Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

Tight-binding model predicts exciton energetics and structure for photovoltaic molecules

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Section A. Materials, General Methods, and Instrumentation

All solvents were used as received from commercial suppliers without further purification. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Supelco). Column chromatography was carried out on silica gel 60A (Sorbtech, 0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer, with a working frequency of 400 MHz (^{1}H). A Cary 60 UV-Visible spectrometer (Aglilent Technologies) was used to record UV-Visible absorption spectra. All reactions were carried out under Argon atmosphere.

Materials: 2-((4-thien-2-yl) phenyl) thiophen, 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5] thiadiazole, and 4,7-di(thiophen-2-yl)benzo[c][1,2,5] thiadiazol were obtained from AmBeed. 4-Bromo benzo[c][1,2,5] thiadiazole, and 2,1,3-Benzothiadiazole were obtained from Sigma Aldrich. 2-phenylthiophen was obtained from Thermoscientific. α-Sexithiophen, 2,5-bis(trimethylstannyl)thiophen,2-thienylboronicacid, 2,2′-bithiophene, 2,2′:5′,2″-Terthiophene, and Quaterthiophen were purchased from Sigma Aldrich. Acetone (ACS grade) was purchased from VWR chemicals. Dichloromethane was purchased from Fisher chemicals. Anhydrous toluene 99.8% and ACS grade hexane was bought from Sigma Aldrich.

General Procedures for the Synthesis of the prepared compounds: compounds 1, 2, and 3 were synthesized according to reported protocols.[S1-S3]

Synthesis of 2,5- bis(7-thiophen-2-yl benzo[c][1,2,5] thiadiazole-4-yl) thiophen (1):

This compound was prepared according to the reported literature with minor modifications.[s1] 2,5-bis(trimethylstannyl) thiophene (61 mg, 0.15 mmoles), 4-bromo-7-(thiophen-2-

yl)benzo[c][1,2,5]thiadiazole (90 mg, 0.3 mmol), and Pd(PPh3)4 (1 mg, 0.0008 mmol) were mixed and dissolved in anhydrous toluene (3 mL) in a two round-bottom flask in argon glovebox. The mixture was then purged with argon for 10 min. The reaction was refluxed for 24 hours. After cooling the reaction, 70 ml of hexane was added. The product precipitated and was filtered by vacuum filtration. To further purify the product, it was washed in a Soxhlet apparatus for 6 hours using acetone and dried in vacuum oven overnight at room temperature, yielding a purple crystalline solid. The product was poorly soluble in organic solvents and only ^{1}H NMR in $CDCl_3$ is reported. The product purty did not improve by extending the washing time in the Soxhlet apparatus, but residual impurities did not affect the UV-Visible spectrum.

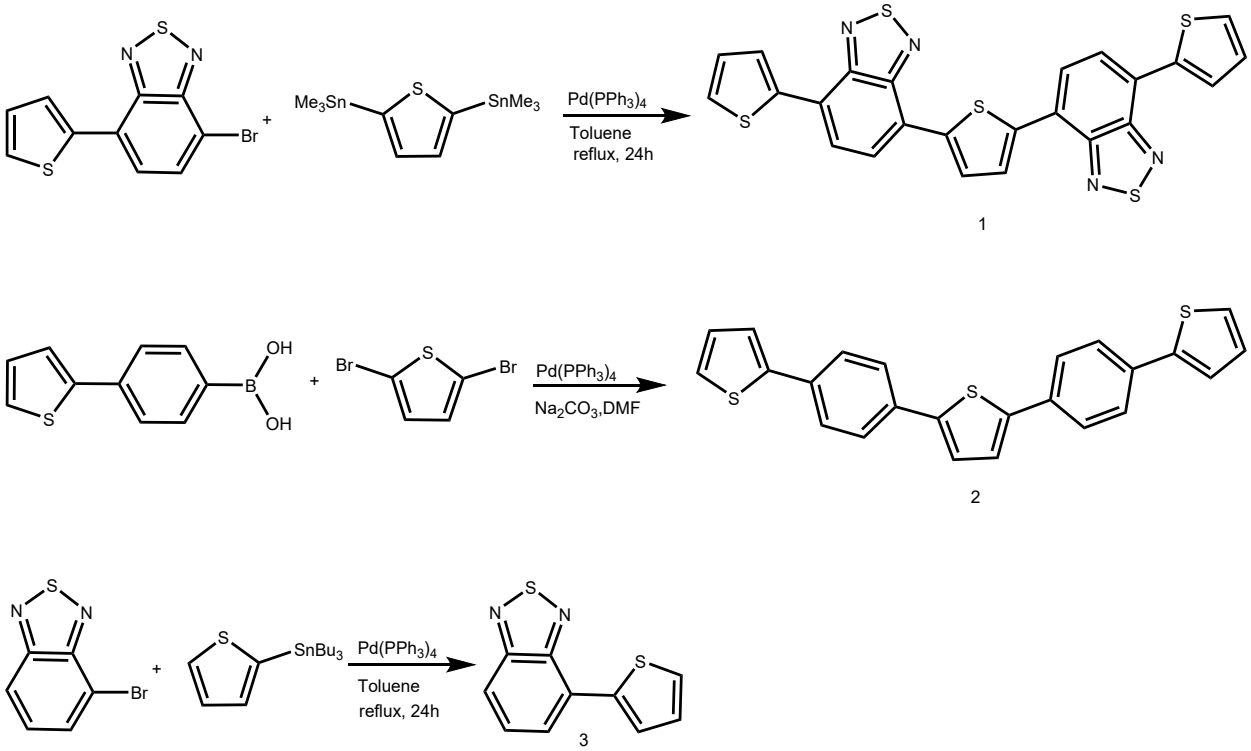
Synthesis of 2,5-bis(4-(thiophen-2-yl)phenyl)thiophene (2):

This compound was prepared according to a previous report.[s2] (4-(Thiophen-2-yl)phenyl)boronic acid (102 mg, 0.5 mmoles), 2,5-dibromothiophene (60 mg, 0.25 mmol), and Pd(PPh3)4 (100 mg, 0.086 mmol) were mixed and dissolved in DMF (20 mL) in a two round-bottom flask in Argon atmosphere glovebox. Then 2ml of aqueous 2M Na_2CO_3 was added to the mixture under an Argon atmosphere outside the glovebox. The mixture was then purged with Argon for 10 min. The reaction heated to 100ºC for 24 hours under reflux. Afterwards, 30 ml of water was added followed by filtration to obtain greenish precipitate. The precipitate was washed with acetone and dichloromethane. The product showed no solubility in common NMR organic solvents and no NMR spectrum is reported.

Synthesis of 4-(2-Thienyl)-2,1,3-benzothiadiazole(3):

This compound was prepared by Stille coupling. 2-tributylstannyl thiophen (400 mg, 1.1 mmol) mixed with 4-Bromo benzo[c][1,2,5] thiadiazol (215mg, 1 mmol), and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in Argon atmosphere glovebox. The mixture dissolved in anhydrous toluene (7 mL) in a two round-bottom flask and purged in Argon for 10 min. The reaction was refluxed for 30 hours. Rotary evaporation was used to remove solvent. The crude was purified using silica chromatography eluted by toluene/ hexane (10:1) to give a yellow precipitate with 56% yield. ^1H NMR was recorded in $CDCl_3$ and matched with previous data.[S3]

Section B. Characterization



Scheme S1. Synthesis schemes for compounds 1,2 and 3.

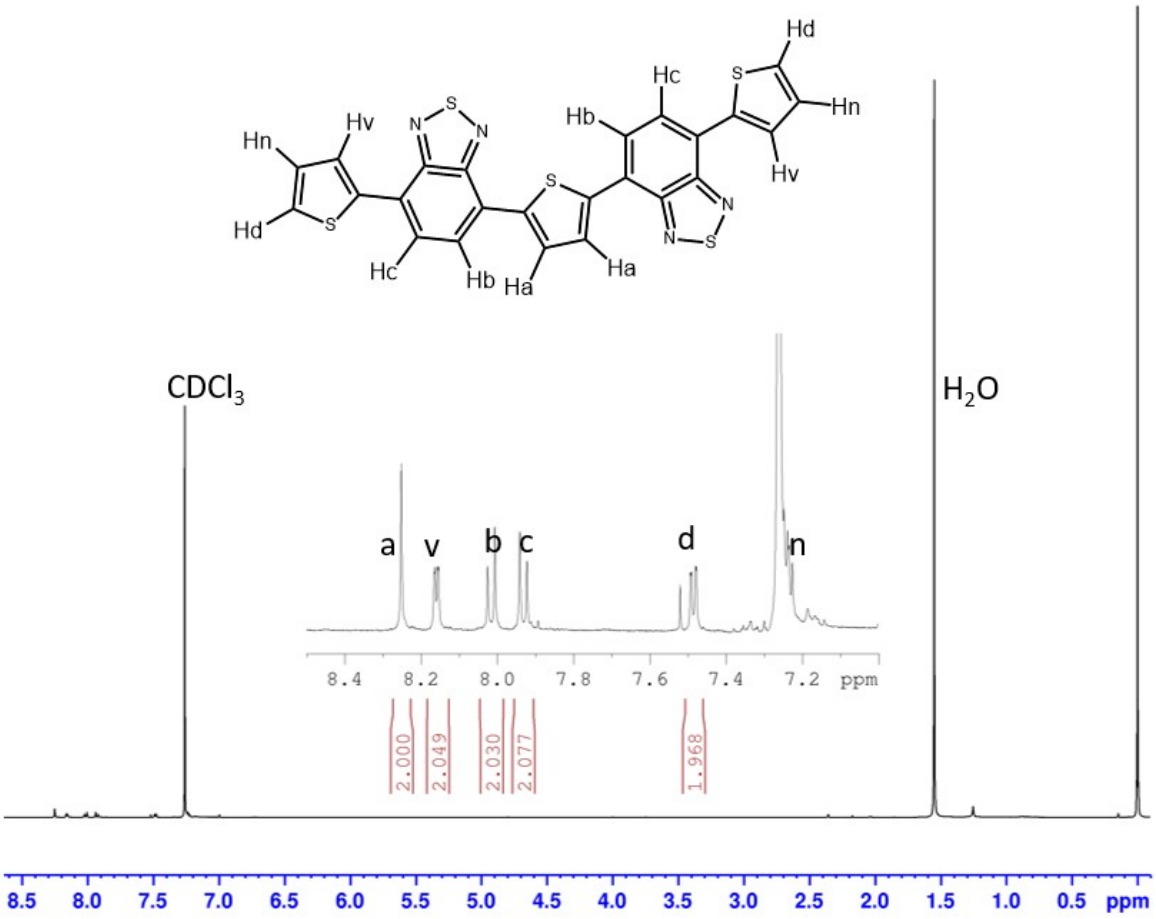


Figure S1: ^{1}H NMR (400 MHz) spectra of 2,5- (bis(7-thiophen-2-yl) benzo[c][1,2,5] thiadiazole-4-yl) thiophen (1) in $CDCl_3$.

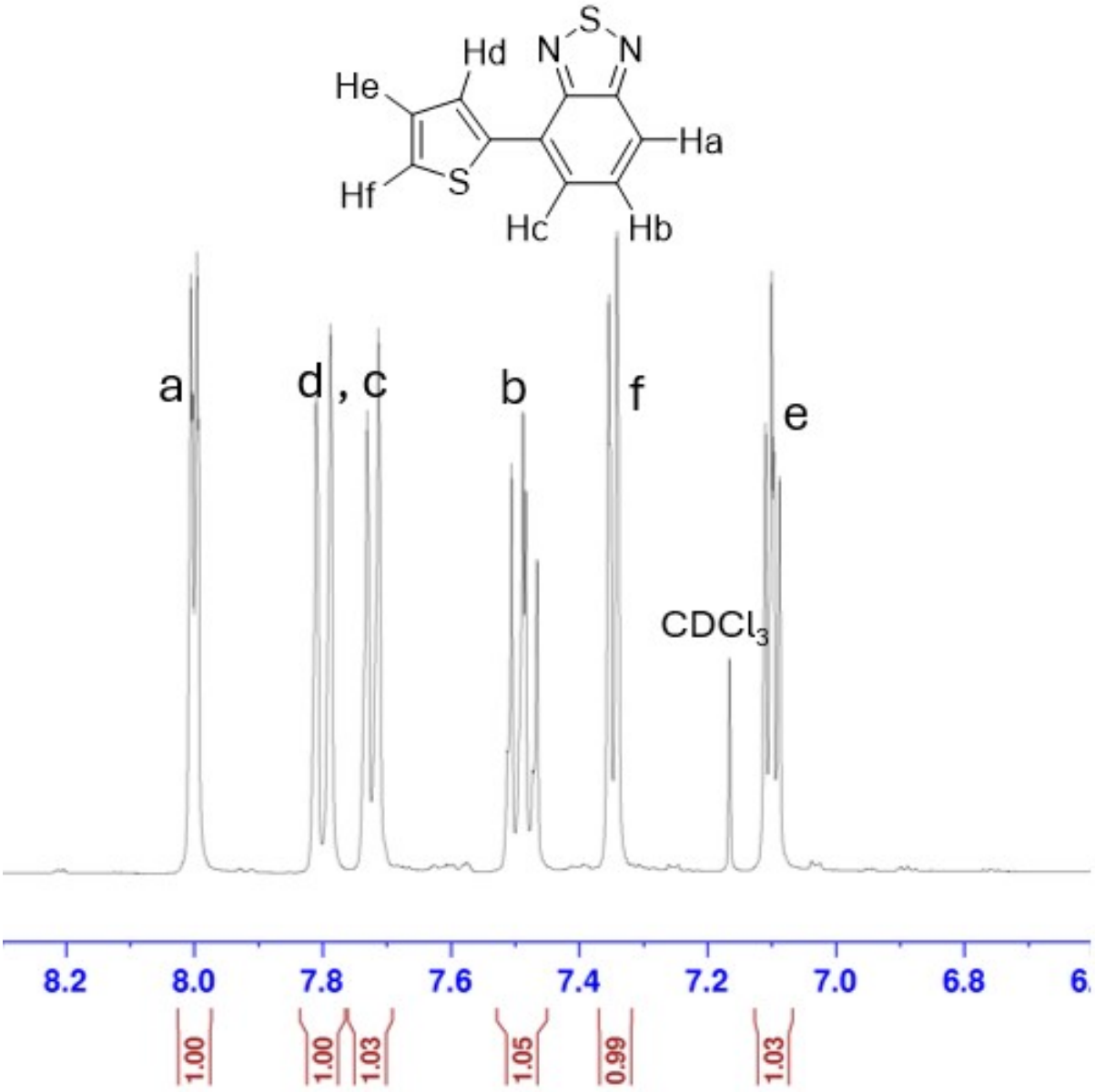


Figure S2: ^{1}H NMR (400 MHz) spectra of 4-(2-Thienyl)-2,1,3-benzothiadiazole(3) in $CDCl_3$.

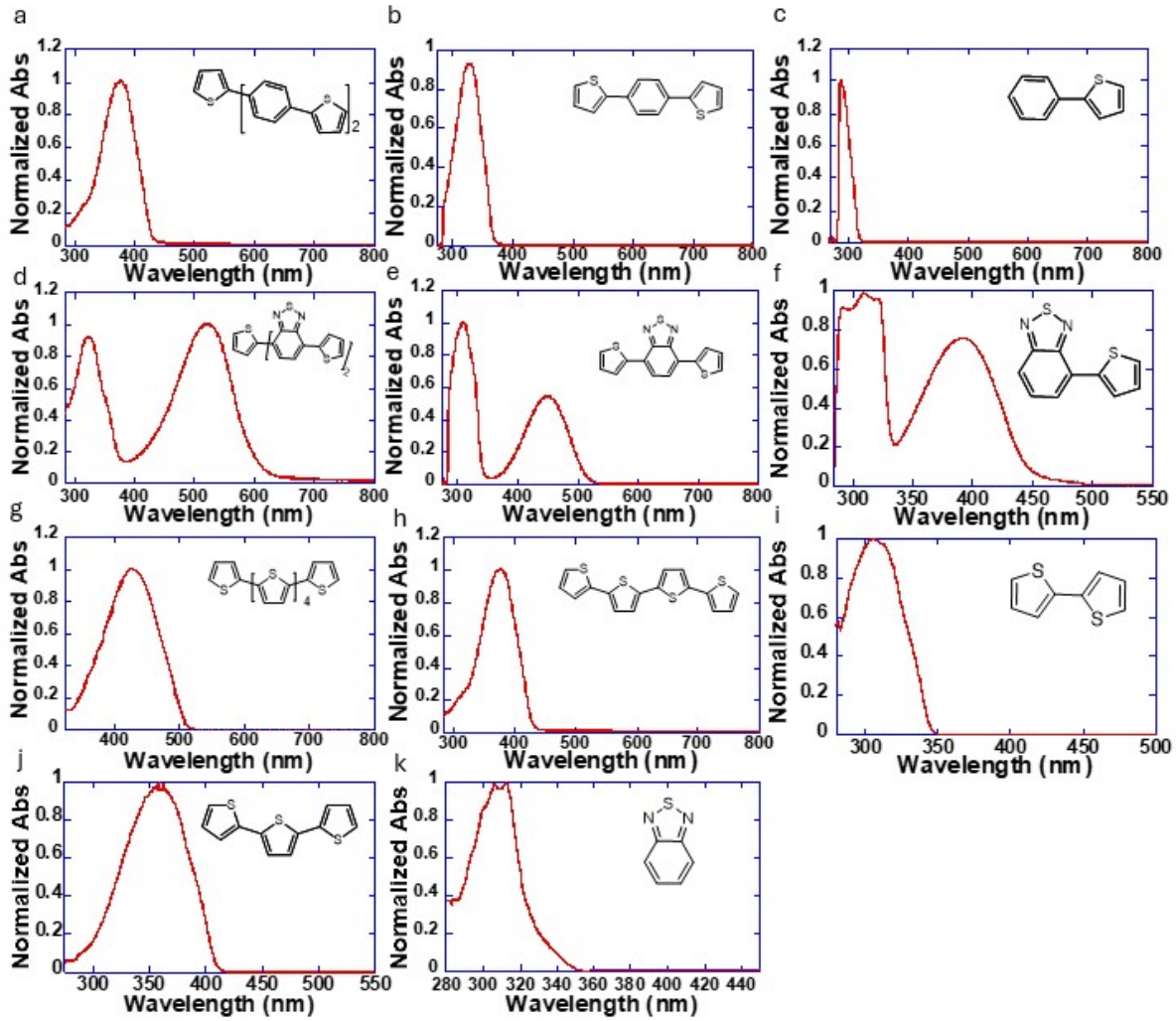


Figure S3. Normalized UV-Visible spectra of (a) 2,5-bis(4-(thiophen-2-yl)phenyl)thiophene (2); (b) 2-((4-thien-2-yl) phenyl) thiophen; (c) 2-phenylthiophen; (d) 2,5- bis(7-thiophen-2-yl benzo[c][1,2,5] thiadiazole-4-yl) thiophen (1); (e) 4,7-di(thiophen-2-yl)benzo[c][1,2,5] thiadiazol; (f) 4-(2-Thienyl)-2,1,3-benzothiadiazole(3); (g) α-Sexithiophen; (h) Quaterthiophen; (i) 2,2′-bithiophene; (j) 2,2′:5′,2″-Terthiophene; (k) 2,1,3-Benzothiadiazole in chlorobenzene (1.0×10^{-5} M).

Section C. Computational Data

Energy terms (in eV)	LC-wPBE	B3LYP
Direct Coulomb (V_{HLLH})	8.24	8.38
Exchange Coulomb (V_{HLHL})	1.71	1.82
Total Coulomb: -(V_{HLLH} - V_{HLHL})	**-6.53**	**-6.56**
TDDFT singlet excitation (A)	5.9	5.68
DFT fundamental gap (B)	10.91	10.40
Coulomb term using DFT (A-B)	**-5.01**	**-4.72**

Table S1: Coulomb terms calculated using DFT (TD-DFT) and integrating HOMO/LUMO cube files for two different exchange-correlation functional for a thiophene monomer.

References

[1] Akkuratov, A. V., et al. "A strong influence of the positions of solubilizing alkyl side chains on optoelectronic and photovoltaic properties of TTBTBTT-based conjugated polymers." *Journal of Materials Chemistry C* 3.7 (2015): 1497-1506.

[2] Yoshida, Ryohei, Takashi Tachikawa, and Suguru Ito. "Mechano-and Thermo-Responsive Luminescence of Crystalline Thienylbenzothiadiazole Derivatives: Stepwise Hypsochromic Switching of Near-Infrared Emission." Crystal Growth & Design 22.1 (2021): 547-558.

[3] Kuiper, Stefan, et al. "Liquid crystalline properties of all symmetric p-phenylene and 2, 5-thiophene pentamers." *Liquid Crystals* 36.4 (2009): 389-396.