

Synthesis and characterization of organic light-emitting molecules possessing 3-(4-methoxyphenyl)thieno[3,2-*b*]thiophene and boron

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Abstract: The donor-acceptor (D–A) system, which is one of the main methods implemented in material chemistry, has been widely used to construct low band-gap semiconductors. It is desirable that donor molecules have π -conjugation in these structures. Thienothiophene (TT) derivatives have been used extensively as donors and are preferred in optoelectronic applications. As a strong acceptor, boron unit with a vacant p orbital is linked to donor TT groups. Bulky tetraphenylethylene (TPE) subunits were appended as end groups to afford an aggregation-induced emission (AIE).

Keywords: Thienothiophene; aggregation induced emission (AIE); organic light emitting diode (OLED); boron. ©2018 ACG Publication. All right reserved.

1. Introduction

Small molecules have attracted great interest in optoelectronic applications as important scaffolds of organic electronic materials.^{1,2} Thiophenes (Ts)³ and thienothiophenes (TTs)^{4,5} have rendered appealing optical and electronic properties, which make them potential candidates in electronics and optoelectronics; organic light-emitting diodes (OLEDs),⁶ field-effect transistors (FET),⁷ and solar cells.⁸ Thiophene rings can easily be modified, which leads to significant effect on electronic and optical properties of organic materials.^{9–11}

Unlike thiophenes, TTs have two fused thiophene rings resulting in more rigid structures with an extended π -conjugation.¹² In addition, their flat molecular structures, stabilities against chemical oxidations and intermolecular nonbonding S \cdots S interactions enhance the electrical properties. Therefore, in the last decade, fused thiophenes have been widely utilized as promising building blocks for the new class of π -conjugated systems for organic semiconductors.^{13–15} Due to the electron rich sulfur atoms incorporated into the five-membered rings, they show electron-rich properties with good electron donating abilities in optoelectronic applications.¹⁶ Moreover, their intermolecular π – π interactions, required for charge carriers and well-organized molecular packings, provide large crystalline domains.

While substituted TTs are used as donors, mesitylboron is preferred as a strong acceptor due to the fact that overlap of empty p-orbital of tricoordinate-boron with pi-orbital of TT results in a strong pi-acceptor effect on boron and extended pi-conjugation of the system.^{10,14} Enhancement of light emitting efficiency can be achieved through the incorporation of bulky tetraphenylethene (TPE)¹⁷ substituent, which induces emission via aggregation known as Aggregation Induced Emission (AIE).¹⁸

Herein, the electronic and optical properties of two type molecules (D–A–D and D–A) possessing TT donors and boron acceptors end capped with TPE bulky units are reported.

2. Experimental

2.1. Computation

Gas phase geometry optimizations were performed without any symmetry constraints at density functional theory (DFT) level using the Gaussian 09 package program.¹⁹ B3LYP²⁰ was employed with Pople's split-valence 6-31+G(d) basis set. The atom-pairwise dispersion correction (D3)²¹ with Becke–Johnson damping (BJ)²² and geometrical counterpoise correction (gCP)^{21a} was used for B3LYP functional.²³ The minima of the calculated structures were verified by analyzing the harmonic vibrational frequencies using analytical second derivatives, which have NImag=0. Solvent effect was incorporated by using self-consistent reaction field (SCRF) with a UFF parametrization of the polarizable continuum model (PCM)²⁴ as implemented in the Gaussian 09 package. Frontier molecular orbitals (FMOs) were constructed using isosurface value of 0.04 au with GaussView 5.0.

2.2. General

3-(4-Methoxyphenyl)thieno[3,2-*b*]thiophen (**1**)²⁵ and 4,4,5,5-tetramethyl-2-[4-(1,2,2-triphenylethenyl)phenyl]-1,3,2-dioxaborolane (**3**)²⁶ were prepared following the literature procedures. 3-Bromothiophene, 2-bromo-4'-methoxyacetophenone, *n*-butyllithium, diphenylmethane, 4-bromobenzophenone, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, dimesitylboron fluoride, 2-mesitylmagnesium bromide solution (1 M), bis(triphenylphosphine)palladium(II)chloride, tetrakis(triphenylphosphine)palladium(0), dichloromethane (Aldrich), trimethylborate diethyl ether, tetrahydrofuran (THF), toluene and sodium bicarbonate, *N*-bromosuccinimide (NBS) were used without further purification, except for diethyl ether and THF, which were dried over metallic sodium.

¹H and ¹³C NMR spectra were recorded on a Varian model NMR (500 MHz). Proton and carbon chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). UV-Vis measurements were studied on HITACHI U-0080D. Mass spectra were recorded on Bruker MICROTOFQ and Thermo LCQ-Deca ion trap mass instruments. Melting points of the compounds were measured by BÜCHI Melting point B-540.

2.3. Synthesis

*2-Bromo-3-(4-methoxyphenyl)thieno[3,2-*b*]thiophene (2)*: To a solution of **1** (300 mg, 1.2 mmol) in 10 mL of DMF was added NBS (230 mg, 1.33 mmol) at 0 °C. The mixture was stirred for 2 h at the same temperature and allowed to stir overnight at room temperature. It was quenched with water and the precipitate was filtered. Then, it was dissolved in DCM and extracted successively with 10% NaHCO₃(aq) and brine (3×50 mL). Column chromatography over silica gel was performed using *n*-hexane/DCM (10:1) as eluent affording a white solid in 90% yield. ¹H NMR (500 MHz, CDCl₃) 7.65 (d, *J*=8.8 Hz, 2H), 7.44 (d, *J*=5.3 Hz, 1H), 7.23 (d, *J*=5.3 Hz, 1H), 7.04 (d, *J*=8.8 Hz, 1H), 3.89 (s, 3H).

*3-(4-Methoxyphenyl)-2-(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-*b*]thiophene (4)*: **2** (200 mg, 600 μmol) and **3** (330 mg, 700 μmol) were dissolved in 32 mL of THF. To the solution were added PdCl₂(PPh₃)₂ (56.0 mg, 48.0 μmol) and K₂CO₃ (2 M, 8.00 mL). The reaction mixture was refluxed for 2 d. It was filtered through a celite pad and solvent was removed under reduced pressure. The residue was dissolved in DCM and extracted with NaHCO₃ (3×50 mL). Column chromatography over silica gel using *n*-hexane/DCM (5:1) as eluent furnished a bright green solid in 40% yield. Mp. 179 – 185 °C. ¹H-NMR (600 MHz, Acetone-*d*₆) 6.81 – 6.79 (m, 1H), 6.64 (d, *J*= 5.2 Hz, 1H), 6.54 – 6.52 (m, 2H), 6.43 – 6.40 (m, 3H), 6.35 (ddd, *J*= 8.1, 7.0, 3.4 Hz, 8H), 6.30 – 6.25 (m, 7H), 6.21 – 6.17 (m, 4H) 3.08 (s, 3H). ¹³C-NMR (150 MHz, Acetone-*d*₆) 160.17, 144.49, 144.21, 142.52, 142.51, 141.36, 139.66, 137.30, 133.80, 132.78, 132.20, 132.04, 131.99, 131.69, 131.91, 130.82, 129.33, 128.73, 128.67, 128.56, 128.29, 128.21, 127.48, 127.46, 127.42, 125.63, 120.96, 115.30, 115.13, 55.63. HRMS (*m/z*): 577.1 (M⁺).

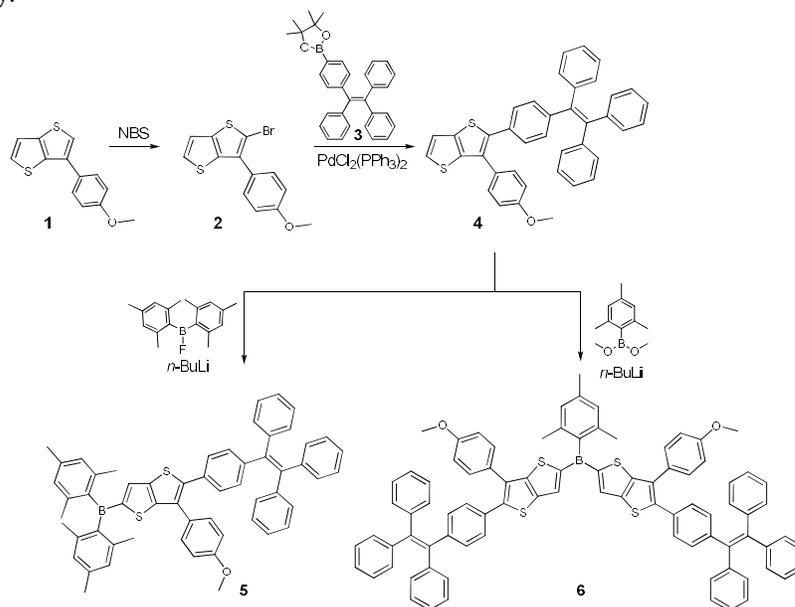
Dimesityl(6-(4-methoxyphenyl)-5-(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-b]thiophen-2-yl)boron (5): To a solution of **4** (350 mg, 60.6 μmol) in 20 mL of THF was added 360 μL of 2.5 M *n*-BuLi at -78 $^{\circ}\text{C}$ and the reaction mixture was stirred for 30 min, after which it was left stirring at room temperature for 1 h. Then, it was cooled down to -78 $^{\circ}\text{C}$ and dimesitylboron fluoride (160 mg, 60.6 μmol) was added. The mixture was stirred for 3 h at the same temperature and overnight at room temperature. The solvent was removed and the residue was dissolved in DCM. It was extracted with aqueous solution of NaHCO_3 . Column chromatography over silica gel using petroleum ether/DCM (10:1) as eluent furnished a bright green solid in 45% yield. Mp. 95.7 $^{\circ}\text{C}$. $^1\text{H-NMR}$ (500 MHz, CDCl_3) 7.58 (s, 1H), 7.32 – 7.29 (m, 2H), 7.14 – 7.08 (m, 11H), 7.07 – 7.01 (m, 6H), 6.94 (d, $J = 8.4$ Hz, 2H), 6.85 – 6.81 (m, 6H), 3.83 (s, 3H), 2.32 (s, 6H), 2.16 (s, 12H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3) 158.89, 153.02, 143.58, 143.57, 143.47, 143.24, 141.53, 140.90, 140.37, 138.57, 138.41, 132.64, 132.47, 131.45, 131.35, 131.33, 131.27, 130.20, 130.14, 129.69, 128.54, 128.15, 127.70, 127.66, 127.63, 127.28, 126.58, 126.56, 126.51, 114.06, 55.20, 30.92, 29.70, 23.51, 21.22.

Mesitylbis(6-(4-methoxyphenyl)-5-(4-(1,2,2-triphenylvinyl)phenyl)thieno[3,2-b]thiophen-2-yl)boron (6): To a solution of **4** (250 mg, 43.3 μmol) in 15 mL of THF was added 800 μL of 1.6 M *n*-BuLi at -78 $^{\circ}\text{C}$ and the reaction mixture was stirred for 30 min. Dimethoxymesityl borane (2.20 mL, 21.5 μmol , 0.1 M) was added and the reaction mixture was stirred for 3 h at the same temperature, after which it was left stirring at room temperature for overnight. The solvent was removed and the residue was dissolved in DCM. It was extracted with aqueous solution of NaHCO_3 . Column chromatography over silica gel using *n*-hexane/DCM (12:1) as eluent provided a bright green solid in 10% yield. Mp. 124 $^{\circ}\text{C}$. $^1\text{H-NMR}$ (500 MHz, CDCl_3) 7.61 (s, 2H), 7.33 (d, $J = 8.8$ Hz, 4H), 7.15 – 7.09 (m, 22H), 7.06 – 7.02 (m, 12H), 6.94 (d, $J = 8.3$ Hz, 4H), 6.88 – 6.85 (m, 6H), 3.86 (d, $J = 2.5$ Hz, 6H), 2.33 (s, 3H), 2.28 (s, 6H).

3. Results and Discussion

3.1. Synthesis

NBS mono-bromination of **1** gave rise to 2-bromo-TT (**2**) in 90% yield, which was followed by cross-coupling reaction of the product with **3** in the presence of Pd(II) catalyst leading to the formation of TPE attached TT (**4**) in 40% yield (Scheme 1). Subsequent reactions with dimesitylboron fluoride and dimethoxymesityl borane resulted in D-A (**5**) and D-A-D (**6**), end-capped with TPE in 45 and 10% yields, respectively.



Scheme 1. Synthesis of D-A (**5**) and D-A-D (**6**) compounds end-capped with TPE units.

3.2. Optical Studies

Optical studies of compounds **5** and **6** were realized in THF and on ITO (Figure 1 and 2). While λ_{\max} value of 392 nm was recorded for **5** with a D–A system in THF, D–A–D type compound **6** had the absorption wavelength of 352 nm, indicating the blue shift effect of second TT-donor (Table 1). This phenomenon can be rationalized by the decrease of acceptor efficiency of boron through the second TT-donor. On the other hand, emission wavelength of **6** (501 nm) appeared at longer wavelength than that of **5** (489 nm) resulting in a large Stokes shift of 149 nm. The same phenomenon was observed in UV-Vis investigations performed on ITO. UV-Vis absorption maxima of **5** and **6** were recorded as 406 and 361 nm, respectively. However, emission wavelengths were detected almost the same; 495 nm for **5**, and 494 nm for **6**, which rendered Stokes shifts of 89 and 133 nm, respectively.

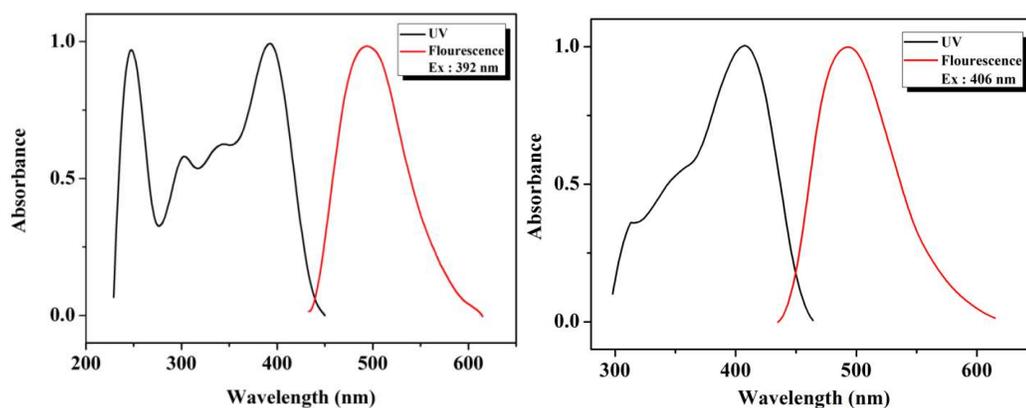


Figure 1. UV-Vis and fluorescence spectra of **5** in THF (left) and on ITO (right).

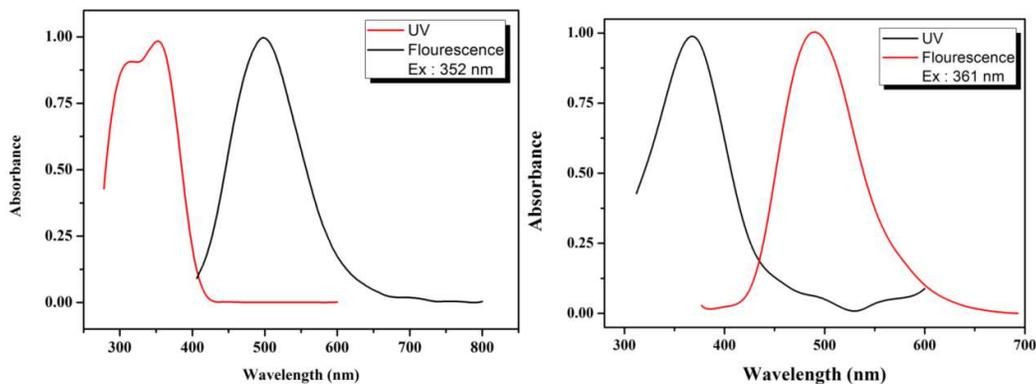


Figure 2. UV-Vis and fluorescence spectra of **6** in THF (left) and on ITO (right).

Table 1. Optical results obtained for compounds **5** and **6** in THF and on ITO.

Compound	THF		ITO	
	λ_{\max}^{abs} [nm]	λ_{\max}^{em} [nm]	λ_{\max}^{abs} [nm]	λ_{\max}^{em} [nm]
5	392 nm	489 nm	406 nm	495 nm
6	352 nm	501 nm	361 nm	494 nm

3.3. Computation

Computations performed on **5** and **6** showed that MeOPh units attached to TT cores are deviating from the plane of TTs by 43° and 49°, respectively, indicating a moderate conjugation between TT and MeOPh groups. On the other hand, TPE units have dihedral angles of 43° for **5** and 41° for **6**,

pointing out the efficient steric hindrance precluding intermolecular π,π -interactions in the solid state. Mesityl units on boron atom did not show perpendicular arrangements in molecule **5**. The predicted dihedral angle is $56\text{--}58^\circ$. However, mesityl group in **6** was estimated to be almost perpendicular to the plane of TT with a deviation of just 4° .

While the HOMOs are localized on TT units spreading over the adjacent phenyl fragments of TPEs, LUMOs of the molecule is localized on boron atoms with small contribution of TT units (Table 2). The HOMOs of **6** are separated by electron deficient boron atom. The estimated HOMO–LUMO gaps are 3.22 and 2.92 eV for molecules **5** and **6**, respectively. MOs noticeably indicate an effective intramolecular charge transfer (ICT) between TT donor and boron acceptor units.

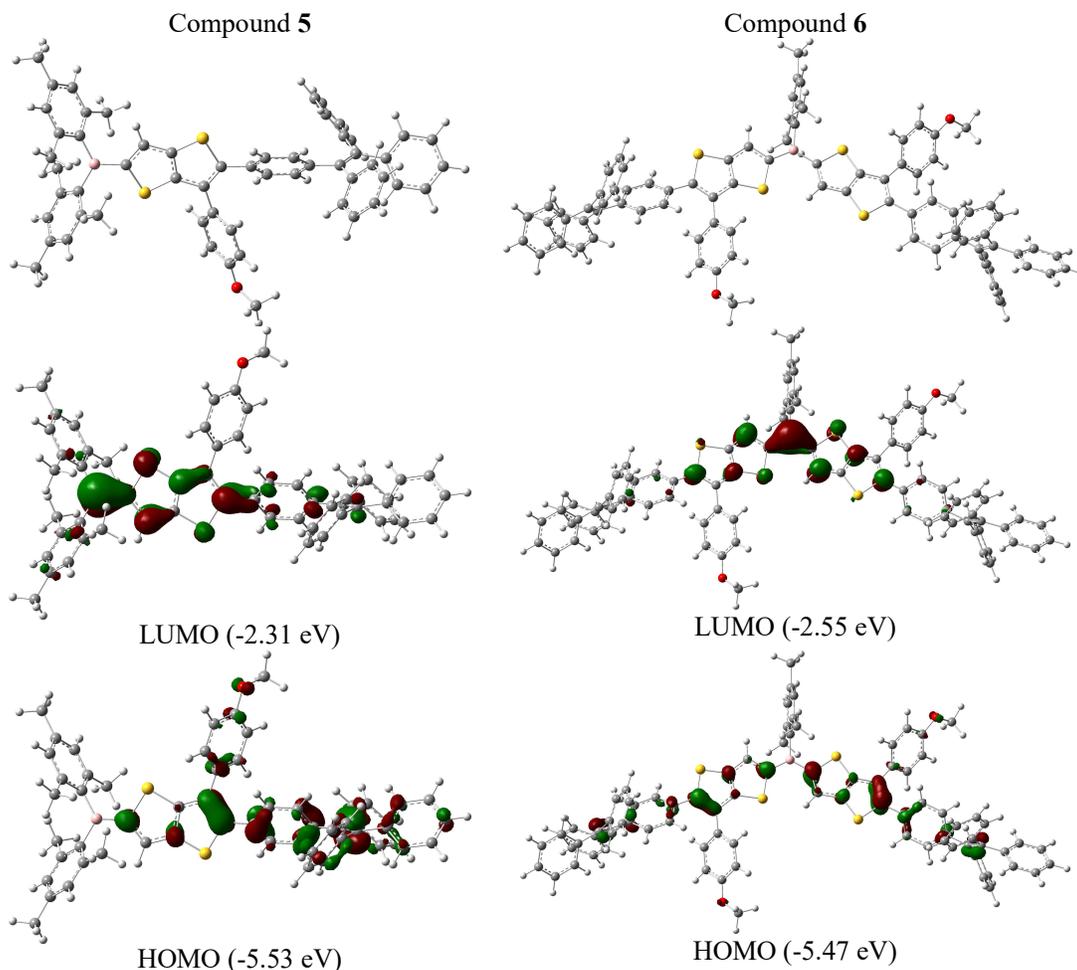


Figure 3. Molecular structures and FMOs of compounds **5** and **6** predicted at (CPCM:THF)-B3LYP-D3(BJ)/6-31+G(d) level.

4. Conclusion

D–A and D–A–D type small molecules were successfully synthesized and their optical investigations were realized in THF and on ITO. Red shift was detected on ITO in UV and fluorescence with respect to the measurements in THF emphasizing the well arrangement of the molecules in solid state. Molecule **6** with D–A–D system gave a broad emission band on ITO from 400 to 650 nm pointing out that it might be utilized as a promising small molecule in OLED applications. DFT computations shed light on their electronic structures and FMOs, which indicated efficient intramolecular charge transfers between TT donors and boron acceptor units.

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