Synthesis, photophysical, electrochemical and single-crystal x-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile

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ABSTRACT
The optical characteristics, redox properties, thermogravimetric stability and single-crystal X-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile are examined using ultraviolet–visible spectrophotometry, cyclic voltammetry, thermal gravimetric analysis–diffraction scanning calorimetry analysis, single-crystal X-ray diffraction and density functional theory calculations. Evidently, the crystal structure of compound 6 is sustained by a number of weak nonconventional intermolecular forces of attraction such as C-H…N, C-H…π donor–acceptor interactions.

Introduction
2,1,3-Benzothiadiazole (BTD) derivatives are outstanding compounds because of their electron-withdrawing properties and have been used as units of electron acceptors for conducting materials. BTD containing compounds are expected to afford well ordered...
crystal structures because of their highly polarized properties, leading to intermolecular interactions such as heteroatom constants or \( \pi-\pi \) interactions.\(^2\) BTD derivatives are also known as efficient fluorophores.\(^3\) In addition to that, polymers containing BTD units have been used as luminescent compounds in electroluminescence devices.\(^4\) The highly electron-deficient BTD unit is one of the most popular building blocks in organic electronics. BTD can conjugatively link with an electron-rich molecule to form low bandgap functional polymers or small molecules, and materials prepared in this manner showed usefulness in organic light-emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs), light harvesting, and other optical or electronic functional devices.\(^5\)

For molecularly hybridized push–pull type materials, where the alternating arrangement of electron-rich and electron-deficient units along the \( \pi \)-conjugated backbone effectively controls the frontier molecular orbitals, BTD is often the electron-deficient unit of choice.\(^6\) Moreover, to further fine-tune the frontier molecular orbital as well as other important materials parameters such as solubility and crystallinity, chemical modifications of the BTD unit have attracted much interest.\(^7\)

Recently, a BTD-based small molecule and its selenium analog showed good efficiency in heterojunction solar cells and photovoltaic cells, respectively.\(^8\) Alternatively, BTD-based small molecules are becoming increasingly popular for devising hybrid solar cells, because of high electron mobility and excellent chemical and physical stability of inorganic semiconductors.\(^9\) Recent studies have demonstrated that formation of self-assembled monolayer of conjugated molecules on the surface of the inorganic semiconductors can lead to the formation of interfacial dipoles, which in turn can improve the work function of substrate materials.\(^9\) These types of small conjugated molecules can act as interfacial modifiers (IMs), which enhance charge injection from metals into organic materials. Yu and coworkers have prepared and examined one of such IMs having cyano-acrylic acid as the anchoring group, and it showed an increase in electron affinity at the polymer–inorganic semiconductor interface and formation of dipoles, which are oriented away from the semiconductor surface.\(^10\)

In this communication, we report the synthesis and photophysical study of dithienobenzothiadiazole \( \text{4} \), dithienobenzoxadiazole \( \text{12} \), and a new conjugated compound having a cyano-benzylic anchoring group, \( (Z)\)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile \( \text{6} \). These compounds were successfully prepared by a multistep synthetic route. All the molecules consisted of donor–acceptor segments. The molecular structure of compound \( \text{6} \) was further confirmed by single-crystal X-ray diffraction study. The thermal and electrochemical properties of synthesized compound \( \text{6} \) were studied.

**Results and discussion**

The BTD-based novel highly conjugated molecule \( \text{6} \) is synthesized in five steps (Scheme 1).\(^10\) In the first step of the synthesis ortho-phenylenediamine \( \text{1} \) was treated with thionyl chloride to achieve 2,1,3-benzthiadiazole \( \text{2} \) in 36\% yield, which was further treated with \( \text{Br}_2 \) in HBr (48\% aqueous) to get 4,7-dibromo-2,1,3-benzothiadiazole \( \text{3} \) in 68\%
yield. Compound 3 was further treated with 2-tributyldithiophene in the presence of PdCl$_2$(PPh$_3$)$_2$ to get compound 4 in 49% yield. Monoformylation of compound 4 gives compound 5 in 56% yield, which was subjected to Knoevenagel condensation reaction with benzyl cyanide to get the desired compound 6 in 62% yield.

In addition, we have also synthesized oxadiazole based compound 12 from ortho-nitroaniline 7 in a five-step synthetic strategy (Scheme 2). Ortho-nitroaniline is oxidatively cyclized to benzofuroxan 8 in excellent yield with commercial bleach, and the latter is used as wet cake without drying. Compound 8 was deoxygenated to 2,1,3-benzooxadiazole 9 with triethylphosphite. Compound 9 is purified by vacuum sublimation. Bromination with molecular bromine in hydrobromic acid (48% aqueous) affords the tetrabromo compound 10, which is further treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in tetrahydrofuran (THF) at room temperature for the hydrodebromination. The resultant compound

Scheme 1. Synthesis of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile.

Scheme 2. Synthesis of dithienobenzooxadiazole.
11 is treated with 2-tributylstannylthiophene in the presence of PdCl$_2$($\text{PPh}_3$)$_2$ to get compound 12 in 47% yield.

**Single-crystal X-ray diffraction (SCXRD)**

The molecular structure for compound 6 was elucidated by SCXRD (Fig. S1). Crystals of compound 6 were obtained from ethyl acetate (solvent). A suitable crystal was selected and data were collected using CuKα ($\lambda = 1.5418$ Å) radiation on an Xcalibur-Eos-Gemini diffractometer. The crystal was kept at 293 K during data collection. The structure was solved and refined using Olex2.$^{[12]}$ The structure was solved with the Superflip$^{[13]}$ structure solution program using charge flipping and refined with the ShelXL$^{[14]}$ refinement package using least squares minimization. Table S1 summarizes the crystal structure and refinement data whereas Tables S2 and S3 summarize selected bond lengths and bond angles, respectively.

The X-ray structure of compound 6 clearly suggests that it crystallizes in monoclinic system with space group P2$_1$/c. Asymmetric unit of this contains full molecules and there are four such molecules present in the unit cell, as shown in Fig. S2. The unit cell parameters for this are $a = 16.9905$ (7), $b = 7.2712$ (3), $c = 16.5005$ (7) and $\alpha = 90.00$, $\beta = 107.130$ (4), and $\gamma = 90.00$.

Notably, the presence of various polar subunits in the molecular framework of compound 6 induces conformational changes in the molecule that apparently changes the nature and number of donor–acceptors sites. For instance, all the heterocyclic and carbocyclic rings present in compound 6 are not coplanar, making differential dihedral angles with one another; for example, a dihedral angle between the least squares planes drawn through peripheral thiophene ring and adjacent benzothiadiazole ring is estimated as 24.24°, whereas a dihedral angle between the least squares planes drawn through internal thiophene ring and adjacent benzothiadiazole ring is estimated 23.18°, and vice versa. In fact, the crystal structure of compound 6 is sustained by a number of weak nonconventional intermolecular forces of attraction such as C-H…N, C-H…π donor–acceptor interactions as shown in Fig. 1.

![Figure 1. Intermolecular force of attraction in compound 6.](image)

Interestingly, C-H…N donor–acceptor interaction limits the growth of molecular packing along the c axis by forming a closed contact. However, C-H…π donor–acceptor interactions arranged the molecules of 6 along the b axis form a zigzag network as shown in Fig. 2.
Photophysical and electrochemical properties of compounds 4, 6, and 12

The photophysical properties of compounds 4, 6, and 12 were studied. The absorption and emission spectra of 4, 6, and 12 were carried out in methanol (Fig. 3). All these compounds possess the dual-band nature; one lower energy band ranges between 250 and 340 nm, which is due to π–π* transition of the conjugated backbones, while a second higher energy band ranges from 400 to 520 nm due to the charge transfer transition between D→A. Compounds 4, 12, and 6 show absorption maxima at 441, 436, and 463 nm with Stokes shifts of 159, 146, and 142. The lower energy charge transfer leads to red shift (bathochromic shift) while going from 4 (441 nm) to 6 (463 nm).

Figure 3. (a) Absorption spectra and (b) emission spectra of 4, 6, and 12 (red, black, and blue solid lines) measured in methanol containing $3.33 \times 10^{-7}$, $3.33 \times 10^{-6}$, and $6.67 \times 10^{-7}$ mol respectively. Photographs of 4, 6, and 12 in methanol under a 365-nm UV lamp.

The band-gap calculation for all three compounds (4, 6, and 12) was carried out using density functional theory\textsuperscript{[15]} as well as electronic spectra. As can be seen in Table 1, there is a slight difference in $E_{\text{band-gap}}$ (theoretical) and $E_{\text{band-gap}}$ (optical) for compounds 4, 6, and 12.
Cyclovoltammetry experiment data for compound 6

The electrochemical properties of compound 6 were studied, in which ferrocene was used as an internal standard. According to Fig. 4, cyclic voltammograms exhibit an irreversible oxidation curve with no reduction wave deducted. The highest occupied molecular orbital (HOMO) was then calculated from the oxidation potential ($E_{\text{oxi}}$), according to the formula of $E_{\text{HOMO}} = -[(E_{\text{oxi}} - E_{\text{Fc}}) + 4.8 \text{ eV}]$, where $E_{\text{Fc}}$ denotes the measured oxidation potential of ferrocene and 4.8 eV is the absolute oxidation potential value of ferrocence under vacuum. Calculated value of $E_{\text{HOMO}}$ for compound 6 is $-5.86 \text{ eV}$ and value of $E_{\text{LUMO}}$ is $-3.59 \text{ eV}$, which is calculated from the formula $E_{\text{LUMO}} = [E_{\text{HOMO}} + E_{\text{Optical}}]$.

![Cyclic voltammogram of compound 6](image)

**Figure 4.** Cyclic voltammogram of compound 6 in anhydrous THF containing 0.1 M tetra butylammoniumhexafluorophosphate as a supporting electrolyte with glassy carbon as working electrode, platinum as counterelectrode, and nonaqueous Ag/AgNO₃ as reference electrode.

Thermogravimetric analysis data of compound 6

Compounds 4, 6, and 12 showed reasonably good thermal stabilities up to 450 °C. The thermogravimetric analysis (TGA) shows high stability of compound 6 (Fig. 5). The DTA curve shows a phase transition at 172.6 °C, which is also in accordance with the melting point of compound 6 (173–175 °C). It shows thermal decomposition at 429.3 °C as suggested by the DTG curve.
Conclusion

In this communication we have reported the synthesis of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile. The synthesized compound was well characterized by \(^1\)H and \(^{13}\)C NMR, mass spectra, IR spectral data, and single-crystal X-ray diffraction analysis data. This compound was screened for its band-gap properties using absorption and emission spectral data and cyclic voltammograms. The experimental value of the band gap was compared with the theoretical band gap. Thermal stability was studied using thermogravimetric analysis. In summary, the synthesized new class of donor–acceptor compound, featuring a benzothiadiazole electron-accepting unit, displays distinct optical, electrochemical, and thermal properties. The experimental data show that compound 6 could be a potential candidate as an interfacial modifier for photovoltaic devices.

Experimental

All the chemicals were reagent grade and used as purchased. Moisture-sensitive reactions were performed under an inert atmosphere of dry nitrogen with dried solvents. Reactions were monitored by thin-layer chromatographic (TLC) analysis using Merck 60 F\(_{254}\) aluminium-coated plates and the spots were visualized under ultraviolet (UV) light. Column chromatography was carried out on silica gel (60–140 mesh). All melting points were determined using Thiele’s tube using paraffin oil and are uncorrected. IR spectra were recorded on a Shimadzu Prestige 21 spectrometer. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument. NMR spectra were recorded on a Bruker Avance-III 400 spectrometer in CDCl\(_3\). Diffraction data were collected using CuK\(_\alpha\) (\(\lambda = 1.5418\) Å) radiation on an Xcalibur, Eos, Gemini diffractometer. CV data were obtained with CH Instruments.
model of CHI 600C with three electrode (glassy carbon as the working electrode, platinum as the counter electrode, and nonaqueous Ag/AgNO₃ as the reference electrode) cells in anhydrous THF solution containing 0.1 M tetra-n-butylammoniumhexafluorophosphate at a scan rate of 100 mV s⁻¹ under nitrogen atmosphere. DFT calculations were performed using Gaussian 09 with B3LYP functional and 6-311G (++) basis set.[15]

**Compounds 2–6**

Compounds 2–5 were prepared by the corresponding literature methods.[10] Compound 2 yield: 36%; mp: 43–45 °C. Compound 3 yield: 68%; mp: 191–194 °C.

**4,7-Dithien-2-yl-2,1,3-benzothiadiazole 4**

4,7-Dibromo 2,1,3-benzothiadiazole (1 g, 3.4 mmol) is taken in dry THF (25 mL). Add to this 2-tributylstannylthiophene (2.37 mL, 7.48 mmol) and PdCl₂(PPh₃)₂ (0.11924 g, 0.17 mmol) and reflux for 10–12 h under nitrogen atmosphere. After cooling the reaction mixture, quench with water and extract in EtOAc. Purify using column chromatography on alumina using EtOAc / petroleum ether (1:20) as eluent and further recrystallize in petroleum ether.

Yield: 49%; mp: 123–124 °C. IR (KBr): 2978, 2885, 2389, 1725, 1562, 1481, 1013, 823, 772, 692. ¹H NMR (400 MHz, CDCl₃): δ 7.22–7.24 (dd, J = 5.2, 4 Hz, 2H), 7.47–7.48 (dd, J = 5.2, 1.2 Hz, 2H), 7.88 (s, 2H), 8.13–8.14 (dd, J = 3.6, 1.2 Hz, 2H). ¹³C NMR: δ 125.8, 126.0, 126.8, 127.5, 128.0, 139.3, 152.6. Mass (EI) m/z: 300 (M⁺, 100%), 299 (90%), 81 (15%), 68 (22%).

**5-(4-(Thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophene-2-carbaldehyde 5**

Take DMF (0.39 mL, 5 mmol) in a round-bottom flask under a nitrogen atmosphere and cool it to 0 °C. To this solution add POCl₃ (0.47 mL, 5 mmol) dropwise and stir it for 15 min at room temperature. After this add compound 4 (0.150 g, 0.5 mmol in 20 mL of DCM) and reflux the reaction mixture for 17 h. After cooling add sodium acetate (50 mL) and stir the reaction mixture for 2 h at room temperature. Extract the compound with DCM and purify by column chromatography on silica gel using EtOAc / petroleum ether (2:10) as eluent.

Yield: 56%; mp: 168–170 °C. IR (KBr, cm⁻¹): 2983, 2888, 2410, 1655, 1440, 1236, 834, 818. ¹H NMR (400 MHz, CDCl₃): δ 7.25–7.27 (m, 1H), 7.53–7.54 (dd, J = 5.2, 1.2 Hz, 1H), 7.86–7.88 (d, J = 4.4 Hz, 1H), 7.9–8.0 (d, J = 7.6 Hz, 1H), 8.02–8.04 (d, J = 7.6 Hz, 1H), 8.19–8.20 (dd, J = 3.6, 0.8 Hz, 1H), 8.23–8.24 (d, J = 4 Hz, 1H), 10.0 (s, 1H). ¹³C NMR: δ 124.3, 125.2, 127.4, 127.8, 127.9, 128.0, 128.2, 128.4, 136.8, 138.8, 143.3, 148.6, 152.4, 152.46, 183.

**(Z)-2-Phenyl-3-(5-(4-(Thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile 6**

Take a mixture of compound 5 (0.1 g, 0.305 mmol) and benzyl cyanide (0.038 g, 0.32 mmol) in 30 mL dry ethanol. To this reaction mixture slowly add a solution of Na metal (0.031 g,
1.53 mmol) in 10 mL dry ethanol. Reflux the reaction mixture for 10–12 h. After completion of the reaction distill the excess of ethanol. The crude product is purified by column chromatography on silica gel using EtOAc / petroleum ether (1:4) as eluent.

Yield: 62%; mp: 173–175 °C. IR (KBr, cm⁻¹): 2983, 2897, 2390, 2289, 1583, 1480, 1439, 828, 801, 756, 720, 690; ¹H NMR (400 MHz, CDCl₃): δ 7.23–7.25 (m, 1H), 7.38–7.42 (m, 1H), 7.45–7.51 (m, 3H), 7.68–7.70 (m, 3H), 7.73–7.74 (d, J = 4 Hz, 1H), 7.89–7.91 (dd, J = 7.6, 0.8 Hz, 1H), 7.97–7.99 (dd, J = 7.2, 0.8 Hz, 1H), 8.15–8.16 (d, J = 4 Hz, 1H), 8.21–8.22 (d, J = 4 Hz, 1H).¹³C NMR: δ 108.2, 118.3, 124.8, 125.5, 125.7, 126.6, 127.1, 127.4, 127.9, 128.1, 129.0, 129.1, 133.7, 133.8, 133.9, 138.5, 139.1, 143.7, 152.5, 152.6. Mass (EI) m/z: 427 (M⁺, 88%), 426 (59%), 400 (70%), 399 (68%), 368 (43%), 298 (63%), 133 (39%), 128 (35%).

**Compounds 9, 10, and 11**

These compounds were prepared by the corresponding literature method.[11] Compound 9: Yield: 20%; mp: 50–51 °C. Compound 10: yield: 46%; mp: 141–143 °C. Compound 11: Yield: 70%; mp: 111–113 °C.

**4,7-Di(thiophen-2-yl)benzo[c][1,2,5]oxadiazole 12**

Take compound 11 (0.2 g, 0.719 mmol), 2-tributylstannylthiophene (0.55 mL, 1.73 mmol), and PdCl₂(PPh₃)₂ (0.025 g, 0.03595 mmol) in dry THF (20 mL) under a nitrogen atmosphere. Reflux the reaction mixture for 10–12 h. After completion of the reaction, quench the reaction mixture in water and extract it with EtOAc. Purify the crude product by column chromatography on alumina using EtOAc / petroleum ether (1:20) as eluent. Yield: 47%; mp: 111–113 °C.[11] IR (KBr, cm⁻¹): 2394, 1663, 1592, 1536, 1430, 1216, 825, 711; ¹H NMR (400 MHz, CDCl₃): δ 7.22–7.24 (dd, J = 4.8, 3.6 Hz, 2H), 7.46–7.48 (dd, J = 5.2, 1.2 Hz, 2H), 7.63 (s, 2H), 8.13–8.14 (dd, J = 3.6, 0.8 Hz, 2H).¹³C NMR: δ 122.1, 126.3, 126.9, 128.6, 128.7, 137.9, 147.8. Mass (EI) m/z: 284 (M⁺, 100%), 283 (64%), 254 (35%), 253 (26%), 90 (22%), 69 (36%).

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