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# **A Solution-Processable *meso*-Phenyl-BODIPY-Based *n*-Channel Semiconductor with Enhanced Fluorescence Emission**

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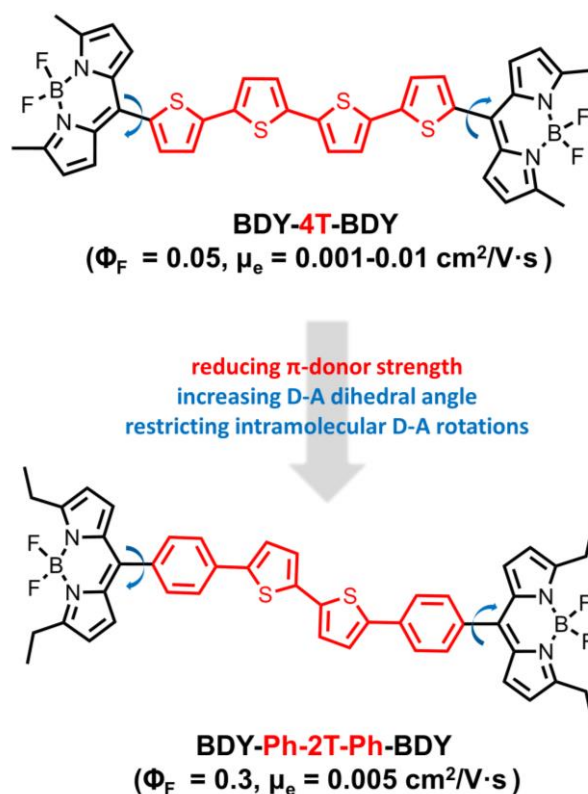
## Abstract

The molecular design, synthesis, and characterization of a new acceptor-donor-acceptor (A-D-A) semiconductor **BDY-Ph-2T-Ph-BDY** comprising a central phenyl-bithiophene-phenyl  $\pi$ -donor and BODIPY  $\pi$ -acceptor end-units is reported. The new semiconductor shows an optical band gap of 2.32 eV with a highly stabilized HOMO/LUMO (-5.74 eV/-3.42 eV). Single-crystal X-ray diffraction (XRD) reveals D-A dihedral angle of  $\sim 66^\circ$  and strong intermolecular "C-H $\cdots\pi$  (3.31 Å)" interactions. Reduced  $\pi$ -donor strength, increased D-A dihedral angle, and restricted intramolecular D-A rotations allows for both good fluorescence efficiency ( $\Phi_F = 0.30$ ) and  $n$ -channel OFET transport ( $\mu_e = 0.005 \text{ cm}^2/\text{V}\cdot\text{s}$ ;  $I_{\text{on}}/I_{\text{off}} = 10^4\text{-}10^5$ ). This indicates a much improved ( $\sim 6\text{-}7$  fold) fluorescence quantum yield compared to *meso*-thienyl BODIPY semiconductor **BDY-4T-BDY**. Photophysical studies reveal important transitions between locally excited (LE) and twisted intramolecular charge-transfer (TICT) states in solution and solid-state, which could be controlled by solvent polarity and nano-aggregation. This is the first time that such high emissive characteristics are reported for a BODIPY-based  $n$ -channel semiconductor.

## Introduction

$\pi$ -Conjugated small molecules with photon absorption/emission properties have attracted great scientific and technological interest as semiconducting materials in organic photovoltaics (OPVs), field-effect transistors (OFETs), and light-emitting transistors (OLETs).<sup>[1–4]</sup> The delocalization of  $\pi$ -electron density over the entire molecular system is very critical to the electronic/photonic properties of molecular semiconductors.<sup>[5–9]</sup> In addition to their promising charge-transport and photophysical properties, the most favorable physical and chemical properties of  $\pi$ -conjugated small molecules are structural versatility, ease of synthesis-purification and fabrication, and synthetic (batch-to-batch) reproducibility.<sup>[10–13]</sup> Among various  $\pi$ -building blocks, 4,4-difluoro-4-bora-3*a*,4*a*-diazas-indacene (BODIPY) has recently attracted attention in the design of molecular semiconductors for optoelectronics.<sup>[14]</sup> In the past few decades, BODIPY-based small molecules have been studied as fluorescent switches/sensors, chemosensors, biochemical labels, and photodynamic therapy agents,<sup>[15–18]</sup> and they have shown remarkable photophysical properties such as high fluorescence quantum yield, large extinction coefficient, small Stokes shifts, high photostability, and tunable absorption/fluorescence profiles.<sup>[19]</sup> The recent optoelectronic applications of BODIPY  $\pi$ -systems include organic photovoltaics (OPVs),<sup>[20]</sup> dye-sensitized solar cells (DSSCs),<sup>[21]</sup> organic thin film transistors (OTFTs),<sup>[22]</sup> light harvesting,<sup>[23]</sup> and near-infrared absorption.<sup>[24]</sup> Owing to its highly  $\pi$ -electron deficient electronic structure resulting in an energetically stabilized frontier orbitals, BODIPY is one of the unique  $\pi$ -acceptor building blocks that could be synthesized and functionalized in a few steps. Thanks to its excellent structural properties including high  $\pi$ -core planarity, large dipole moment ( $\mu \sim 3\text{--}4$  D), good  $\pi$ -delocalization, and high solubility, BODIPY is an ideal building block to form solution-processable donor-acceptor (D-A) type *n*-channel semiconductor architectures.<sup>[25–28]</sup> In addition to these structural features, the electronic properties of BODIPY-based

semiconductors are unique because the majority charge carrier is highly dependent on its  $\pi$ -architecture. While aromatic substitution on BODIPY's *meso*-position yields *n*-channel (electron-transporting) semiconductivity,<sup>[29]</sup>  $\pi$ -extension through 2,6-positions leads to hole-transport (*p*-channel) characteristics.<sup>[26]</sup> Facile synthetic modifications on BODIPY have been demonstrated to finely tune chemical/photophysical and charge-transport characteristics, which then allows the development of optimized BODIPY  $\pi$ -structures for specific optoelectronic applications such as OLETs and OPVs.<sup>[29,30]</sup> To this end, we have recently demonstrated that when *meso*-thienyl BODIPYs are used as  $\pi$ -acceptor end-units in acceptor-donor-acceptor (A-D-A) type  $\pi$ -architectures (e.g., **BDY-4T-BDY**, Figure 1), highly efficient electron-transport ( $\mu_e \sim 0.001\text{-}0.01 \text{ cm}^2/\text{V}\cdot\text{s}$ ) characteristics in *n*-channel OFETs could be achieved.<sup>[31]</sup> In this design, we took advantage of the negative inductive (*-I*) and mesomeric (*-M*) effects provided by the BODIPY  $\pi$ -core, which enabled electron injection/stabilization/transport across the corresponding molecular solid-state. Despite all these recent efforts, there is still only a handful example of BODIPY-based *n*-channel semiconducting molecules reported for use in optoelectronics.<sup>[32]</sup> Furthermore, for the known BODIPY-based *n*-channel molecular semiconductors, emissive properties have either not been studied or reported to be very low as a result of strong D-A electronic structures. For instance, our previously reported high-performance small molecule **BDY-4T-BDY** showed meager fluorescence quantum yields ( $\Phi_F \sim 0.04\text{-}0.05$ ).<sup>[31]</sup> Therefore, from a materials development/functionality standpoint, it is still precious to design and develop novel BODIPY-based semiconducting  $\pi$ -systems with improved photophysical properties. This way, good electron-transport characteristics and emissive properties could be simultaneously achieved to open new avenues for next-generation solution-processed optoelectronics.



**Figure 1.** The chemical structures of **BDY-Ph-2T-Ph-BDY** developed in this study and the reference compound, **BDY-4T-BDY**, developed in our earlier study<sup>[31]</sup> showing  $\pi$ -donor (in red) and  $\pi$ -acceptor (in black) building blocks.

In this study, we demonstrate the design, synthesis, and characterization of a new solution-processable A-D-A  $\pi$ -conjugated small molecule, **BDY-Ph-2T-Ph-BDY** (Figure 1), employing phenyl-bithiophene-phenyl (Ph-2T-Ph) central  $\pi$ -donor unit and BODIPY  $\pi$ -acceptor end units. The molecular design rationales used here are: (i) attaching BODIPY end units to the  $\pi$ -donor unit through *meso*-positions to facilitate electron-transport, (ii) decreasing  $\pi$ -donor strength (Ph-2T-Ph vs. 4T in **BDY-4T-BDY**) and (iii) increasing D-A dihedral angle/rotational barrier (BODIPY-Ph vs. BODIPY-T in **BDY-4T-BDY**) to minimize non-radiative decays and the formation of twisted intramolecular charge-transfer (TICT).<sup>[33–36]</sup> The new semiconductor shows a large dihedral angle ( $\sim 66^\circ$ ) between BODIPY and *meso*-phenyl units and large local dipoles ( $\mu = 3\text{-}4 \text{ D}$ ); both provide good solubility in common organic solvents. This solution processibility enables convenient purification and thin-film fabrication for the new semiconductor. Also, the absence of long lipophilic substitution and

the presence of significant local dipoles could lead to efficient intermolecular interactions favoring solid-state ordering. The new molecule was characterized by  $^1\text{H}/^{13}\text{C}$  NMR, mass spectrometry, elemental analysis, and thermogravimetric analysis. The single-crystal structure of the key intermediate compound **BDY-Ph-Br** reveals crucial structural properties in the design of the new semiconductor. **BDY-Ph-2T-Ph-BDY** shows an optical band gap of 2.32 eV with highly stabilized HOMO/LUMO energies of -5.74 eV/-3.42 eV. **BDY-Ph-2T-Ph-BDY** was studied in solution-processed OFETs; it shows *n*-channel semiconductor behavior with electron mobility of  $0.005\text{ cm}^2/\text{V}\cdot\text{s}$  and  $I_{\text{on}}/I_{\text{off}}$  ratio of  $10^4$ - $10^5$ . The detailed photophysical characterizations show significant transitions between locally excited (LE) and twisted intramolecular charge-transfer (TICT) states via solvent polarity change and nano-aggregation. Significantly enhanced fluorescence characteristics (~6-7 fold increase in quantum yield) were achieved compared to the previously developed *n*-channel BODIPY semiconductors. To the best of our knowledge, this is the first time that such high emissive characteristics are reported for a BODIPY-based *n*-channel semiconductor. This is undoubtedly the result of rational molecular design employed here, which demonstrates an essential step towards the development of solution-processable highly fluorescent BODIPY-based *n*-channel semiconductors for next-generation optoelectronics.

## Experimental Section

### Materials and Methods

The reactions were carried out under  $\text{N}_2$  unless otherwise noted by using Schlenk techniques. All reagents were obtained from commercial sources and used without any further purification unless otherwise noted.  $^1\text{H}/^{13}\text{C}$  NMR characterizations were performed by a Bruker 400 spectrometer ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz). Elemental analyses were done by a LecoTruspec Micro model instrument. MALDI-TOF was performed by a Bruker Microflex LT MALDI-TOF-MS Instrument. Thermal properties of compounds were investigated by a

Mettler Toledo TGA/SDTA 851 Thermogravimetric Analysis (TGA) Instrument and Differential Scanning Calorimeter DSC 821 equipped with METTLER TOLEDO STAR software at a heating rate of 10 °C/min under nitrogen. UV-Vis absorption and fluorescence emission measurements were performed by a Shimadzu, UV-1800 UV-Vis Spectrophotometer and Varian Eclipse spectrofluorometer, respectively. The fluorescence quantum yield was determined in dichloromethane as compared to the fluorescence of Rhodamine 6G standard ( $\Phi_F = 0.76$  in water). Electrochemistry was performed by a C3 cell stand electrochemical station equipped with BAS-Epsilon software (Bioanalytical Systems, Inc. Lafayette, IN). Dynamic light-scattering (DLS) measurements were performed on a Malvern, Nano ZS Zetasizer (Abdullah Gül University-Central Research Facility (AGU-CRF)). SEM images were taken using the ZEISS GeminiSEM 300 – Field Emission Scanning Electron Microscope at a 3 kV accelerating voltage (Abdullah Gül University-Central Research Facility (AGU-CRF)).

### *The parameters for fluorescence quantum yields*

The fluorescence quantum yield values for **BDY-4T-BDY** and **BDY-Ph-2T-Ph-BDY** were determined in benzene by comparing to the fluorescence of Rhodamine 6G as a standard. Fluorescence quantum yields ( $\Phi_F$ ) were calculated by the comparative method (Eq. 1).<sup>[37]</sup>

$$\Phi_F = \Phi_F(\text{Std}) \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \quad (1)$$

where  $\Phi_F(\text{Std})$  is the fluorescence quantum yield of standard. Rhodamine 6G is employed as the standard ( $\Phi_F = 0.76$  in water)<sup>[38]</sup>.  $F$  and  $F_{\text{Std}}$  are the areas under the fluorescence emission curves of samples (**BDY-4T-BDY** and **BDY-Ph-2T-Ph-BDY**) and the standard, respectively.  $A$  and  $A_{\text{Std}}$  are the respective absorbance of the samples and standard at the excitation wavelengths.  $n^2$  and  $n_{\text{Std}}^2$  are the refractive indices of solvents used for the sample and standard, respectively. The concentration of the solutions at the excitation wavelength was



fixed at  $1 \times 10^{-5}$  M.

## Synthesis and Characterization

The synthesis of **BDY-4T-BDY** was performed following our previously reported procedure.<sup>[31]</sup>

*Synthesis of 8-(4-bromo-1-phenyl)-3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BDY-Ph-Br):* To a flask containing  $\text{CH}_2\text{Cl}_2$  (300 mL), 4-bromobenzaldehyde (1150 mg, 6.25 mmol) and N-ethylpyrrole (1.3 mL, 12.5 mmol) were added, respectively, under nitrogen, followed by the addition of 3 drops of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 12 h. Next, *p*-chloranil (1500 mg, 6.25 mmol) was added to the reaction medium, and the mixture was stirred at room temperature for an additional 30 min. Then, triethyl amine (5 mL) and boron trifluoride diethyl etherate ( $\text{BF}_3 \cdot \text{OEt}_2$ ) (5 mL) were added, sequentially. The reaction mixture was stirred at room temperature for an additional 3 h. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and water. Organic layer was dried with  $\text{Na}_2\text{SO}_4$  and evaporated to dryness to give a crude product. The crude product was purified by silica gel column chromatography using  $\text{CH}_2\text{Cl}_2$ :Hexanes (3:1) as the eluent to give **BDY-Ph-Br** as a red solid (495 mg, 20% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.63-7.61 (d,  $J = 8.4$  Hz, 2H), 7.37-7.35 (d,  $J = 8.4$  Hz, 2H), 6.71-6.70 (d,  $J = 4.2$  Hz, 2H), 6.36-6.35 (d,  $J = 4.2$  Hz, 2H), 3.10-3.05 (q,  $J = 7.6$  Hz, 4H), 1.36-1.33 (t,  $J = 7.6$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.2, 141.4, 134.1, 133.2, 131.9, 131.6, 130.3, 124.6, 117.7, 22.2, 12.9. MS (MALDI-TOF)  $m/z$   $[\text{M}]^+$ : calcd for  $\text{C}_{19}\text{H}_{18}\text{BBrF}_2\text{N}_2$ : 402.07; found: 402.280  $[\text{M}]^+$ , 383.357  $[\text{M}-\text{F}]^+$ .

*Synthesis of 8,8'-([2,2'-bithiophene]-5,5'-diylbis(4,1-phenylene))bis(3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) (BDY-Ph-2T-Ph-BDY):* The solution of **BDY-Ph-Br** (150 mg, 0.372 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (89.2 mg, 0.181 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (10.5 mg, 9.1  $\mu\text{mol}$ ) in anhydrous toluene (15 mL) was stirred at 110 °C for 24

hours. Then, the reaction mixture was allowed to warm to room temperature and evaporated to dryness to give a crude solid. The dark colored crude solid was isolated and washed with methanol; then, it was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>:Hexanes (2:1) as the eluent to afford **BDY-Ph-2T-Ph-BDY** as a dark red solid (112 mg, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.73 (d, 2H, J = 8.0 Hz), 7.55 (d, 2H, J = 8.0 Hz), 7.39 (d, 1H, J = 4.0 Hz), 7.28 (d, 1H, J = 4.0 Hz), 6.83 (d, 2H, J = 4.0 Hz), 6.39 (d, 2H, J = 4.0 Hz), 3.08 (q, 4H, J = 22.8 Hz), 1.35 (t, 6H, J = 15.2 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 163.6, 142.1, 137.5, 135.6, 134.1, 133.5, 131.2, 130.2, 125.2, 125.1, 124.9, 117.4, 22.1, 12.8. MS (MALDI-TOF) *m/z* [M]<sup>+</sup>: calcd for C<sub>46</sub>H<sub>40</sub>B<sub>2</sub>F<sub>4</sub>N<sub>4</sub>S<sub>2</sub>: 810.28; found: 810.11[M]<sup>+</sup>, 791.085 [M-F]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>46</sub>H<sub>40</sub>B<sub>2</sub>F<sub>4</sub>N<sub>4</sub>S<sub>2</sub>: C, 68.16; H, 4.97; N, 6.91; found: C, 67.89; H, 5.03; N, 7.01.

### Field-Effect Transistor Fabrication and Characterization

Top contact/bottom gate (TC/BG) OFETs were fabricated on highly *n*-doped silicon wafers having thermally grown 300 nm oxide layer (areal capacitance; C<sub>i</sub> = 11.4 nF cm<sup>-2</sup>). The substrates were sonicated in acetone for 10 min and then treated with air plasma for 5 min (Harrick plasma, PDC-32G, 18 W). PS-brush (M<sub>w</sub> = 1.7 – 28 kg mol<sup>-1</sup>) treatments were implemented on the cleaned substrates following the conventional procedure.<sup>[39]</sup> The solution-shearing method was employed to form organic semiconductor layers on PS-brush-treated substrates where the concentration of the organic solution, solvent type, substrate temperature, and shearing speed were optimized. The substrates were placed in a vacuum oven to remove residual solvent. Finally, Au source and drain electrodes (40 nm) were thermally evaporated to define the semiconductor channel width (W) and length (L) of 1000 and 50 μm, respectively. Electrical characteristics of OFETs were measured in vacuum conditions at room temperature with a semiconductor parameter analyzer (Keithley 4200-SCS). The

saturation charge-carrier mobility ( $\mu_{\text{sat}}$ ) for an OFET device was calculated in the saturation regime as the average value of at least 10 OFET devices using the formula:

$$\mu_{\text{sat}} = (2I_{\text{DS}}L)/[WC_i(V_G - V_{\text{th}})^2]$$

where  $I_{\text{DS}}$  is the source-drain current,  $L$  is the channel length,  $W$  is the channel width,  $C_i$  is the areal capacitance ( $11.4 \text{ nF}\cdot\text{cm}^{-2}$ ) of the gate dielectric,  $V_G$  is the gate voltage, and  $V_{\text{th}}$  is the threshold voltage. The voltage ranges used in charge carrier mobility calculations are between 50-80 V. The thin-film microstructure and surface morphology were analyzed by atomic force microscopy (AFM, NX10, Park systems) and wide-angle X-ray diffraction (XRD, Ultima IV, Rigaku).

## Results and Discussion

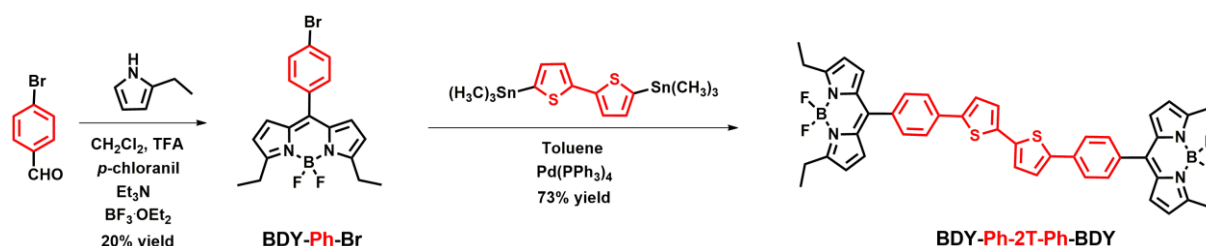
### Computational Modeling, Synthesis, Characterization, and Single Crystal X-ray Analysis

The density functional theory (DFT) calculations performed at the B3LYP/6-31G\*\*<sup>[40]</sup> level of theory indicates that the central Ph-2T-Ph  $\pi$ -donor unit in **BDY-Ph-2T-Ph-BDY** is coplanar with small inter-ring dihedral angles of  $\sim 15\text{-}19^\circ$  (Figure 2A). This angle is below the threshold value of torsional angle ( $\sim 30\text{-}35^\circ$ ) at which  $\pi$ -conjugation breaks,<sup>[41]</sup> and it provides a very efficient  $\pi$ -orbital delocalization through the donor unit. Indeed, the HOMO completely delocalizes on this  $\pi$ -donor framework with no contribution from BODIPY acceptor  $\pi$ -system. On the other hand, sizeable inter-ring dihedral angle of  $\sim 61^\circ$  is calculated between “boron-dipyrromethene” and “*meso*-phenyl”  $\pi$ -units, which matches well with the single-crystal structure of the **BDY-Ph-Br** intermediate compound (Figure 2B). As a result of this mostly broken  $\pi$ -conjugation between donor and acceptor units, the LUMO has significantly larger electron densities on the terminal BODIPY  $\pi$ -acceptors with minimal contributions from phenyl/thienyl units. The HOMO and LUMO energies for **BDY-Ph-2T-Ph-BDY** were calculated to be  $-5.50 \text{ eV}$  and  $-2.71 \text{ eV}$ , respectively, which are relatively higher than those calculated for the reference compound **BDY-4T-BDY** ( $E_{\text{HOMO}}/E_{\text{LUMO}} = -5.58/-3.17 \text{ eV}$ ). The nonsymmetric increase in frontier orbital energies results in increased HOMO-LUMO energy gap for the new compound ( $E_{\text{HOMO-LUMO}}$  for **BDY-Ph-2T-Ph-BDY** =

2.79 eV) as compared with **BDY-4T-BDY** ( $E_{\text{HOMO-LUMO}} = 2.41$  eV), most likely a result of lowered  $\pi$ -donor strength (Ph-2T-Ph vs. 4T) and increased dihedral twist (Ph-BDY vs. T-BDY) between donor and acceptor units.

The synthetic route to **BDY-Ph-2T-Ph-BDY** is outlined in Scheme 1. In order to prevent potential instability of the dipyrromethene  $\pi$ -core, the BODIPY structure employed in this study is synthesized bearing two ethyl substituents at  $\alpha$ -positions. **BDY-Ph-Br** was synthesized in 20% yield by first reacting 4-bromobenzaldehyde with 2-ethyl pyrrole in the presence of catalytic amount of trifluoroacetic acid, followed by oxidization with tetrachloro-*p*-benzoquinone and coordination with trifluoroborane-dietherate ( $\text{BF}_3 \cdot \text{OEt}_2$ ) in the presence of *N,N*-diisopropylethylamine. **BDY-Ph-2T-Ph-BDY** was synthesized via Stille cross-coupling reaction between **BDY-Ph-Br** and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene in the presence of tetrakis(triphenylphosphine)palladium(0) catalysts in toluene at 110 °C. The good solubility of the target compound, **BDY-Ph-2T-Ph-BDY**, enabled convenient purification via column chromatography (silica gel/ $\text{CH}_2\text{Cl}_2$ :Hexanes (2:1)), and the pure product was obtained as a dark red solid in 73% yield. Consistent with the previously developed BODIPY semiconductors, **BDY-Ph-2T-Ph-BDY**'s A-D-A  $\pi$ -system is found to be highly soluble in common organic solvents despite the absence of long lipophilic alkyl substituents. This points to the combined effects of large molecular dipoles of BODIPY units and increased inter-ring torsions between D and A units enhancing interactions with the solvent molecules. The chemical structures and purities of **BDY-Ph-Br** and **BDY-Ph-2T-Ph-BDY** were established by  $^1\text{H}/^{13}\text{C}$  NMR (Figures S1, S2, S4, S5), MALDI-TOF mass spectrometry (MS) (Figures S3 and S6), and elemental analysis. The thermogravimetric analysis (TGA) (10 °C min<sup>-1</sup> heating rate, under nitrogen) of the new molecule indicates excellent thermal stability with the decomposition onset (5% mass loss) temperature at 367 °C (Figure S7). However, standard

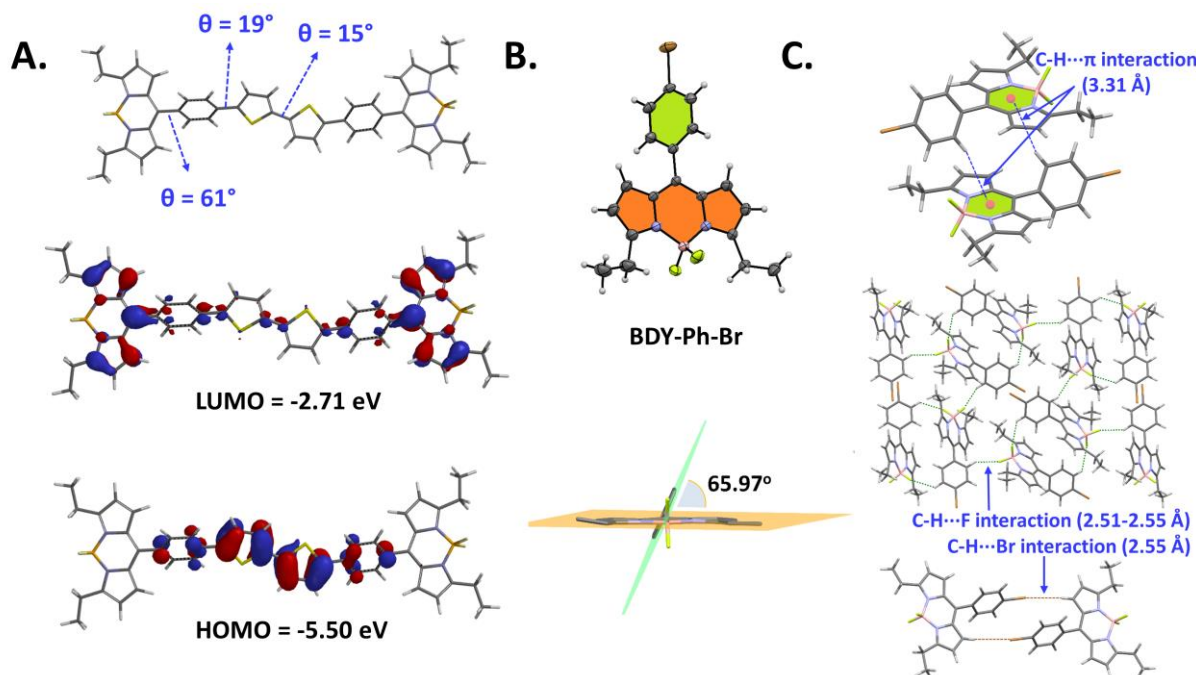
melting temperature measurement and differential scanning calorimetry (DSC) analysis did not show any thermal transition prior to the molecular decomposition.



**Scheme 1.** Synthetic route to **BDY-Ph-2T-Ph-BDY**.

Although single-crystals of the final molecular structure, **BDY-Ph-2T-Ph-BDY**, could not be obtained, red crystals of the intermediate compound **BDY-Ph-Br** (Scheme 1) suitable for single-crystal analysis were grown by diffusion of hexane into a chloroform solution at room temperature (Figure 2). **BDY-Ph-Br** crystallizes in the monoclinic  $P2_1/n$  space group, and the solid-state structure reveals highly coplanar “boron-dipyrromethene” core ( $C_9BN_2$ ) subunit with two ethyls ( $-C_2H_5$ ) lying nearly in the same plane with tilt angles of  $1.57^\circ$  and  $9.16^\circ$ . The “B-F” bond distances and “F-B-F”, “N-B-N”, and “N-N-F” bond angles match closely with those of previously reported BODIPY-based  $\pi$ -conjugated small molecules<sup>[31,42]</sup> As shown in Figure 2B, the dihedral angle between the *meso*-phenyl group and the boron-dipyrromethene  $\pi$ -core was found to  $65.97^\circ$ , which matches well with the computationally optimized geometries. This angle is large as compared to that of *meso*-thiophene substituted BODIPY ( $\theta_{\text{dihedral}} = 48.8^\circ$ ) in **BDY-4T-BDY**, which doubtless reflects sterically encumbered nature of the six-membered phenyl ring having “C-H” bonds pointing towards the BODIPY’s 1,7-positions. Note that this observed dihedral angle is in the range of those previously reported *meso*-phenyl substituted BODIPY small molecules<sup>[43,44]</sup> Although  $\pi$ - $\pi$  stacking interactions in the solid-state are not effective showing relatively large centroid-to-centroid distances of  $> 4.6 \text{ \AA}$ , strong “C-H $\cdots\pi$ ” ( $3.31 \text{ \AA}$ ) interactions and short “C-H $\cdots\text{Br}$ ” ( $2.55 \text{ \AA} \ll r_{\text{vdw}}(\text{Br}) + r_{\text{vdw}}(\text{H}) = 3.09 \text{ \AA}$ ) and “C-H $\cdots\text{F}$ ” ( $2.51\text{-}2.55 \text{ \AA} \ll r_{\text{vdw}}(\text{F}) + r_{\text{vdw}}(\text{H}) =$

2.67 Å) contacts are found to play key roles in forming three-dimensional crystal packing (Figure 2C). Specifically, “C-H $\cdots\pi$ ” interactions (*herringbone-type packing*) between aromatic moieties of the final  $\pi$ -structure could be quite advantageous for three-dimensional charge transport in **BDY-Ph-2T-Ph-BDY** thin-film.

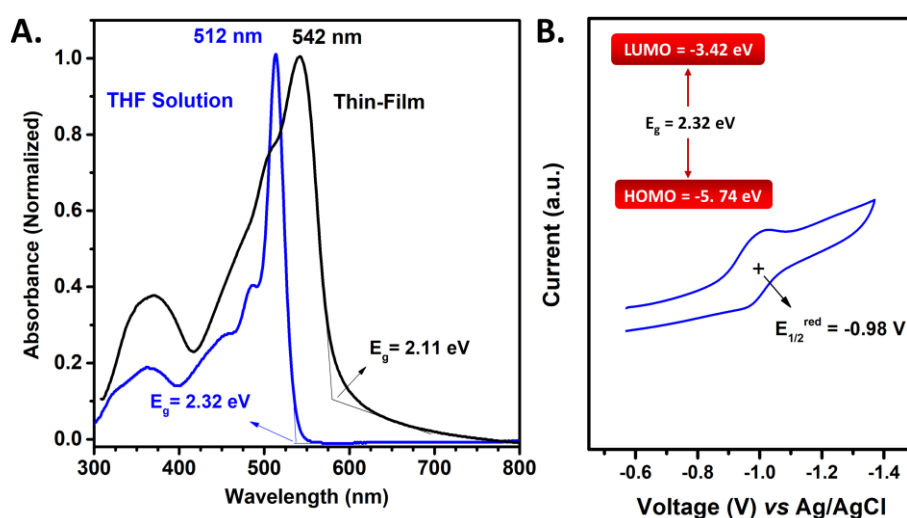


**Figure 2.** A. Optimized molecular geometry for **BDY-Ph-2T-Ph-BDY** showing inter-ring torsional angles ( $\theta$ ), computed HOMO/LUMO energies, and frontier molecular orbital topographies. B. X-ray single-crystal structure of **BDY-Ph-Br** with 50% ellipsoids and the perspective view of the inter-ring dihedral angle between “boron-dipyrromethene” and “*meso*-phenyl”  $\pi$ -units. (The grey, blue, pink, yellow, and white coloured atoms represent C, N, B, F, and H, respectively) C. The perspective views of the short “C-H $\cdots\pi$ ”, “C-H $\cdots$ Br”, and “C-H $\cdots$ F” contacts. (CCDC 1876266 (**BDY-Ph-Br**) contains the supplementary crystallographic data for this paper, and these data can be obtained free of charge from The Cambridge Crystallographic Data Centre)

### Optical and electrochemical properties

The optical properties and electronic structure of the new small molecule were studied by optical absorption/fluorescence spectroscopies and cyclic voltammetry. As shown in Figure 3A, **BDY-Ph-2T-Ph-BDY** shows an absorption maximum at 512 nm with the out-of-plane vibronic features at 484/451 nm (1129/2641  $\text{cm}^{-1}$  from the maximum). This is the unique absorption profile of *meso*-aromatic BODIPY's  $\pi$ - $\pi^*$  transition ( $S_0 \rightarrow S_1$ ).<sup>[45]</sup> The

optical band gap is estimated as 2.32 eV from the low energy absorption onset. When compared with the reference compound **BDY-4T-BDY** ( $\lambda_{\text{max}} = 526 \text{ nm}$ ,  $E_{\text{g}}^{\text{opt}} = 2.19 \text{ eV}$ ), the absorption maximum for **BDY-Ph-2T-Ph-BDY** shifts to higher energy and the optical band gap increases. This reflects the combined effects of lowered  $\pi$ -donor strength (Ph-2T-Ph vs. 4T) and increased dihedral angle (lowered  $\pi$ -conjugation) between *meso*-aromatic and BODIPY moieties ( $\sim 66^\circ$  for phenyl vs.  $\sim 49^\circ$  for thienyl) in the new molecule. UV-Vis absorption spectra of the corresponding solution-processed **BDY-Ph-2T-Ph-BDY** thin-film exhibits a significantly red-shifted absorption profile with the maximum located at 542 nm. The solid-state optical band gap is estimated as 2.11 eV. This result points to intramolecular  $\pi$ -core planarization and enhanced intermolecular interactions in **BDY-Ph-2T-Ph-BDY**'s solid-state, which is consistent with the observed thin-film crystallinity (*vide infra*). Cyclic voltammetry measurement in THF solution shows a reversible reduction for **BDY-Ph-2T-Ph-BDY** with the half-wave potential ( $E_{1/2}^{\text{red}}$ ) located at -0.98 V (*vs* Ag/AgCl). This indicates a stable *n*-doping/undoping characteristics with a low LUMO energy level of -3.42 eV for **BDY-Ph-2T-Ph-BDY**. The HOMO energy level is estimated as low as -5.74 eV. Based on the frontier orbital energetics and electrochemical behavior, it is evident that **BDY-Ph-2T-Ph-BDY** is a potential *n*-channel semiconductor in field-effect transistors.

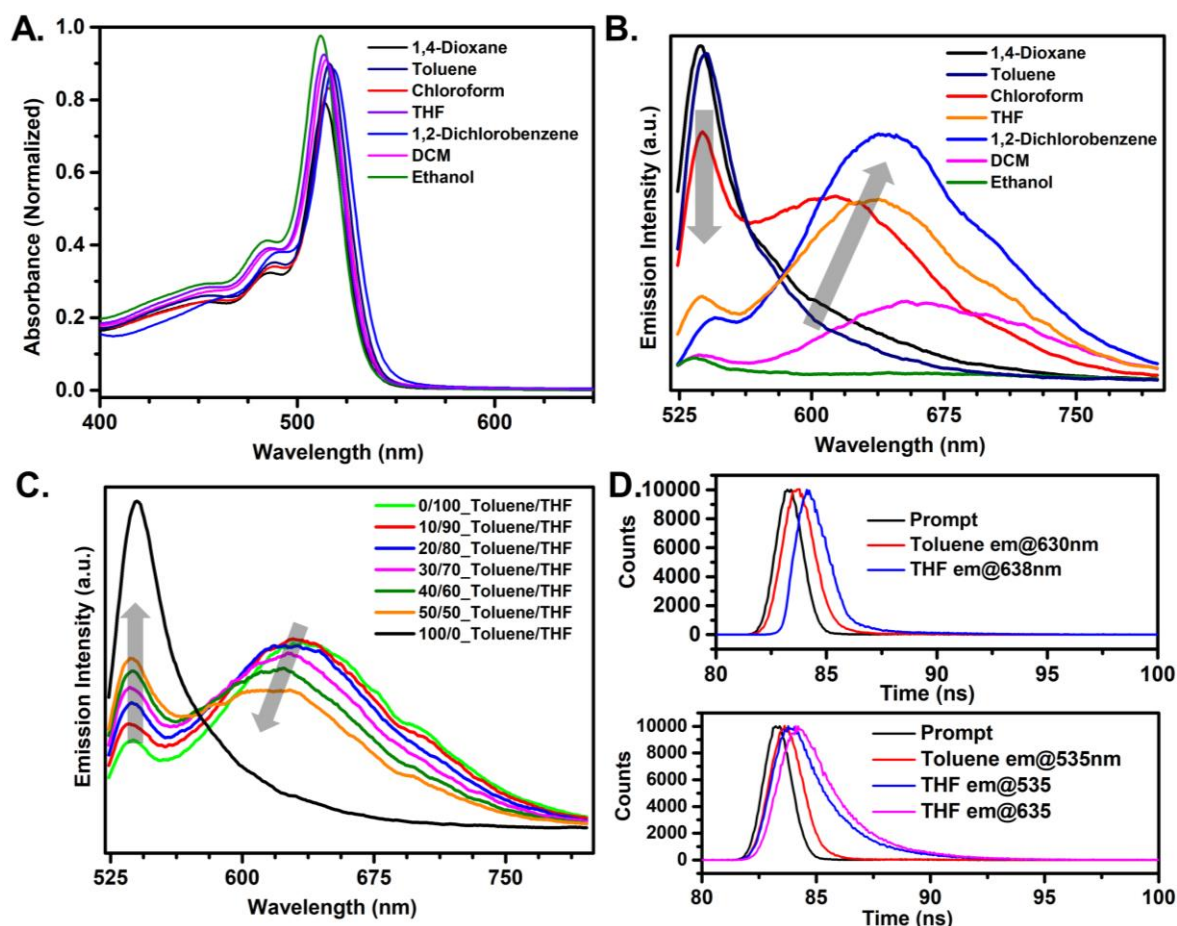


**Figure 3.** A. Optical absorption spectra of **BDY-Ph-2T-Ph-BDY** in THF solution ( $1 \times 10^{-5}$  M) and as thin-film, and the corresponding optical band gaps ( $E_g$ ). B. Cyclic voltammogram of **BDY-Ph-2T-Ph-BDY** in THF (0.1 M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$ , scan rate =  $50 \text{ mV} \cdot \text{s}^{-1}$ ) and experimental HOMO-LUMO energy levels.

The fluorescence properties of the new molecule were explored by both steady-state and time-resolved fluorescence spectroscopy techniques. Although the absorption profile of the new molecule remains nearly the same ( $\Delta\lambda_{\text{max}} \sim 3\text{-}4 \text{ nm}$ ) in several solvents of different polarity (Figure 4A), the corresponding fluorescence spectra show dramatic changes upon polarity increase (Figure 4B). This indicates that the ground-state of **BDY-Ph-2T-Ph-BDY** has much less polarity than the excited state. The fluorescence spectrum of **BDY-Ph-2T-Ph-BDY** ( $1 \times 10^{-5}$  M in solution,  $\lambda_{\text{exc}} = 510 \text{ nm}$ ) shows a single sharp emission peak  $\lambda_{\text{max}}$  located at 536-538 nm (Stokes shift  $\sim 25 \text{ nm}$ ) in a low polarity solvent (e.g., 1,4-dioxane and toluene). When the fluorescence spectrum is taken in a more polar medium (e.g., chloroform, dichloromethane, THF), the intensity of the emission peak at higher energy significantly decreases, and a new broad highly red-shifted (Stokes shift  $\sim 103\text{-}138 \text{ nm}$ ) emission peak appears with  $\lambda_{\text{max}}$  located at 615-660 nm. Based on these fluorescence characteristics, while the higher energy peak is attributed to a locally excited (LE) state, lower energy peak originates from a twisted intramolecular charge transfer (TICT) state.<sup>[33,34,46]</sup> The higher wavelength peak shows a pronounced solvatochromism indicating energetic stabilization of polar TICT state in polar solvents. To further explore the effect of medium polarity on fluorescence characteristics of **BDY-Ph-2T-Ph-BDY**, the emission measurements were carried out by admixing nonpolar toluene and polar THF at different ratios. As shown in Figure 4C, reduction of solvent polarity by gradual addition of toluene into THF solution (volume fraction: from 0 to 100%) progressively increases the intensity of the emission peak at higher energy ( $\sim 536 \text{ nm}$ ) and decreases the lower energy emission peak intensity along with a hypsochromic shift ( $\lambda_{\text{em}} = 635 \text{ nm} \rightarrow 613 \text{ nm}$ ). In solvent mixtures of  $>30\%$  toluene, the higher energy peak exhibits higher intensities relative to the lower energy peak and



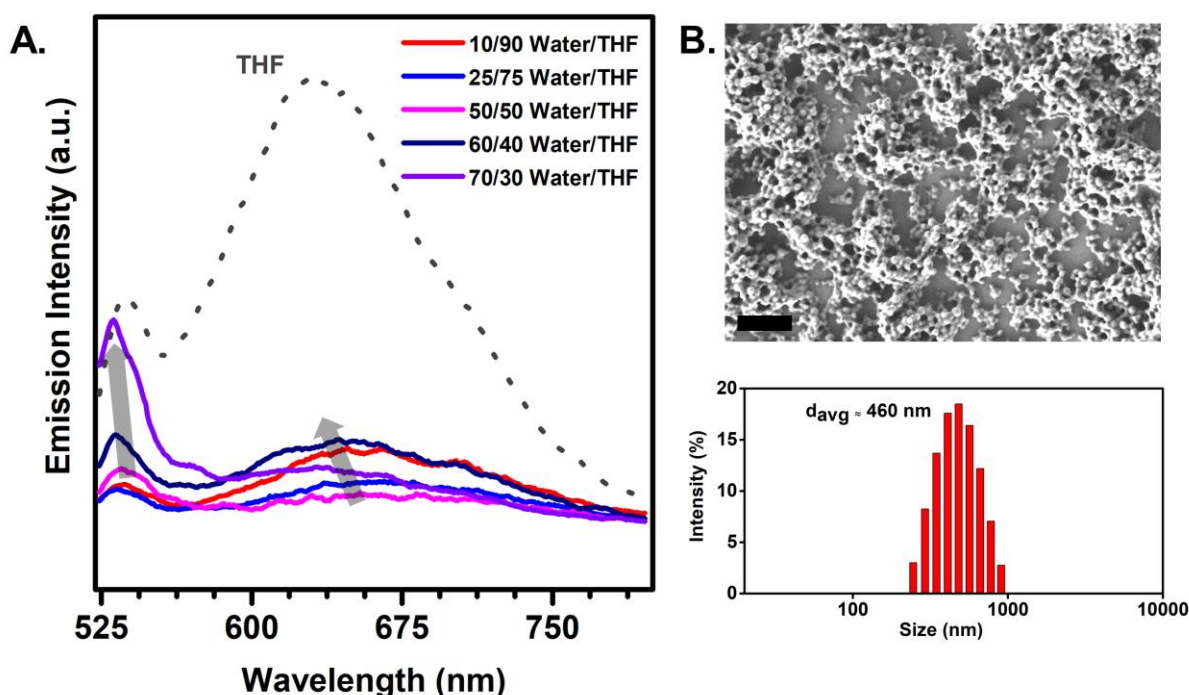
eventually becomes the only peak observed in the emission spectra in pure toluene. All these observations corroborate the assignments of LE and TICT states for **BDY-Ph-2T-Ph-BDY**.



**Figure 4.** (A, B) Optical absorption and fluorescence emission spectra of **BDY-Ph-2T-Ph-BDY** in solvents with varied polarities. (C) Fluorescence emission spectra of **BDY-Ph-2T-Ph-BDY** in Toluene/THF mixtures (solution concentration =  $1 \times 10^{-5}$  M; excitation wavelength = 510 nm). (D) Fluorescence decay plots along with fitted data for **BDY-4T-BDY** (top curve) and **BDY-Ph-2T-Ph-BDY** (bottom curve) solutions in THF and Toluene upon excitation at 390 nm.

These fluorescence characteristics are in sharp contrast to those of **BDY-4T-BDY** that exhibits only broad emission peaks with highly red-shifted (Stokes shift ~ 104-152 nm) maxima at 630/678 nm (in Toluene/THF) with no observable high-energy emission (Figure S8). Therefore, **BDY-4T-BDY** fluorescence seems to originate only from a twisted intramolecular charge transfer (TICT) state. These observations clearly indicate that highly emissive locally excited (LE) state becomes more effective in the new molecule while non-

radiative decay pathways are minimal as a result of increasing D-A dihedral angle ( $\sim 66^\circ$  for *meso*-phenyl vs.  $\sim 49^\circ$  for *meso*-thienyl), reducing  $\pi$ -donor strength (Ph-2T-Ph vs. 4T), and restricting intramolecular D-A rotations (higher rotational barrier for *meso*-phenyl vs. *meso*-thienyl).<sup>[35,36]</sup> However, note that higher polarity medium is still found to facilitate LE-state  $\rightarrow$  TICT-state transition in the new molecular structure, and concurrent emissions from both emissive states could be observed in relatively polar solvents (Figures 4B and 4C).<sup>[34]</sup> The fluorescence quantum yield ( $\Phi_F$ ) and lifetime ( $\tau_F$ ) measurements point to improved fluorescence characteristics in the new molecular design, and they align well with the proposed fluorescence mechanisms. Much larger quantum yields of 0.30/0.25 (in THF/Toluene) are measured for **BDY-Ph-2T-Ph-BDY** indicating  $\sim 6$ -7 fold increase compared to the reference compound **BDY-4T-BDY** ( $\Phi_F = 0.053/0.055$  in THF/Toluene). Also, fluorescence lifetimes of 1.72 ns ( $\lambda_{em} = 535\text{nm}$ ) and 1.84 ns ( $\lambda_{em} = 635\text{nm}$ ) are measured in THF for **BDY-Ph-2T-Ph-BDY**, which are much larger than those of **BDY-4T-BDY** (0.4-0.5 ns) (Figure 4D and Table S3). Furthermore, **BDY-Ph-2T-Ph-BDY** exhibits much shorter lifetime of 0.40 ns ( $\lambda_{em} = 535\text{nm}$ ) in toluene since the emission originates only from LE state with no contribution of charge-transfer.



**Figure 5.** (A) Fluorescence emission spectra of **BDY-Ph-2T-Ph-BDY** in water/THF mixtures (solution concentration =  $1 \times 10^{-5}$  M; excitation wavelength = 510 nm). Arrows indicate the spectral changes upon nonsolvent water addition. (B) The size distribution of the nano-aggregates in water/THF (70:30, v/v) solution determined by dynamic light-scattering (DLS) and the SEM image of the **BDY-Ph-2T-Ph-BDY** nanoparticles/aggregates as film drop-casted on Si(100) from the same solution. Scale bar denotes 1  $\mu$ m.

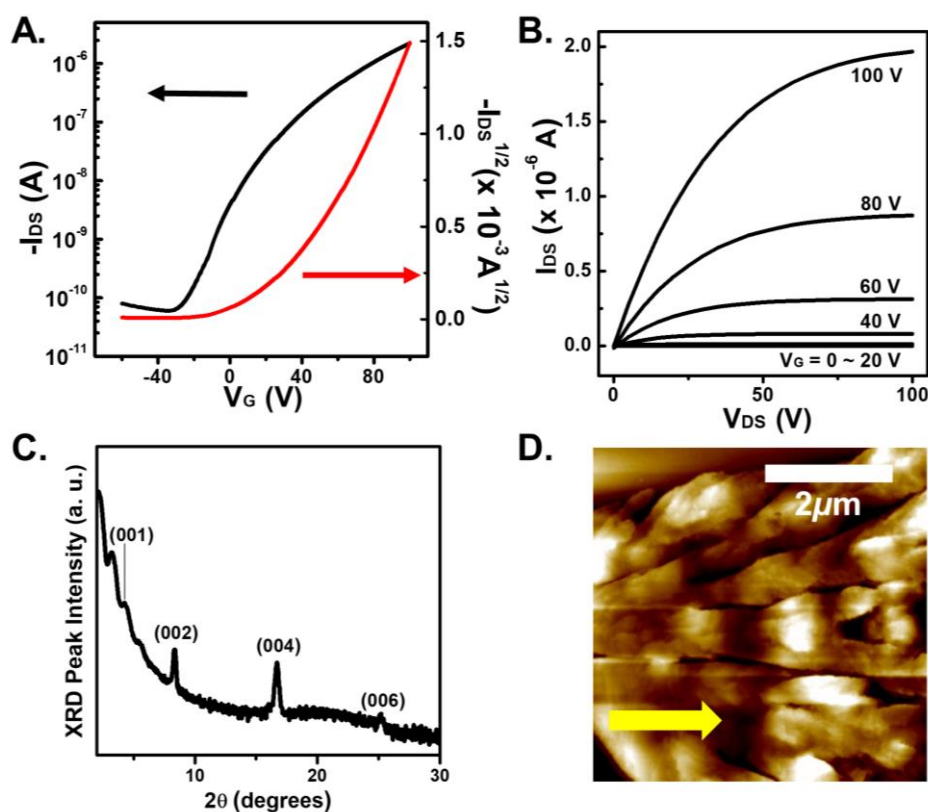
**BDY-Ph-2T-Ph-BDY** also demonstrates aggregation induced emission (AIE) behavior, which – when combined with charge-transport properties – has been very crucial to design novel photonic applications.<sup>[47,48]</sup> The AIE behavior was studied by adding a nonsolvent (water) to a well-dissolved solution of the new molecule in THF. As shown in Figure 5A, upon increasing water volume fraction from 0% to 25%, the lower energy emission peak initially shows a bathochromic shift of ~40-50 nm as a result of the energetic stabilization of the TICT state due to the effect of polarity increase. The fluorescence intensity is observed to be severely quenched at the same time. When nonsolvent water volume fraction further increases to 50-70% yielding a low-solubility environment for **BDY-Ph-2T-Ph-BDY**, hypsochromic shift (~30-40 nm) of the lower energy maximum was observed along with a significant fluorescence intensity increase in the higher energy peak at 536 nm. This obviously reveals that **BDY-Ph-2T-Ph-BDY** molecules transform into solid-state forming

nano-aggregates, which leads to restricted intramolecular D-A rotations and reduced medium polarity around the molecules.<sup>[33,49]</sup> As a result, LE emission becomes dominant with minimal contribution from the TICT state. Dynamic Light-Scattering (DLS) measurement in water/THF (70:30, v/v) solution confirms the formation of **BDY-Ph-2T-Ph-BDY** nano-aggregates in sizes of ~200-900 nm ( $d_{\text{avg}} \sim 460$  nm) (Figure 5B). The scanning electron microscope (SEM) image (Figure 5B) of the corresponding drop-casted film prepared from this solution on Si(100) shows a 3D network morphology of micron-sized aggregates that consist of nearly spherical **BDY-Ph-2T-Ph-BDY** nanoparticles (~200-600 nm), which is consistent with the DLS particle size distribution.

### Thin-Film Microstructure/Morphology and Field-Effect Transistor Characterization

The charge transport characteristics of the new BODIPY small molecule was studied in top-contact/bottom-gate (TC/BG) OFET devices by solution-shearing **BDY-Ph-2T-Ph-BDY** solution (1 mg/mL in chlorobenzene) on PS-brush treated  $n^{++}$ -Si/SiO<sub>2</sub> substrates. The microstructure and surface morphology of the solution-sheared **BDY-Ph-2T-Ph-BDY** thin-film were characterized by  $\theta$ -2 $\theta$  X-ray diffraction (XRD) measurement and atomic force microscopy (AFM). XRD scans for the semiconductor thin-film showed multiple peaks for the same diffraction family up to the sixth-order suggesting a reasonably crystalline microstructure (Figure 6C). The primary diffraction peak (001) was observed at  $2\theta = 4.26^\circ$  corresponding to  $d$ -spacing of 20.7 Å, which is smaller than the computed molecular length (28.8 Å) of **BDY-Ph-2T-Ph-BDY**. Therefore, it is very probable that the semiconductor molecules adopt tilted edge-on orientation on the surface with a  $\sim 44^\circ$  tilting angle from the substrate normal. As shown in Figure 6D, AFM characterization reveals the presence of micrometer-sized crystalline domains aligned along the shearing direction. The OFET devices were completed by thermally evaporation of Au source-drain electrodes on the semiconductor layer. OFETs demonstrated typical  $n$ -channel transistor characteristics under vacuum with

appreciable electron mobility of  $0.0054 \text{ cm}^2/\text{V}\cdot\text{s}$  and  $I_{\text{on}}/I_{\text{off}}$  ratio of  $3.7 \times 10^4$  (Figures 6A and B), which correlate well with **BDY-Ph-2T-Ph-BDY**'s computed/measured electronic structure and the observed solid-state microstructure/morphology. The semiconducting performance of **BDY-Ph-2T-Ph-BDY** is among the highest of previously reported *n*-channel BODIPY semiconductors ( $\mu_e \sim 10^{-4}$ - $0.01 \text{ cm}^2/\text{V}\cdot\text{s}$ ).<sup>[14]</sup> The small decrease in electron mobility, as compared with the best results of **BDY-4T-BDY** ( $\mu_e = 0.01 \text{ cm}^2/\text{V}\cdot\text{s}$ ), could be attributed to increased LUMO energy level, narrower  $\pi$ -delocalization, and increased D-A backbone twist in the new molecular structure. Increasing D-A backbone twists lead to a decrease in effective  $\pi$ -conjugation and charge carrier  $\pi$ -delocalization across the molecular backbone, which results in slightly lowered charge-transport characteristics for the new molecule.<sup>[41]</sup> Increased emissive properties of the new molecule could be combined with its appreciable electron mobility to enable novel photonic applications.



**Figure 6.** Representative transfer (A) and output (B) curves for *n*-channel OFETs based on solution-sheared **BDY-Ph-2T-Ph-BDY** semiconductor layer.  $\theta$ - $2\theta$  XRD scan (C) and AFM

topographic image ( $5 \times 5 \mu\text{m}^2$ ) of solution-sheared **BDY-Ph-2T-Ph-BDY** thin-film. The arrow shows the shearing direction.

## Conclusions

We have described the molecular design, synthesis, and characterization of a new acceptor-donor-acceptor (A-D-A) semiconductor **BDY-Ph-2T-Ph-BDY** comprising a central phenyl-bithiophene-phenyl  $\pi$ -donor and BODIPY  $\pi$ -acceptor end-units. Single-crystal X-ray diffraction (XRD) analysis of the key intermediate compound **BDY-Ph-Br** shows an increased D-A dihedral angle of  $\sim 66^\circ$  and strong intermolecular “C-H $\cdots\pi$  (3.31 Å)” interactions. **BDY-Ph-2T-Ph-BDY** exhibits an optical band gap of 2.32 eV with highly stabilized HOMO and LUMO energies of -5.74 eV and -3.42 eV, respectively. Detailed photophysical studies reveal important transitions between locally excited (LE) and twisted intramolecular charge-transfer (TICT) states in solution and solid-state, which could be controlled by solvent polarity and nano-aggregation. Restricted intramolecular D-A rotations, reduced  $\pi$ -donor strength, and increased D-A dihedral angle allows for both good fluorescence efficiency ( $\Phi_F = 0.30$ ) and *n*-channel OFET transport ( $\mu_e = 0.005 \text{ cm}^2/\text{V}\cdot\text{s}$ ;  $I_{\text{on}}/I_{\text{off}} = 10^4\text{-}10^5$ ) for **BDY-Ph-2T-Ph-BDY**, which indicates a much improved ( $\sim 6\text{-}7$  fold) fluorescence quantum yield compared to *meso*-thienyl BODIPY semiconductor **BDY-4T-BDY**. To the best of our knowledge, considering its electron mobility and emission characteristics, **BDY-Ph-2T-Ph-BDY** is among the highest performing BODIPY-based emissive *n*-type small molecules. Undoubtedly, our results provide important guidelines towards designing solution-processable highly fluorescent BODIPY-based molecular semiconductors for next-generation organic optoelectronics.

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## Keywords

BODIPY, fluorescence, organic field-effect transistor, organic semiconductor, small molecule

## Supporting Information

Chemical characterizations ( $^1\text{H}$  NMR/ $^{13}\text{C}$  NMR/MALDI TOF-MS spectra) for **BDY-Ph-Br** and **BDY-Ph-2T-Ph-BDY**; thermogravimetric analysis (TGA) of **BDY-Ph-2T-Ph-BDY**; single crystal structure data and structure refinement details for **BDY-Ph-Br**; fluorescence emission spectra of **BDY-4T-BDY** in toluene and THF solutions.

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