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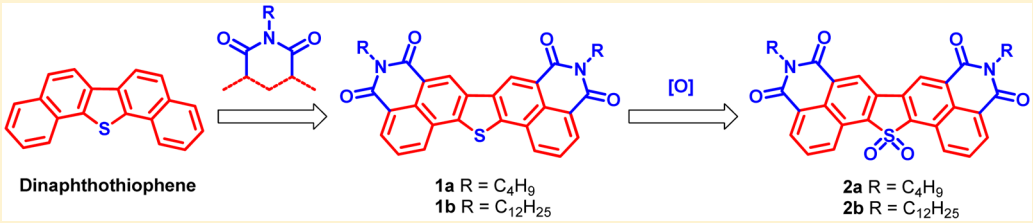
Imide-Modified Dinaphtho[1,2-*b*:2′,1′-*d*]thiophene and Dinaphtho[1,2-*b*:2′,1′-*d*]thiophene 13,13-Dioxide: Synthesis and Optoelectronic Properties

Di Wu, Zhao Chen, Yufeng Zhang, Jing Zhang, Sheng Hua Liu,* and Jun Yin*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P.R. China

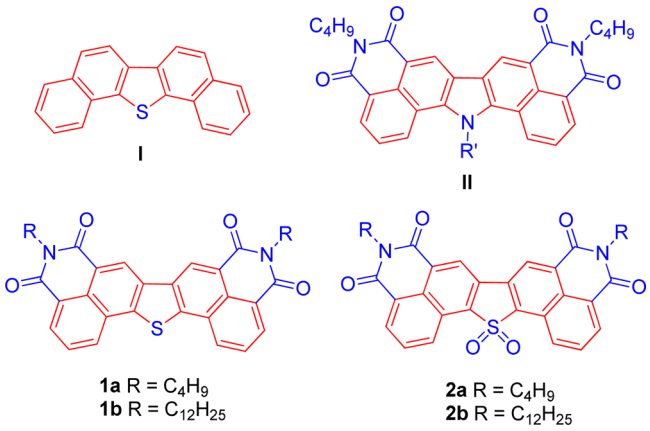
Supporting Information



ABSTRACT: Dinaphthothiophene has been reported as a promising p-type semiconductor. The development of high-performance n-type semiconductors is highly desirable. The introduction of an imide group into polycyclic aromatic hydrocarbons can lower their LUMO levels to meet the basic requirement of n-type organic semiconductor materials. In this work, we have synthesized four imide-modified dinaphthothiophenes and dinaphthothiophenedioxides. Their optoelectronic properties have been investigated. Their low-lying LUMO levels make them potential n-type semiconductor candidates.

Heteroarenes, which are constructed by replacing one (or more) carbon atom in a polycyclic aromatic hydrocarbon (PAH) with a group III and V element, have been developed as promising organic semiconductors (OSCs) for applications in a variety of electronic devices due to their outstanding optoelectronic properties.[1] A large number of heteroarenes have been synthesized and applied in OSCs over the past few decades.[2] Dinaphtho[1,2-*b*:2′,1′-*d*]thiophene (**I**, Scheme 1), which contains four benzene rings and one thiophene ring, has been reported by many groups who have used different synthetic strategies to prepare this compound.[3] Recently, Takeya and co-workers reported dinaphtho[1,2-*b*:2′,1′-*d*]-chalcogenophenes, including **I**, as a new class of highly promising p-type semiconductors,[4] which is a great improvement on phenacene-type PAHs based p-type OSCs.[5] Since both p-type and n-type OSCs with comparable performance are required for ambipolar transistors, p−n junctions, and organic complementary circuits, the development of high-performance ambient-stable n-type OSCs is highly desirable.[6] There is no doubt that providing more n-type candidates is required. Introducing electron-withdrawing substituents to p-type OSCs can decrease the LUMO energy level and improve the efficiency of electron transport. For example, the introduction of an imide group not only lowers the LUMO but also improves the solubility of the PAHs in some cases due to the alkyl or aryl groups on the imide unit.[7] Recently, we reported a series of dibenzocarbazolediimides (**II**, Scheme 1), whose low-lying LUMO levels make them potential candidates for n-type organic semiconductor applications.[8] Motivated by the aforementioned advancements and our previous work, we envisaged that introducing two imide groups into dinaphthothiophene **I** could also make it a potential n-type OSC candidate. We chose dinaphthothiophene **I** on the basis of the following considerations: (1) It is capable of introducing S···S, S···H, and S···π intermolecular interactions, which originate from the high polarizability of sulfur atoms, which not only are preferred for charge transport but also largely change the

Scheme 1. Structures of Dinaphthothiophene I, Dibenzocarbazole Diimides II, Dinaphthothiophenediimides 1a,b, and Dinaphthothiophenedioxidediimides 2a,b



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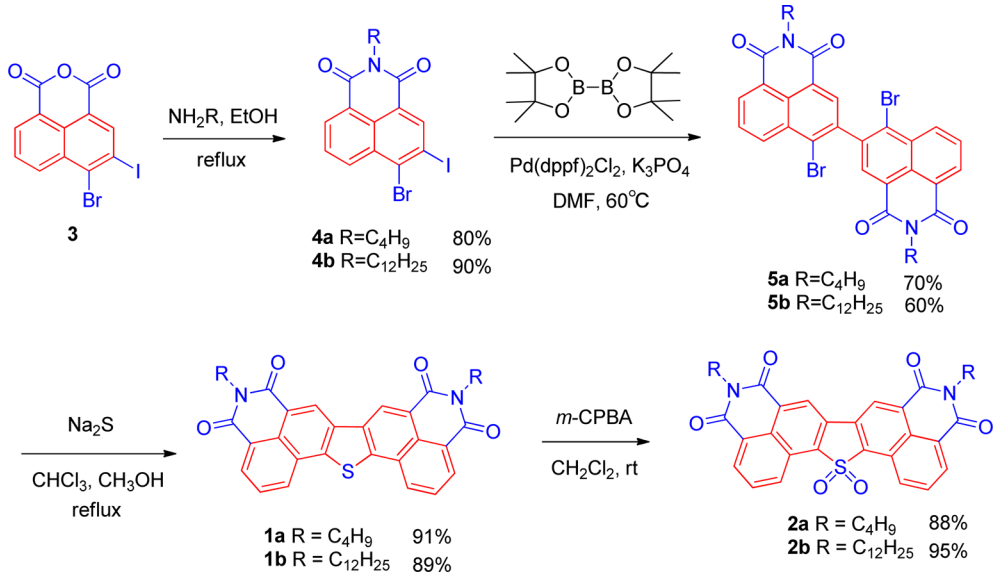
Scheme 2. Synthesis of Compounds 1a,b and 2a,b



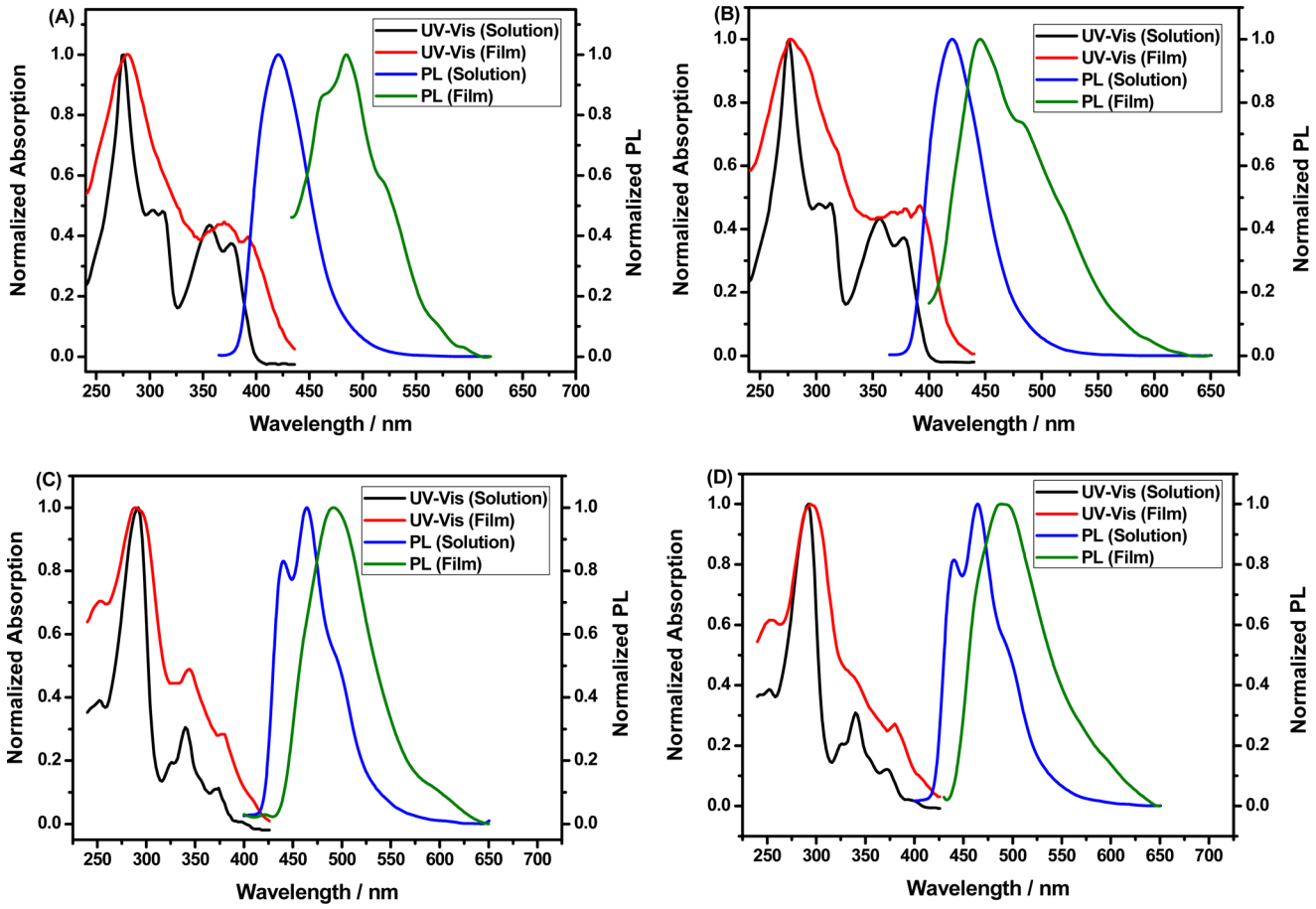


Figure 1. Normalized UV−vis absorption and photoluminescence spectra of (A) **1a**, (B) **1b**, (C) **2a**, and (D) **2b** in DCM (1.0×10^{-5} M) and in thin film.

packing motifs of such systems;[9] and (2) the S atoms can be easily oxidized to sulfones (or (*S*,*S*)-dioxides), which will lead to much lower LUMO levels.[10] Herein, we report the synthesis and optoelectronic properties of two dinaphthothiophenediimides (**1a**,**b**, Scheme 1) and two dinaphthothiophenedioxidediimides (**2a**,**b**, Scheme 1).

The syntheses of compounds **1a**,**b** and **2a**,**b** are illustrated in Scheme 2. Compound **3** was prepared using the commercially available 4-bromo-1,8-naphthalic anhydride as the starting material according to a reported procedure.[11] The syntheses of compounds **4a** and **5a** have been reported in our previous work.[12] In order to improve the solubility, longer alkyl chains

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Table 1. Optical and Electrochemical Data of Dibenzocarbazolediimides 1a,b and 2a,b

compound	λ_{Abs}[a] (nm)	λ_{max}(PL)[a] (nm)	ε_{max}[b] (M^{-1} cm^{-1})	E_{red}^{onset} (V)	HOMO[c] (eV)	LUMO[d] (eV)	E_g[e] (eV)	E_g[f] (eV)
1a	275, 355, 376 (S[g])	420 (S)	31600	−1.47	−6.41	−3.33	3.08	3.82
	278, 371, 393 (F[h])	485 (F)						
1b	275, 356, 377 (S)	420 (S)	32500	−1.47	−6.41	−3.33	3.08	3.71
	277, 380, 393 (F)	445 (F)						
2a	290, 340, 372 (S)	439, 464 (S)	76000	−0.88	−6.94	−3.92	3.02	3.29
	290, 344, 479 (F)	491 (F)						
2b	290, 340, 372 (S)	439, 464 (S)	79000	−0.88	−6.94	−3.92	3.02	3.30
	290, 382 (F)	491 (F)						

[a]Wavelength of absorption and photoluminescence in CH_2Cl_2 (1.0×10^{-5} M). [b]Molar extinction coefficient. [c]HOMO energy levels were calculated from the LUMO energy levels according to the equation HOMO = LUMO − E_g. [d]LUMO = −(4.8 + E_{red}^{onset}) eV. [e]E_g was calculated from the low-energy absorption onset in the absorption spectra according to the equation $E_g = 1240/\lambda_{onset}$.[16] [f]Obtained from theoretical calculation by TD-DFT. [g]S = solution. [h]F = film.

were introduced and the synthetic procedures used to prepare **4b** and **5b** were similar to that described for compounds **4a** and **5a**. Subsequently, **5a** and **5b** were reacted readily with an excess of sodium sulfide in a chloroform−methanol solution to give compounds **1a** and **1b** in 91 and 89% yields, respectively. This strategy was a combination of previously reported methods.[13] Then, we chose *m*-CPBA as the oxidizer to form dinaphthothiophenedioxidediimides **2a,b** in 88 and 95% yield, respectively, due to its convenient availability and mild reaction conditions.

The optical properties were investigated using UV−vis absorption and fluorescence spectrometry. All four compounds showed well-resolved absorption bands in the UV region with long-wavelength absorption maxima at 376, 377, 372, and 372 nm in dichloromethane, and a blue shift of around 40 nm was observed in comparison to that of our previously reported analogues **II**.[8] This may due to stronger electron affinity of sulfur heterocycles. The UV−vis absorption spectra of **1a,b** and **2a,b** were also measured in thin film. As can be seen in Figure 1 and Table 1, the spectra for the thin films were broader than those measured in solution, indicating that the chromophores had a strong tendency to aggregate in the solid state. We also measured their photoluminescence spectra, and compounds **1a** and **1b** had almost the same photoluminescence spectra in dichloromethane. The photoluminescence quantum yields of **1a,b** and **2a,b** in dichloromethane were 0.35, 0.37, 0.56 and 0.59, respectively, using quinine sulfate as a standard. Their photoluminescence spectra broadened and were red-shifted relative to those found in solution. However, the extent of red shift was different. It was 65 nm for **1a**, and 25 nm for **1b**. This may be attributed to the different length of the alkyl chains on the imide groups, leading to different self-assembly behaviors. Compounds **2a** and **2b** had almost the same photoluminescence spectra, both in dichloromethane and in thin film. They displayed a main emission peak at 464 nm with a shoulder peak at 439 nm in dichloromethane and a single peak at 491 nm in thin film. The intermolecular interaction of **2a** and **2b** was examined by concentration-dependent ^{1}H NMR spectroscopy in $CDCl_3$, as shown in Figure S1. For **2a**, all four signals of the aromatic protons and methylene group protons attached to the nitrogen atom shifted upfield as the concentration increased from 0.5 to 10 mM at room temperature. The upfield shifts observed for the signals are a result of shielding from the ring current of the neighboring aromatic molecules by cofacial stacking.[14] However, **2b** has no obvious proton shifts as the concentration increased. This may be attributed to the lower extent of aggregation in **2b** compared to that found in **2a**, for which ^{1}H NMR spectroscopy could not detect.

The electrochemical properties of these four compounds were investigated using cyclic voltammetry (CV). The measurements were carried out in dry dichloromethane at room temperature. As shown in Figure 2, all of these four

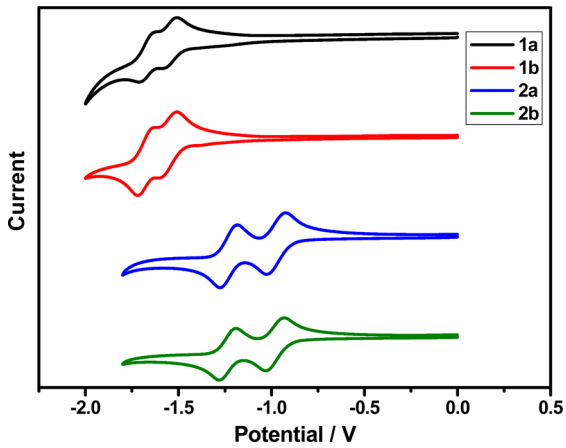

Figure 2. Cyclic voltammograms of **1a,b** and **2a,b** in dry DCM with 0.1 M Bu_4NPF_6 as supporting electrolyte.

compounds showed two reversible reduction processes. The reversible reduction processes of **1a,b** indicated that the molecules can be reduced to monoanionic and dianionic species, which are stabilized by the two imide groups.[15] However, no obvious oxidation waves were observed upon an anodic scan up to 2.00 V. The LUMO levels were determined from the E_{onset} values of the reduction peaks to be −3.33 eV for **1a,b** and −3.92 eV for **2a,b**. The LUMO levels of **2a,b** are much lower than those of **1a,b** and **II**, and the low LUMO levels are beneficial for the efficiency of n-type semiconductors. The HOMO levels were calculated to be −6.41 eV for **1a,b** and −6.94 eV for **2a,b** from the difference between the LUMO and optical gap.[16] The low-lying LUMO levels make these compounds potential candidates for n-type materials. It is worth noting that **2a,b** have LUMO levels approaching the requirement for ambient stable n-type semiconductors, of which LUMO levels should be less than or equal to −4.0 eV (a value between −4.3 and −4.4 is preferred).[6c,d,17]

The reversible redox behavior of **1b** and **2b** suggests that they can be controllably reduced to stable radical monoanionic and dianionic species with distinctive optical properties. To confirm this, the absorption spectra of the radical monoanionic

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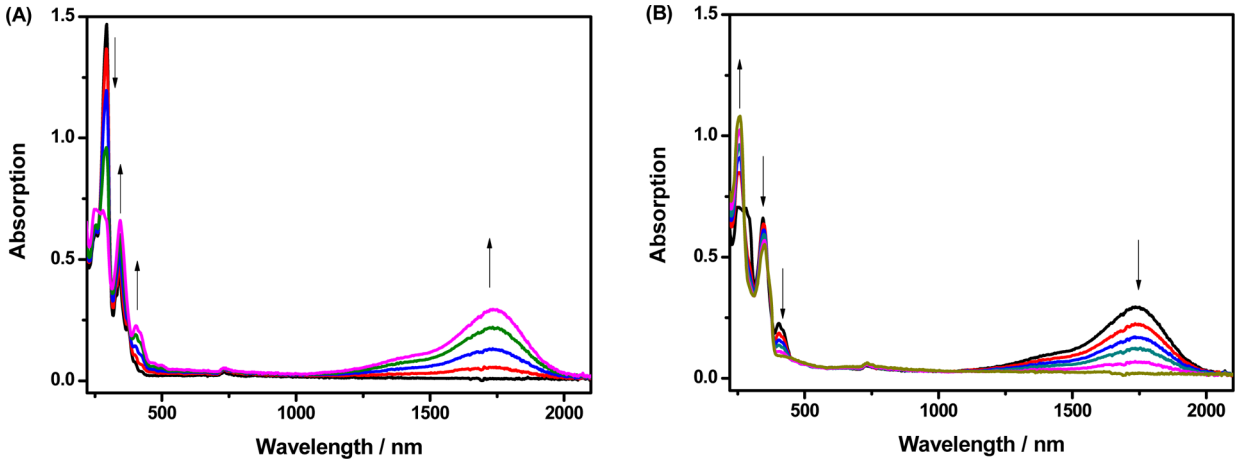

Figure 3. Spectroelectrochemistry of **2b**. (A) Neutral state to monoanionic species. (B) Monoanionic species to dianionic species.

and dianionic species of **1b** and **2b** were measured by implementing a potentiostatic electrochemical experiment with an in situ spectroelectrochemistry measuring technique.[18] According to the CV results, reduction potentials of −1.40, −1.50, −1.60, −1.70, and −1.80 V were applied separately to compound **1b** for 80 s before the absorption spectra were obtained. As shown in Figure S2, with the increasing of the potential from −1.40 to −1.60 V, the intensity of the initial absorptions of **1b** decreased, which indicated the formation of the anion species. While the potential increased from −1.60 to −1.80 V, the initial absorptions continued to decrease and a new broad band located at 430 nm emerged and increased in intensity. The spectral change during the cyclic scans between −1.40 and −1.60 V was reversible, while the transformation between −1.60 and −1.80 V was irreversible. This result suggests that the one-electron-reduced species had good stability. Compound **2b** shows a different spectroelectrochemistry property, as shown in Figure 3. When reduction potentials from −0.85 to −1.15 V were applied, the bands located at 340 and 372 nm increased while the band at 290 nm decreased. Besides the changes in the UV region, a new peak at 1470 in the NIR region emerged and increased synchronously. Upon further increase in the reduction potential, the absorption spectrum changes in an opposite direction. The spectral changes were reversible and suggest that both the monoanionic and dianionic species of **2b** have good stability. In all, the oxidation of the S atom to a sulfone can lower the LUMO energy level and stabilize the dianionic species of compound **2b**.

To gain a better insight into the molecular orbitals of **1a**,**b** and **2a**,**b**, the structures and frontier molecular orbital profiles of these molecules were optimized using DFT and TD-DFT calculations at the B3LYP/6-31G* level in the Gaussian 09 suite of programs. Figure 4 presents the frontier molecular orbitals, which show that the dinaphthothiophene and dinaphthothiophenedioxide cores possess the largest HOMO and LUMO coefficients, while the imide groups have a contribution to the LUMO coefficient. The optimized structures (Figure S3) showed that the double bonds in the sulfone were perpendicular to the plane of the central core. The computational data containing tables of the atom coordinates, absolute energies, and calculated UV−vis spectra based on TD-DFT calculations were recorded in the Supporting Information (Tables S1−S4).[19] TD-DFT calculations predicted two major absorption bands at 367 nm (f = 0.2588, dominated by a

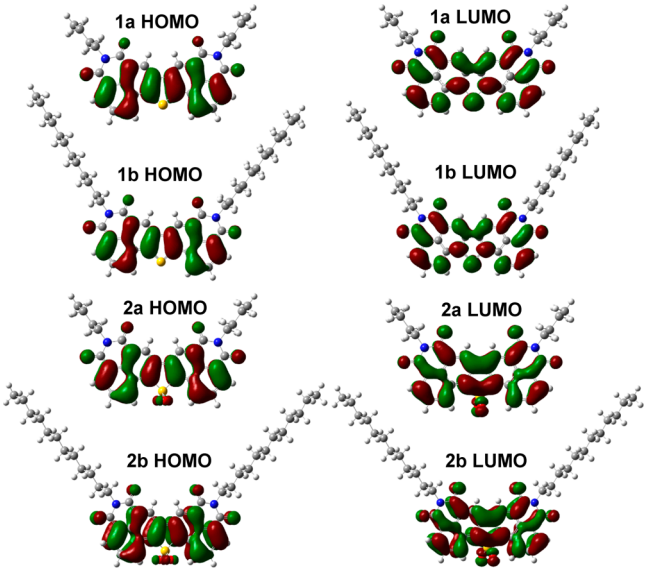

Figure 4. Frontier molecular orbital profiles of molecules based on DFT (B3LYP/6-31G*) calculations.

HOMO−1 to LUMO+1 transition) and 347 nm (f = 0.1607, HOMO−1 to LUMO) for **1a**. It displayed some charge-transfer character from the dinaphthothiophene core to the two imide groups. Compound **1b** has a calculated result similar to that of **1a**, as shown in Tables S5 and S6. For **2a**,**b**, TD-DFT calculations also predicted two major absorption bands at 365 nm (f = 0.1048 (**2a**), f = 0.1012 (**2b**), dominated by a HOMO−2 to LUMO transition) and 352 nm (f = 0.1906 (**2a**), f = 0.1957 (**2b**), HOMO to LUMO+1), as shown in Tables S7 and S8. Additionally, the calculated results of frontier molecular orbital levels and energy gaps are in agreement with the experimental data.

In summary, four imide-modified dinaphthothiophene and dinaphthothiophenedioxide have been synthesized. Their optoelectronic properties and intermolecular interaction have also been investigated. The LUMO levels of these imide-modified compounds could well meet the basic requirement of n-type organic semiconductor materials. It is worth noting that the lower LUMO energy levels of compounds **2a** and **2b** support their potential as promising candidates for ambient-stable n-type semiconductors. In addition, their good photoluminescence quantum yields make them promising π-frame-

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works for bioimaging and biolabeling. We believe that the present results will promote the development of the conjugated system with novel backbones and excellent optical behavior.

■ EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques, unless otherwise stated. All commercial products were used as received without further purification. ^{1}H and ^{13}C NMR spectra were collected on a 400 MHz spectrometer. UV−vis and fluorescence spectra were obtained on a UV or fluorescent spectrophotometer, respectively. Mass spectra were measured in the EI mode. Elemental analyses were performed by investigation of C, H, and N. CV was performed on a potentiostat. A three-electrode one-compartment cell was used to contain the solutions of **1a**,**b** and **2a**,**b** (0.001 M) and supporting electrolyte in dry CH_2Cl_2. Deaeration of the solution was achieved by bubbling argon through the solution for about 10 min before measurement. A 500 μm diameter platinum disk working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode were used. The Ag/Ag^+ reference electrode contained an internal solution of 0.01 M $AgNO_3$ in acetonitrile and was incorporated into the cell with a salt bridge containing 0.1 M n-Bu_4NPF_6 in CH_2Cl_2. All electrochemical experiments were carried out under ambient conditions. The theoretical calculation in the present studies was performed at the B3LYP/6-31G* level by using the Gaussian 09 program.

Synthesis of 4b. A mixture of **3** (2.01 g, 4.99 mmol) and dodecylamine (1.02 g, 5.50 mmol) in ethanol (80 mL) was refluxed under argon for 3 h. The resulting solution was evaporated under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane−petroleum ether (1:3, v/v) as the eluent to afford the pure product as a white solid: 2.56 g, 90%; mp = 84−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.93 (s, 1H), 8.60−8.65 (m, 2H), 7.83 (t, J = 8.06 Hz, 1H), 4.15 (t, J = 7.42 Hz, 2H), 1.71−1.72 (b, 2H), 1.24−1.38 (b, 18H), 0.88 (t, J = 6.04 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 14.0, 22.6, 27.0, 28.0, 29.3, 29.6, 31.8, 40.6, 97.6, 121.8, 123.1, 127.8, 128.6, 129.5, 131.1, 131.6, 140.5, 142.4, 162.0, 163.0; MS (EI) m/z calcd for $C_{24}H_{29}BrINO_2$ 569.04, found 569.38. Anal. Calcd for $C_{24}H_{29}BrINO_2$: C, 50.54; H, 5.13; N, 2.46. Found: C, 50.48; H, 5.20; N, 2.51.

Synthesis of 5b. A suspension of **4b** (569.0 mg, 1.00 mmol), $Pd(dppf)_2Cl_2$ (36.6 mg, 0.05 mmol), and K_3PO_4 (636.8 mg, 3.00 mmol) in DMF (30 mL) was degassed with nitrogen for 15 min at room temperature. Bis(pinacolato)diboron (139.7 mg, 0.55 mmol) in DMF (20 mL) that was degassed with nitrogen was added to the mixture dropwise with stirring. The mixture was stirred at 60 °C for 4 h, and then the volatile solvents were removed under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane−petroleum ether (3:1, v/v) as an eluent to afford the pure product as a white solid. The solubility of **5b** was not good, so it was difficult to obtain its ^{13}C NMR: 531.8 mg, 60%; mp = 216−217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 8.72−8.76 (m, 4H), 8.55 (s, 2H), 7.95 (t, J = 7.92 Hz, 2H), 4.19 (t, J = 7.58 Hz, 4H), 1.71−1.77 (m, 4H), 1.25−1.43 (b, 36H), 0.87 (t, J = 6.80 Hz, 6H). Anal. Calcd for $C_{48}H_{58}Br_2N_2O_4$: C, 65.01; H, 6.59; N, 3.16. Found: C, 65.11; H, 6.51; N, 3.21.

General Synthetic Procedure for 1a,b. A suspension of **5a** or **5b** (0.1 mmol) and excess sodium sulfide (1.0 mmol) in a mixture of trichloromethane (10 mL) and methanol (5 mL) was degassed with nitrogen for 15 min at room temperature. The mixture was stirred at reflux for 36 h, and then the volatile solvents were removed under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane/petroleum ether (6:1, v/v) as eluent to afford pure products as pale yellow solid.

*Compound **1a**:* Pale yellow solid; 48.8 mg, 91%; mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.38 (s, 2H), 8.67−8.69 (d, J = 7.28 Hz, 2H), 8.53−8.55 (d, J = 8.20 Hz, 2H), 7.93 (t, J = 7.78 Hz, 2H), 4.24 (t, J = 7.56 Hz, 4H), 1.74−1.81 (m, 4H), 1.47−1.53 (m, 4H), 1.02 (t, J = 7.34 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 13.8, 20.4, 30.1, 40.3, 121.1, 123.9, 125.0, 126.8, 126.9, 128.0, 129.5, 131.1,133.8, 142.1, 163.6, 163.7; MS (EI) m/z calcd for $C_{32}H_{26}N_2O_4S$ 534.16, found 534.24. Anal. Calcd for $C_{32}H_{26}N_2O_4S$: C, 71.89; H, 4.90; N, 5.24. Found: C, 71.67; H, 4.84; N, 5.31.

*Compound **1b**:* Pale yellow solid; 88.7 mg, 89%; mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.07 (s, 2H), 8.54−8.57 (d, J = 7.16 Hz, 2H), 8.35−8.38 (d, J = 8.00 Hz, 2H), 7.83 (t, J = 7.78 Hz, 2H), 4.15 (t, J = 7.54 Hz, 4H), 1.73−1.79 (m, 4H), 1.26−1.47 (b, 36H), 0.88 (t, J = 6.38 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 14.1, 22.7, 27.2, 28.0, 29.4, 29.7, 31.9, 40.6, 120.2, 123.1, 123.3, 125.5, 125.6, 127.6, 128.6, 130.5, 132.4, 140.9, 162.6, 162.7; MS (EI) m/z calcd for $C_{48}H_{58}N_2O_4S$ 758.41, found 758.76. Anal. Calcd for $C_{48}H_{58}N_2O_4S$: C, 75.95; H, 7.70; N, 3.69. Found: C, 75.68; H, 7.76; N, 3.71.

General Synthetic Procedure for 2a,b. To a 25 mL round-bottom flask equipped with a stir bar were added **1a** or **1b** (0.1 mmol) and dichloromethane (15 mL). Then m-CPBA (5.0 mmol) was added. The reaction vessel was covered in foil and stirred for 24 h. The reaction mixture was quenched with 10 mL of saturated $NaHCO_3$ solution. The organic layer was washed with saturated $NaHCO_3$ solution and dried using $MgSO_4$. The volatile solvents were removed under reduced pressure. The residue was purified by column chromatography packed with silica gel using dichloromethane/petroleum ether (8:1, v/v) as eluent to afford pure products as yellow solid.

*Compound **2a**:* Yellow solid; 49.9 mg, 88%; mp > 300 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ_H = 9.17 (s, 2H), 8.78−8.80 (d, J = 8.40 Hz, 2H), 8.73−8.75 (d, J = 6.48 Hz, 2H), 8.60 (t, J = 7.80 Hz, 2H), 4.24 (t, J = 7.62 Hz, 4H), 1.73−1.79 (m, 4H), 1.45−1.49 (m, 4H), 1.01 (t, J = 7.38 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 13.8, 20.3, 30.1, 40.8, 123.2, 123.8, 125.0, 128.5, 128.9, 129.4, 130.0, 130.5, 132.8, 136.8, 162.5, 162.9; MS (EI) m/z calcd for $C_{32}H_{26}N_2O_6S$ 566.15, found 566.22. Anal. Calcd for $C_{32}H_{26}N_2O_6S$: C, 67.83; H, 4.63; N, 4.94. Found: C, 71.67; H, 4.84; N, 5.31.

*Compound **2b**:* Yellow solid; 75.1 mg, 95%; mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H = 9.15 (s, 2H), 8.76−8.78 (d, J = 8.24 Hz, 2H), 8.72−8.74 (d, J = 7.16 Hz, 2H), 8.04 (t, J = 7.82 Hz, 2H), 4.22 (t, J = 7.24 Hz, 4H), 1.74−1.76 (m, 4H), 1.26−1.44 (b, 36H), 0.88 (t, J = 6.36 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C = 14.1, 22.7, 27.1, 28.0, 29.3, 29.6, 31.9, 41.0, 123.2, 123.5, 124.6, 128.1, 128.7, 129.0, 129.7, 130.3, 132.6, 136.4, 162.2, 162.6; MS (EI) m/z calcd for $C_{48}H_{58}N_2O_6S$ 790.40, found 790.09. Anal. Calcd for $C_{48}H_{58}N_2O_6S$: C, 72.88; H, 7.39; N, 3.54. Found: C, 72.76; H, 7.43; N, 3.60.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01341.

Characterization, NMR, MS spectra of intermediates, dinaphthothiophenediimides, and dinaphthothiophene-dioxidediimides (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: chshliu@mail.ccnu.edu.cn.

*E-mail: yinj@mail.ccnu.edu.cn.

Notes

The authors declare no competing financial interest.

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