 130.3 (C*p*), 128.1 (C*m*), 127.9 (C-7), 122.9 (C-2), 92.0 (C-9), 82.2 (C-8).

2.3 Theoretical calculations

Density functional theory computations were performed using the Gaussian 09 program [24] with the B3LYP functional and the triple-zeta quality basis set 6-311+G(d,p). The polarizable continuum model was employed for implicit solvation with the dielectric constant of chloroform.

2.4 Structural characterization.

Suitable crystals for SXRD experiments of BTD derivatives 4 and 5 were obtained during slow evaporation of p-xylenes solutions in partially open glass vials. The XRD data were collected on an Oxford Diffraction Xcalibur Atlas Gemini diffractometer with CCD area detector ($\lambda_{CuKa} = 1.54184$ Å, monochromator: graphite) at 293 (2) K for 4, and on a Bruker APEX-II CCD ($\lambda_{MoKa} = 0.71073$ Å, monochromator: graphite) at 293 (2) K for 5. CrysAlisPro and CrysAlis RED [25] software packages were used for data collection and data integration. All reflection data set was corrected for Lorentz and polarization effects. The first structure solution was obtained using the SHELXS-97 programs and then the SHELXL-97 program was applied for refinement and output data [26] by using OLEX2 software environment [27]. The programs Mercury [28] and ORTEP-3 [29] were used to prepare artwork representations. Crystallographic data are summarized in Table S2. CCDC 1560958 (4) and 1560959 (5) contains the supplementary crystallographic data for this paper, these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. See DOI: 10.1039/x0xx00000x

3. Results and Discussion

3.1 Synthesis and characterization.

BTD central core **6** and trityl type derivative **2** were synthesized according reported literature procedures in good yields [5b, 30]. BTD derivatives **4**, **5**, **7** and **8** were synthesized using Sonogashira cross-coupling reactions mediated with Pd(0) catalyst under basic conditions (Scheme 1) in moderate to good yields.



The presence of BTD-derivatives **4**, **5**, **7** and **8** was corroborated by solution NMR experiments as shown in Figure S1. All the ¹H NMR spectra showed a singlet between $\delta =$ 7.69-7.80, corresponding to the hydrogen atom (H-3) of the BTD central core; in addition, trityl type molecules appeared as multiple signals in the aromatic region of the spectrum.

For compounds **7** and **8**, ¹H NMR spectra displayed two doublets signals at *ca*. $\delta = 7.87$ (H-6) and 7.71 ppm (H-5), corresponding to the hydrogen's of the extended phenyl rings. In the case of ¹³C NMR experiments, all expected signals for each BTD derivative were observed and assigned as depicted in Figure S2. The BTD carbon atoms were observed between $\delta = 153-155$ ppm (C-1), 117-123 ppm (C-2), and 132-133 ppm (C-3), confirming the obtention of the featured compounds. FT-Infrared experiments were carried out by using ATR technique as solid samples (Figure S3); in all the cases, the most relevant bands are those derived from CAr-H stretching between 3000-2900 cm⁻¹, as well as the bands corresponding to substituted alkyne -C=C- stretching in the range of 2260 to 2100 cm⁻¹. For the silylated BTD-derivatives **5** and **8**, the stretch bands –Si-C- were observed between 850-650 cm⁻¹.

3.2 UV-Vis Absorption studies and TDDFT electronic excitations

Absorption profiles of BTD-derivatives **4-5** and **7-8** are shown in Figure 1, relevant data is summarized in Table S1. BTD derivatives **4-5** and **7-8** show the typical absorption band of the BTD core around 390 nm in both solvents (there is no evidence of aggregate formation in the selected solvents).



Figure 1. Absorption profiles of BTD-derivatives 4-5 and 7-8.

Molecules in solution display absorption spectra where the features of the BTD core persist, being remarkably insensitive to functionalization. We can ascribe this behavior to two main factors: (i) the amphidynamic nature of these compounds lead to different regimes of rotation between the central core and the bulky flanking groups, such difference may hinder conjugation with the extended π -system of the lateral branches; and (ii) the phenyl rings of the potentially more conjugated systems **7-8** are sterically hindered and thus π -overlap suboptimal. However, conjugation can be present in the solid-state if rotation is suppressed by densely packed environments. To estimate this hypothesis we carried out density functional theory (DFT) computations of BTD derivatives **4-5** and **7-8**.

Molecular geometries were optimized with the B3LYP functional and the 6-311+G(d,p) basis set, using the polarizable continuum model for implicit salvation, with the dielectric constant of CHCl₃. On top of the optimized geometries, TDDFT calculations were applied to estimate vertical excitation energies, with the same basis and salvation scheme used for

optimization (Figure 2). The lowest 20 singlet states derived from the computation were kept for inspection. The main features we observe in this study are: a) for all systems, the main excitation is HOMO \rightarrow LUMO+1 and the corresponding absorption profiles are insensitive to the lateral groups in good agreement with experimental data, and b) for the optimized structures, vertical excitation is predicted to shift slightly toward red as conjugation increases. Their implementation of molecular semiconductors in optoelectronic devices relies on the match between the working function of the chosen electrode with the frontier orbital energies of the material. Thus, these parameters are of special significance as they will impact the efficient injection of charges.



Figure 2. Main TDDFT excitations of BTD derivatives **4-5** and **7-8**. Transition energies are shown along with the orbitals involved with 0.04 isosurfaces. Computed at the TDDFT B3LYP 6-311+G(d,p) in implicit chloroform.

3.3 Structural analyses of BTD derivatives 4 and 5

The weak intermolecular interactions holding together make the hoping mechanism of carrier transport dominant. Tailored self-assembly leading to controlled aggregation of pure and dense solid is a desirable characteristic in the development of organic semiconducting solids for organic electronics; by using BTD derivatives with dumbbell-like molecular architectures it is possible to leverage the interdigitation of trityl-like groups to tailor aggregation into compact, solvent-free organic solids with heterocyclic units such as benzothiadiazole and its π -extended derivatives.

Molecular structure of BTD derivative **4** was solved in the monoclinic space group C 2/c with Z = 8 and Z' = 1 (Figure 3A). The measured angles (<C6-BTD centroid-C6', 175.8 °) and (<C6-C2-C2'-C6', 93.6 °) confirmed that the 4,7-diethynylbenzo[*c*][1,2,5]thiadiazole axle was slightly deviated from linearity. Aromatic trityl rings are partially eclipsed and presented lower angles than those expected for a tetrahedron (< *Ci*-C6-BTD centroid, 105.3 °, 107.7 ° and 110.0 °), which is an indicative for the presence of phenyl embrace interactions. Therefore, π -stacking interactions established between adjacent aromatic trityl rings [C-H… π , 2.85 and 2.90 Å] dominate the crystal packing of BTD derivative **4**, these interactions connected neighboring BTD molecules along the crystallographic *bc* plane forming a 2D arrangement complemented by S… π [3.40 Å] (Figure 3B). The inclusion of a BTD central core favors a densely packed supramolecular self-assembly as shown in figure 3C, this molecular organization could enhance electron delocalization over different modes and axles, a desirable characteristic to increase electron delocalization in organic semiconductive materials [31].



Figure 3. A) Crystalline structure with unit cell (thermal ellipsoids are drawn at 30 % probability level for all atoms except hydrogen), B) π -interactions between adjacent BTD molecules (phenyl embraces), and C) supramolecular arrangement found in BTD derivative **4** (hydrogen atoms were omitted for clarity purposes).

For BTD-derivative **5**, the molecular structure was solved in the monoclinic space group P $2_1/c$ with Z = 4 and Z' = 1 (Figure 4A). In comparison with BTD-derivative **4**, introduction of a silicon atom produced a larger distance between the BTD central core and trityl fragments [C6-C2 4.11 Å for **4**, and Si-C2 4.46 Å for **5**]; as expected, this structural modification was reflected in a more distorted 4,7-diethynylbenzo[*c*][1,2,5]thiadiazole axle, as verified by the measured angles [<Si-BTD centroid-Si', 176.3 ° and <Si-C2-C2'-Si'. 136.9 °] [32]. Analogously, the main interactions found in BTD-derivative **5** were C-H… π [2.80 Å]) as well as complementary four phenyl embraces (4PE) between neighboring trityl fragments [2.89 and 2.90 Å] (Figure 4B). These π -interactions produced that the BTD-

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derivative molecules being stacked in an antiparallel mode, creating a 2D layer arrangement that grows along the crystallographic a axis. While the phenyl embraces connect different 2D-layers (that are rotated 82 ° relative to the crystallographic c axis) favoring a less dense supramolecular array as shown in Figure 4C.



Figure 4. A) Crystalline structure with unit cell (thermal ellipsoids are drawn at 30 % probability level for all atoms except hydrogen), B) π -interactions (C-H··· π and phenyl embraces), and C) supramolecular arrangement found in BTD derivative **5** (hydrogen atoms were omitted for clarity purposes).

3.4 Hirshfeld Surface Analysis of BTD derivatives 4-5.

An interesting approach to explore insights into crystal packing has been the so-called Hirshfeld surface analysis; in brief, it provides a way to define the boundary of a molecule within a crystal in terms of electron density. In this context, non-covalent intermolecular interactions within a crystalline network can be analyzed and quantified by Hirshfeld

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Surface Analysis (HSA) deriving 2D fingerprintplots; surfaces were generated using CrystalExplorer software based on experimental CIF data employing the BLYP 6-31G(d) scheme [33-36].

Both BTD-derivatives **4** and **5** display different *edge-to-face* stacking due to diverse phenyl embraces; particularly for compound **5**, the inclusion of the silicon atoms favored the appearance of these interactions. In general, is expected that increasing total stackable surface through the covalent linkage of additional aromatic results could result in prevailing extensive stacking as in compounds **7** and **8**. Although no high quality single crystals for BTD-derivatives **7** and **8** have been obtained, crystallization attempts with benzene yielded weakly diffracting crystals that could not be further refined to acceptable publication standards; therefore, consequences of increasing the stackable surface in a molecule could not be evaluated in the solid state.

Hirshfeld surfaces were used to analyze the nature of contacts present in each BTDderivative; non-classical H-bonding interactions were distinguished for both compounds, in the case of **4**, S- π contacts were found; overall, near all contacts involve hydrogen atoms which make 92.9 % (**4**) and 93.1 % (**5**) of the total Hirshfeld surfaces. Accordingly, Hisrhfeld surfaces mapped over shape index indicate the presence of complementary stacking interactions established by electron-deficient BTD rings as well as between aromatic trityl fragments. Decomposed Hirshfeld 2D fingerprint plots show that H····H is the main interaction in the crystal packing of BTD-derivatives **4** and **5** (figures 5-6), supported by non-classical hydrogen-bonding interactions (C-H···*π*). Extensive stacking is present in both crystals (estimated as the sum of the C---C, C---S, C---N and N---N intermolecular contact areas: 7.1 % for **4**, and 3.7 % for **5**); nevertheless, the presence of the

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silicon atoms decrease the stacking percentage by increasing C-H $\cdots \pi$ interactions, this behavior could affect the electronic properties of the studied derivatives.



Figure 5. Hirshfeld surfaces and decomposed 2D fingerprint plots of BTD-derivative 4.



Figure 6. Hirshfeld surfaces and decomposed 2D fingerprint plots of BTD-derivative 5.

Conclusions

Four novel BTD-derivatives with dumbbell-like shape were synthesized in moderate to good yields starting from readily available molecular units. Two unreported crystal structures of BTD-derivatives **4** and **5** were obtained and described; both crystal packings are dominated by cooperative phenyl embraces (C-H… π) and π -stacking interactions, favoring interdigitation between BTD cores and aromatic trityl rings and producing highly dense supramolecular arrangements, which confirms the applicability of the interdigitation criterion for the self-assembly of organic solids.

These systems could be useful as candidates for organic semiconductor materials with extended electron delocalization; the studied BTD-derivatives possess desirable characteristics for this purpose, such as synthetic accessibility, solution processability and supramolecular self-assembly *via* H-bonding combined with π -stacking. These results open the possibility to vary the molecular architecture introducing electron-donor or electron-withdrawing groups at the BTD-central core, in order to fine-tune the semiconductor character. Experimental work to explore electronic properties of these systems is currently underway, trying to produce solution-processable organic semiconductor materials.

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Highlights

Four novel BTD-based organic building blocks were synthesized and characterized.

BTD-derivatives are synthetically accessible and solution processable.

Crystal structures **4** and **5** were solved in the C2/c and P2₁/c space groups.

Self-assembly is directed by non-classical H-bonding and π -stacking.

Interdigitation between BTD-based dumbbell-like molecules was found.