

# Air-Stable Benzo[c]thiophene Diimide *n*-Type $\pi$ -Electron Core

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**Supporting Information** 

**ABSTRACT:** In this paper, the molecular design of the first deep-lowest unoccupied molecular orbital (LUMO) level diimide  $\pi$ -electron core, benzo[*c*]thiophene diimide (**BTDI**), as a novel *n*-type organic semiconductor was determined. An original synthetic sequence was devised to obtain the target cyclohexyl-**BTDI** (**Cy**<sub>6</sub>-**BTDI**) derivative. **Cy**<sub>6</sub>-**BTDI** demonstrated completely reversible reduction waves and a stable radical anionic state. Favorable brickwork molecular assembly and two-dimensional charge transport properties of **Cy**<sub>6</sub>-**BTDI** 



were exhibited in the solid state. As a result, air-stable electron mobilities were obtained from the BTDI organic field-effect transistors under ambient conditions.

rganic field-effect transistors (OFETs) are promising candidates for lightweight, low-cost, and flexible electronics,<sup>1</sup> such as sensors<sup>2</sup> and radio frequency identifier (RF-ID) tags.<sup>3</sup> To achieve these high-performance electronic devices with organic materials, both hole-transporting (*p*-type) and electron-transporting (n-type) components are required to construct bipolar transistors and complementary logic circuits.<sup>4</sup> To date, a large number of *p*-type organic semiconductors have been reported such as [1]benzothieno[3,2-b][1]-benzothiophene (BTBT),<sup>5</sup> dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT),<sup>6</sup> dinaphtho[2,3-b:2',3'-d]thiophene (DNT-V),<sup>7</sup> dinaphtho[2,3-d:2',3'-d']benzo[1,2-b:4,5-b'] dithiophene (DNBDT),<sup>8</sup> and chryseno[2,1-b:8,7-b']dithiophene  $(ChDT)^9$  with charge-carrier mobility ( $\mu$ ) values higher than 10 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which are promising for sensor and RF-ID tag applications. However, contemporary n-type organic semiconductors, on the other hand, suffer from low-performance and instability drawbacks due to oxidation of charge carriers by ambient oxidants such as  $O_2$  and  $H_2O$  upon charge injections.<sup>10-12</sup> As a general design principle suggested by numerous studies, lowering the lowest unoccupied molecular orbital (LUMO) energy level below -4.0 eV protects the *n*type organic semiconductors against detrimental oxidation in the charge-carrying states.<sup>13</sup>

To date, a large number of electron-deficient molecules have been synthesized to obtain low-lying LUMO energy levels required for air-stable *n*-channel OFET performances,<sup>14</sup> and a significant portion of the molecular designs so far has been based on naphthalene diimide  $(NDI)^{15}$  (Figure 1a) and perylene diimide  $(PDI)^{16}$   $\pi$ -cores for their relatively low LUMO levels (ca. -3.80 eV). However, the parent NDI and PDI  $\pi$ -cores cannot achieve air-stable OFET operations, and chemical modifications such as incorporations of highly electron-withdrawing substituents<sup>17</sup> and lateral expansion of the rylene framework<sup>18</sup> are required to obtain LUMO energy levels below -4.0 eV. However, the total number of distinct  $\pi$ cores remains limited, which impedes the overall development of the urgently demanded *n*-channel OFETs.

Herein, we report the first deep-LUMO level diimide  $\pi$ -core, benzo[*c*]thiophene diimide (**BTDI**) (Figure 1a), as an airstable *n*-type organic semiconductor without the requirement of any chemical modifications. In contrast to naphthalene ( $E_{LUMO} = -1.33$  eV), which is the main  $\pi$ -conjugated moiety of NDI, the quinoidal-like benzo[*c*]thiophene possesses a respectably deeper LUMO energy level (-1.67 eV). Thus, the relatively deep LUMO energy level of benzo[*c*]thiophene can be potentially harnessed to design deep-LUMO level *n*-type organic semiconductors for air-stable OFETs. Albeit having seemingly intriguing optoelectronic properties, benzo[*c*]thiophene has been reported to be unstable and tends to

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**Figure 1.** (a) Molecular structure of **BTDI** (left), the LUMO coefficients of **BTDI** (middle), and the structure of NDI (right) and (b) molecular orbital energy levels of benzo[c]thiophene, **BTDI**, NDI, and naphthalene.

self-polymerize in air due to its highly reactive 1,3-positions, which makes it challenging to study its structure for functional materials purposes.<sup>19</sup> However, by fusing benzo[c]thiophene with the electron-deficient imide groups, we stabilize the highly reactive 1,3-positions, making **BTDI** a stable compound under ambient conditions. Furthermore, our initial density functional theory (DFT) calculation shows a LUMO level of -4.17 eV for **BTDI** (Figure 1b), which renders air-stable *n*-channel OFET operations as a  $\pi$ -core without the installation of any substituents. Large LUMO coefficients are observed on the benzo[c]thiophene sulfur (Figure 1a), which suggests the

Scheme 1. Synthetic Route toward BTDI

protruding sulfur is likely to participate in intermolecular orbital overlap for electron transports. Thus, our current **BTDI** design features aim to (1) develop a brand-new deep-LUMO  $\pi$ -core via ring-fusion between benzo[*c*]thiophene and imide moieties and obtain air-stable *n*-channel OFET operations, (2) achieve effective intermolecular orbital overlaps in the solid-state and high electron mobility, and (3) obtain highly soluble semiconducting materials through the large dipole moment of benzo[*c*]thiophene (1.38 debye).

The synthetic route to Cy<sub>6</sub>-BTDI is illustrated in Scheme 1. Compound 1 was prepared according to the previously reported procedure in good yield. As previously mentioned, the unsubstituted benzo[c]thiophene is highly reactive and prone to self-polymerization. Thus, compound 2 was generated in situ by the strong reducing agent lithium bis(trimethylsilyl)amide (LiHMDS) under argon, and its formation was determined by <sup>1</sup>H NMR. Intermediate 2 was lithiated in the 1,3-positions, and it is worth mentioning that the regioselectivity of lithiation could be significantly improved by the addition of tetramethylethylenediamine (TMEDA). The dilithiated benzo[c]thiophene was then trapped by dimethylcarbamoyl chloride to yield the diamide compound 3 in 42% yield. By installing the electron-withdrawing amides at the 1,3positions of benzo[c]thiophene, 3 exists as a perfectly stable compound. Regioselective bromination performed by dibromoisocyanuric acid in concentrated H<sub>2</sub>SO<sub>4</sub> gave 4,7dibromobenzo[c]thiophene 4 in 83% yield. Manabe and coworkers previously reported the use of trichlorophenyl formate to serve as a highly reactive CO surrogate in Heck reactions.<sup>20</sup> The electron-deficient formate can later be readily hydrolyzed under basic conditions. Hence, we adopted this method and converted the dibromo compound 4 to afford compound 5 via a Pd-catalyzed cross-coupling reaction using palladium acetate and Xantphos. A subsequent hydrolysis was done using an aqueous solution of NaOH to hydrolyze both the amide and formate groups to give the tetracarboxylic acid 6, followed by a condensation reaction in acetic anhydride to furnish the key precursor 7 in an excellent 90% yield.

We intend to compare our **BTDI** properties and device performance with the well-studied  $N_{,}N'$ -biscyclohexylnaphthalene diimide (Cy<sub>6</sub>-NDI). Since compound 7 adopts a





Figure 2. (a) NICS values of benzo[c]thiophene and Cy<sub>6</sub>-BTDI in ppm, (b) molecular packing structure of Cy<sub>6</sub>-BTDI along the *a*-axis, and (c) mean-plane intermolecular distances and transfer integrals of the LUMO; alkyl chains are omitted for clarity.

slightly distorted geometry due to the five-membered thiophene moiety, common imidization methods for sixmembered imides only lead to the ring-opened amide intermediate. Thus, we attempted the synthesis of  $Cy_6$ -BTDI in a stepwise fashion by first treating the anhydride 7 with cyclohexylamine and using acetic anhydride/pyridine to catalyze the ring-closing step in one pot. The imidization was successfully completed using this method and furnished  $Cy_6$ -BTDI in 64% yield at room temperature as a bright yellow solid.  $Cy_6$ -BTDI demonstrated superior solubility in common organic solvents such as toluene and anisole compared to the  $Cy_6$ -NDI counterpart due to the large internal dipole moment of the benzo[c]thiophene moiety (Table S2). The high solubility of BTDI allows for purification with column chromatography and solution-processable OFET fabrications.

Large platelet-shaped single-crystals of Cy6-BTDI were obtained by physical vapor transport (PVT). The BTDI  $\pi$ core appears to be planar. However, the five-membered thiophene moiety causes the  $\pi$ -core to slightly bend toward the sulfur atom at an angle of 3.8°. Using the molecular geometry obtained from the single-crystal X-ray diffraction, we calculated the nucleus-independent chemical shifts (NICS)<sup>21</sup> values of the BTDI  $\pi$ -core (Figure 2a). The benzene and thiophene moieties of BTDI exhibit NICS values of -6.6 and -14.2, respectively, which are consistent with those of the DFToptimized BTDI structure and lower than those of the parent benzo[c]thiophene. Cy6-BTDI adopts a brickwork packing motif where the molecules are stacked antiparallel to the *b*-axis, and each plane is tilted to the *a*-axis so the distances to the upper and lower stacked molecules along the b-axis are different (Figure 2b). Similar to the reported single-crystal structure of Cy<sub>6</sub>-NDI,<sup>22</sup> adjacent **BTDI** molecules are held by C-H…O interactions, but with a shorter distance of 2.519 Å. Mean plane intermolecular distances of Cy6-BTDI were measured to be 3.801, 3.762, and 3.838 Å. Transfer integral (t) values of the LUMO are calculated at the PBEPBE/6-31G(d) level of theory. Cy<sub>6</sub>-BTDI exhibits t value of +14.6 meV in the lateral direction, and large negative t values of -71.1, -39.0, and -99.3 meV in the vertical directions (Figure 2c). From our effective mass calculations at the PBEPBE/6-31G(d) level, Cy<sub>6</sub>-BTDI shows a two-dimensional anisotropic charge transport behavior in the a and b axes with effective masses of  $m_{\rm a} = 2.83$  and  $m_{\rm b} = 4.64$ .

In contrast to the previously reported Cy<sub>6</sub>-NDI, Cy<sub>6</sub>-BTDI showed a pronounced reduction in the optical HOMO–LUMO energy gap attributed to the quinoidal characteristic of the benzo[c]thiophene core.<sup>23</sup> Cy<sub>6</sub>-BTDI exhibits a  $\lambda_{max}$  at 460

nm in CHCl<sub>3</sub>, which is dramatically red-shifted with respect to  $Cy_6$ -NDI (382 nm) (Figure 3a). From the absorption onset,



Figure 3. (a) UV-vis absorption spectra of  $Cy_6$ -NDI and  $Cy_6$ -BTDI and (b) time-dependent UV-vis of  $Cy_6$ -BTDI in CHCl<sub>3</sub>.

the optical energy gap of Cy<sub>6</sub>-BTDI was calculated to be 2.58 eV. Cy<sub>6</sub>-BTDI demonstrates its chemical stability under ambient conditions as its solution-state time-dependent UV-vis absorption spectra remain unchanged over 30 days (Figure 3b). In addition, Cy<sub>6</sub>-BTDI appears to be emissive in the solution state with a  $\lambda_{em}$  at 467 nm, as opposed to the nonemissive NDI (Figure S13). Cy<sub>6</sub>-BTDI exhibits two fully reversible reduction waves in cyclic voltammetry (CV) experiments with the first half-width reduction potential  $E_{1/2}$  at -0.79 V, which corresponds to a LUMO energy level of -4.01 eV (Figure 4). Compared to the electrochemical LUMO energy level of Cy<sub>6</sub>-BTDI shows the potential for achieving air-stable electron mobility in OFETs. Thermogravimetry-differential thermal analysis (TG-DTA) experiment reveals the thermal stability of Cy<sub>6</sub>-BTDI with its



**Figure 4.** Cyclic voltammograms of Cy<sub>6</sub>-NDI (0.1 mM) and Cy<sub>6</sub>-**BTDI** (0.5 mM) in benzonitrile with 0.1 M of NBu<sub>4</sub>PF<sub>6</sub> at a scan rate of 100 mV s<sup>-1</sup>.



Figure 5. (a) Schematic diagram of the Cy<sub>6</sub>-BTDI single-crystal OFET architecture, (b) transfer characteristic of Cy<sub>6</sub>-BTDI single-crystal OFET at  $V_D = 40$  V, and (c) output characteristic of Cy<sub>6</sub>-BTDI single-crystal OFET.

5% weight loss temperature  $(T_{95})$  at 296 °C, and it exhibits an endothermic phase transition peak higher than its  $T_{95}$  value at 336 °C (Figure S14). We observed no apparent phase transitions from 20 °C to 260 °C for **Cy<sub>6</sub>-BTDI** in the differential scanning calorimetry (DSC) measurement (Figure S15). The excellent thermal stability of **Cy<sub>6</sub>-BTDI** ensures its consistent crystalline structures during the high-temperature device fabrication processes.

To evaluate the intrinsic charge-carrier properties of BTDI, we fabricated bottom-gate/top-contact OFETs with PVTgrown Cy6-BTDI single crystals as the active semiconductor layer (Figure 5a). The crystals were carefully picked up and laminated via electrostatic adhesion on the olefin layer above the SiO<sub>2</sub>/Si substrate with gold as the source and drain electrodes. Cy6-BTDI single-crystal OFETs exhibit negligible hysteresis between the forward and reverse sweeps and constant threshold voltages in the transfer characteristic curves (Figure 5b), which demonstrate reproducible *n*-channel OFET operations. Cy6-BTDI transistors achieved an air-stable electron mobility of  $\mu_e = 0.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the saturation regime, and the OFET performances remained consistent over 1 week of exposure in air. We examined the X-ray diffraction patterns of the semiconductor layer in Cy<sub>6</sub>-BTDI-based OFET and found the channel direction corresponded to neither the  $a^*$  nor  $b^*$  charge-transporting axis. In fact, the OFET channel is in either the  $+2a^* + b^*$  or  $-2a^* + b^*$  direction, which resulted in low electron mobility. Other essential OFET parameters, device stability data, as well as solution-processed  $Cy_6$ -BTDI OFET results via the edge-casting method<sup>24</sup> are summarized in Tables S3 and S4.

**Cy<sub>6</sub>-BTDI** OFETs demonstrated superior stability under ambient conditions compared to Cy<sub>6</sub>-NDI,<sup>22,25</sup> which suggests **BTDI** may be a promising  $\pi$ -core for future development of air-stable *n*-type semiconductors. It is noteworthy that the maximum drain current ( $[II_D]^{1/2}]^2 = 2.56 \ \mu$ A) in the transfer characteristic of the **Cy<sub>6</sub>-BTDI** OFET is consistent with that of the output characteristic (Figure 5c), which indicates **Cy<sub>6</sub>-BTDI** *n*-channel OFETs are insensitive toward bias-stress from charge trapping in transistor channels and confirms no overestimation of the electron mobility.<sup>26,27</sup>

In summary, a novel air-stable electron-deficient BTDI  $\pi$ core is reported in the current work, and we have developed an original synthetic route toward possible BTDI derivatives. Compared to the well-studied NDI core, BTDI has shown remarkable improvements in photophysical and electronic properties. The X-ray single-crystal packing structure of BTDI reveals strong intermolecular interactions as well as effective orbital overlaps. Thermal studies also suggest Cy<sub>6</sub>-BTDI derivative possesses high thermal stability and stabilized crystal phase. Air-stable single-crystal *n*-channel OFETs of  $Cy_6$ -BTDI have been fabricated using lamination and edge-casting methods, and the highest electron mobility of 0.16 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> is achieved. From our preliminary results herein, BTDI is a promising  $\pi$ -core for air-stable *n*-channel OFETs. Prospective studies involving BTDI such as tuning of electronic structures and packing structures via chemical modifications and side-chain engineering are anticipated. Optimizations of device architecture and fabrications are likewise expected to further improve the semiconductor performance of the BTDI  $\pi$ -core.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b01239.

Experimental procedures and spectroscopic data (PDF)

### Accession Codes

CCDC 1901392 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) (a) Bao, Z.; Locklin, J. Organic Field-Effect Transistors, 1st ed.; CRC Press: Boca Raton, FL, 2007. (b) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting  $\pi$ -Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. Chem. Rev. **2012**, 112, 2208–2267. (c) Root, S. E.; Savagatrup, S.; Printz, A. D.; Rodriquez, D.; Lipomi, D. J. Mechanical Properties of Organic Semiconductors for Stretchable, Highly Flexible, and Mechanically Robust Electronics. Chem. Rev. **2017**, 117, 6467–6499. (d) Mei, J.; Diao, Y.; Appleton, A. L.; Fang, L.; Bao, Z. Integrated Materials Design of Organic Semiconductors for Field- Effect Transistors. J. Am. Chem. Soc. **2013**, 135, 6724–6746.

(2) (a) Das, A.; Dost, R.; Richardson, T.; Grell, M.; Morrison, J. J.; Turner, M. L. A Nitrogen Dioxide Sensor Based on an Organic Transistor Constructed from Amorphous Semiconducting Polymers. *Adv. Mater.* 2007, *19*, 4018–4023. (b) Torsi, L.; Magliulo, M.; Manoli, K.; Palazzo, G. Organic Field-Effect Transistor Sensors: A Tutorial Review. *Chem. Soc. Rev.* 2013, *42*, 8612–8628. (c) Lin, P.; Yan, F. Organic Thin-Film Transistors for Chemical and Biological Sensing. *Adv. Mater.* 2012, *24*, 34–51. (d) Li, H.; Shi, W.; Song, J.; Jang, H. J.; Dailey, J.; Yu, J.; Katz, H. E. Chemical and Biomolecule Sensing with Organic Field-Effect Transistors. *Chem. Rev.* 2019, *119*, 3–35.

(3) (a) Yamamura, A.; Matsui, H.; Uno, M.; Isahaya, N.; Tanaka, Y.; Kudo, M.; Ito, M.; Mitsui, C.; Okamoto, T.; Takeya, J. Painting Integrated Complementary Logic Circuits for Single-Crystal Organic Transistors: A Demonstration of a Digital Wireless Communication Sensing Tag. *Adv. Electron. Mater.* **2017**, *3*, 1600456. (b) Myny, K.; Steudel, S.; Smout, S.; Vicca, P.; Furthner, F.; van der Putten, B.; Tripathi, A. K.; Gelinck, G. H.; Genoe, J.; Dehaene, W.; Heremans, P. Organic RFID Transponder Chip with Data Rate Compatible with Electronic Product Coding. *Org. Electron.* **2010**, *11*, 1176–1179.

(4) (a) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. Ultralow-Power Organic Complementary Circuits. *Nature* 2007, 445, 745–748.
(b) Crone, B.; Dodabalapur, A.; Lin, Y. Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarpeshkar, R.; Katz, H. E.; Li, W. Large-Scale Complementary Integrated Circuits Based on Organic Transistors. *Nature* 2000, 403, 521–523. (c) Usta, H.; Facchetti, A.; Marks, T. n. Channel Semiconductor Materials Design for Organic Complementary Circuits. *Acc. Chem. Res.* 2011, 44, 501–510.

(5) Ebata, H.; Izawa, T.; Miyazaki, E.; Takimiya, K.; Ikeda, M.; Kuwabara, H.; Yui, T. Highly Soluble [1]Benzothieno[3,2- b]-Benzothiophene (BTBT) Derivatives for High-Performance, Solution- Processed Organic Field-Effect Transistors. J. Am. Chem. Soc. 2007, 129, 15732–15733.

(6) Yamamoto, T.; Takimiya, K. Facile Synthesis of Highly  $\pi$ -Extended Heteroarenes, Dinaphtho[2,3-b:2',3'-f]chalcogenopheno-[3,2- b]chalcogenophenes, and Their Application to Field-Effect Transistors. J. Am. Chem. Soc. **2007**, 129, 2224–2225.

(7) Okamoto, T.; Mitsui, C.; Yamagishi, M.; Nakahara, K.; Soeda, J.; Hirose, Y.; Miwa, K.; Sato, H.; Yamano, A.; Matsushita, T.; Uemura, T.; Takeya, J. V-Shaped Organic Semiconductors with Solution Processability, High Mobility, and High Thermal Durability. *Adv. Mater.* **2013**, *25*, 6392–6397.

(8) Mitsui, C.; Okamoto, T.; Yamagishi, M.; Tsurumi, J.; Yoshimoto, K.; Nakahara, K.; Soeda, J.; Hirose, Y.; Sato, H.; Yamano, A.; Uemura, T.; Takeya, J. High-Performance Solution-Processable N-Shaped Organic Semiconducting Materials with Stabilized Crystal Phase. *Adv. Mater.* **2014**, *26*, 4546–4551.

(9) Yamamoto, A.; Murata, Y.; Mitsui, C.; Ishii, H.; Yamagishi, M.; Yano, M.; Sato, H.; Yamano, A.; Takeya, J.; Okamoto, T. Zigzag-Elongated Fused  $\pi$ -Electronic Core: A Molecular Design Strategy to Maximize Charge-Carrier Mobility. *Adv. Sci.* **2018**, *5*, 1700317.

(10) de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. Stability of n-Type Doped Conducting Polymers and Consequences for Polymeric Microelectronic Devices. *Synth. Met.* **1997**, *87*, 53–59.

(11) Würthner, F. Plastic Transistors Reach Maturity for Mass Applications in Microelectronics. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037–1039.

(12) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. Tuning Orbital Energetics in Arylene Diimide Semiconductors. Materials Design for Ambient Stability of n-Type Charge Transport. *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278.

(13) (a) Zaumseil, J.; Sirringhaus, H. Electron and Ambipolar Transport in Organic Field-Effect Transistors. *Chem. Rev.* **2007**, *107*, 1296–1323. (b) Newman, C. R.; Frisbie, D.; Da, D. A.; Filho, S.; Brédas, J.- L.; Ewbank, P. C.; Mann, K. R. Introduction to Organic Thin Film Transistors and Design of n-Channel Organic Semiconductors. *Chem. Mater.* **2004**, *16*, 4436–4451. (c) Zhou, K.; Dong, H.; Zhang, H.-L.; Hu, W. High Performance n-Type and Ambipolar Small Organic Semiconductors for Organic Thin Film Transistors. *Phys. Chem. Chem. Phys.* **2014**, *16*, 22448–22457. (d) Facchetti, A.  $\pi$ -Conjugated Polymers for Organic Electronics and Pho- tovoltaic Cell Applications. *Chem. Mater.* **2011**, *23*, 733–758.

(14) Liang, Z.; Tang, Q.; Xu, J.; Miao, Q. Soluble and Stable N-Heteropentacenes with High Field-Effect Mobility. *Adv. Mater.* **2011**, 23, 1535–1539.

(15) (a) Al Kobaisi, M.; Bhosale, S. V.; Latham, K.; Raynor, A. M.; Bhosale, S. V. Functional Naphthalene Diimides: Synthesis, Properties, and Applications. *Chem. Rev.* 2016, 116, 11685-11796.
(b) Bhosale, S. V.; Jani, C. H.; Langford, S. J. Chemistrty of Naphthalene Diimides. *Chem. Soc. Rev.* 2008, 37, 331-342.
(c) Würthner, F.; Stolte, M. Naphthalene and Perylene Diimides for Organic Transistors. *Chem. Commun.* 2011, 47, 5109-5115.

(16) (a) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. Rylene and Related Diimides for Organic Electronics. *Adv. Mater.* **2011**, *23*, 268–284. (b) Horowitz, G.; Kouki, F.; Spearman, P.; Fichou, D.; Nogues, C.; Pan, X.; Garnier, F. Evi- dence for n-Type Conduction in a Perylene Tetracarboxylic Diimide De- rivative. *Adv. Mater.* **1996**, *8*, 242–245. (c) Zhao, X.; Xiong, Y.; Ma, J.; Yuan, Z. Rylene and Rylene Diimides: Comparison of Theoretical and Experimental Results and Prediction for High-Rylene Derivatives. *J. Phys. Chem. A* **2016**, *120*, 7554–7560.

(17) (a) Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. Cyanonaphthalene Diimide Semiconductors for Air-Stable, Flexible, and Optically Transparent n-Channel Field-Effect Transistors. Chem. Mater. 2007, 19, 2703-2705. (b) Yuan, Z.; Ma, Y.; Geßner, T.; Li, M.; Chen, L.; Eustachi, M.; Weitz, R. T.; Li, C.; Müllen, K. Core-Fluorinated Naphtha- lene Diimides: Synthesis, Characterization, and Application in n-Type Organic Field-Effect Transistors. Org. Lett. 2016, 18, 456-459. (c) He, T.; Stolte, M.; Würthner, F. Air-Stable n-Channel Organic Single Crystal Field- Effect Transistors Based on Microribbons of Core-Chlorinated Naphtha- lene Diimide. Adv. Mater. 2013, 25, 6951-6955. (d) Oh, J. H.; Suraru, S.-L.; Lee, W. Y.; Könemann, M.; Höffken, H. W.; Röger, C.; Schmidt, R.; Chung, Y.; Chen, W. C.; Würthner, F.; Bao, Z. High-Performance Air- Stable n-Type Organic Transistors Based on Core-Chlorinated Naphtha- lene Tetracarboxylic Diimides. Adv. Funct. Mater. 2010, 20, 2148-2156. (e) Tang, M. L.; Oh, J. H.; Reichardt, A. D.; Bao, Z. Chlorination: A General Route Toward Electron Transport in Organic Semiconductors. J. Am. Chem. Soc. 2009, 131, 3733-3740. (f) Huang, C.; Barlow, S.; Marder, S. R. Perylene-3,4,9,10-Tetracarboxylic Acid Diimides: Synthesis, Physical Properties, and Use in Organic Electronics. J. Org. Chem. 2011, 76, 2386-2407. (g) Delgado, M. C. R.; Kim, E. G.; da Silva Filho, D. A.; Brédas, J. L. Tuning the Charge-Transport Parameters of Perylene Diimide Single Crystals via End and/or Core Functionalization: A Density Functional Theory Investigation. J. Am. Chem. Soc. 2010, 132, 3375-3387. (h) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. Effects of Ar- ylene Diimide Thin Film Growth Conditions on n-Channel OFET Performance. Adv. Funct. Mater. 2008, 18, 1329-1339. (i) Chang, J.; Ye, Q.; Huang, K. W.; Zhang, J.; Chen, Z. K.; Wu, J.; Chi, C. Stepwise Cyanation of Naphthalene Diimide for n-Channel Field-Effect Transistors. Org. Lett. 2012, 14, 2964-2967.

(18) (a) Katsuta, S.; Tanaka, K.; Maruya, Y.; Mori, S.; Masuo, S.; Okujima, T.; Uno, H.; Nakayama, K. I.; Yamada, H. Synthesis of Pentacene-, Tetracene- and Anthracene Bisimides Using Double-Cyclization Reaction Mediated by Bismuth(III) Triflate. Chem. Commun. 2011, 47, 10112-10114. (b) Yue, W.; Gao, J.; Li, Y.; Jiang, W.; Di Motta, S.; Negri, F.; Wang, Z. One-Pot Synthesis of Stable NIR Tetracene Diimides via Double Cross-Coupling. J. Am. Chem. Soc. 2011, 133, 18054-18057. (c) Gao, X.; Di, C. A.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. Core-Expanded Naphthalene Diimides Fused with 2-(1,3-Dithiol-2-Ylidene)-Malonitrile Groups for High-Performance, Am- bient-Stable, Solution-Processed n-Channel Organic Thin Film Transis- tors. J. Am. Chem. Soc. 2010, 132, 3697-3699. (d) Cui, X.; Xiao, C.; Winands, T.; Koch, T.; Li, Y.; Zhang, L.; Doltsinis, N. L.; Wang, Z. Hexacene Diimide. J. Am. Chem. Soc. 2018, 140, 12175-12180. (e) Endres, A. H.; Schaffroth, M.; Paulus, F.; Reiss, H.; Wadepohl, H.; Rominger, F.; Krämer, R.; Bunz, U. H. F. Coronene-Containing N-Heteroarenes: 13 Rings in a Row. J. Am. Chem. Soc. 2016, 138, 1792-1795. (f) Fukutomi, Y.; Nakano, M.; Hu, J. Y.; Osaka, I.; Takimiya, K. Naphthodithiophenediimide (NDTI): Synthesis, Structure, and Applications. J. Am. Chem. Soc. 2013, 135, 11445-11448. (g) Jaggi, M.; Blum, C.; Marti, B. S.; Liu, S. X.; Leutwyler, S.; Decurtins, S. Annulation of Tetrathiafulvalene to the Bay Region of Perylenediimide. Org. Lett. 2010, 12, 1344-1347. (h) Nakano, M.; Sawamoto, M.; Yuki, M.; Takimiya, K. N, N '-Unsubstituted Naphthodithiophene Diimide: Synthesis and Derivatization via N -Alkylation and -Arylation. Org. Lett. 2016, 18, 3770-3773. (i) Chen, W.; Nakano, M.; Kim, J.-H.; Takimiya, K.; Zhang, Q. Naphtho [2,3-b] Thiophene Diimide (NTI): A Mono-Functionalisable Core-Extended Naphthalene Diimide for Electron-Deficient Architectures. J. Mater. Chem. C 2016, 4, 8879-8883. (j) Ye, Q.; Chang, J.; Huang, K.-W.; Shi, X.; Wu, J.; Chi, C. Cyanated Diazatetracene Diimides with Ultrahigh Electron Affinity for n-Channel Field Effect Transistors. Org. Lett. 2013, 15, 1194-1197. (k) Ye, Q.; Chang, J.; Huang, K.-W.; Chi, C. Thiophene-Fused Tetracene Diimide with Low Band Gap and Ambipolar Behavior. Org. Lett. 2011, 13, 5960-5963. (1) Chang, J.; Shao, J.; Zhang, J.; Wu, J.; Chi, C. A Phthalimide-Fused Naphthalene Diimide with High Electron Affinity for a High Performance n-Channel Field Effect Transistor. RSC Adv. 2013, 3, 6775-6778. (m) Shao, J.; Chang, J.; Chi, C. Solution-Processable n-Type Semiconductors Based on Unsymmetrical Naphthalene Imides: Synthesis, Characterization, and Applications in Field-Effect Transistors. Chem. - Asian J. 2014, 9, 253-260.

(19) (a) Mayer, R.; Kleinert, H.; Richter, S.; Gewald, K. Schwefel-Heterocyclen. XI. Isothionaphthen. J. Prakt. Chem. 1963, 20, 244– 249. (b) Cava, M. P.; Pollack, N. M.; Mamer; Mitchell, O. A. Synthetic Route to Benzo[c]thiophene and the Naphtho[c]thiophenes. J. Org. Chem. 1971, 36, 3932–3937. (c) King, G.; Higgins, S. J. Synthesis and Characterisation of Novel Substituted Benzo[c]thiophenes and Polybenzo[c]thiophenes: Tuning the Potentials for n- and p-Doping in Transparent Conducting Polymers. J. Mater. Chem. 1995, 5, 447–455.

(20) Ueda, T.; Konishi, H.; Manabe, K. Trichlorophenyl Formate: Highly Reactive and Easily Accessible Crystalline CO Surrogate for Palladium-Catalyzed Carbonylation of Aryl/Alkenyl Halides and Triflates. *Org. Lett.* **2012**, *14*, 5370–5373.

(21) Schleyer, P. V. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Van Eikema Hommes, N. J. R. Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

(22) Kakinuma, T.; Kojima, H.; Ashizawa, M.; Matsumoto, H.; Mori, T. Correlation of Mobility and Molecular Packing in Organic Transistors Based on Cycloalkyl Naphthalene Diimides. *J. Mater. Chem. C* 2013, *1*, 5395–5401.

(23) (a) Kawabata, K.; Saito, M.; Osaka, I.; Takimiya, K. Very Small Bandgap  $\pi$ -Conjugated Polymers with Extended Thienoquinoids. *J. Am. Chem. Soc.* **2016**, *138*, 7725–7732. (b) Zhang, C.; Zang, Y.; Gann, E.; McNeill, C. R.; Zhu, X.; Di, C.; Zhu, D. Two-Dimensional  $\pi$ -Expanded Quinoidal Terthiophenes Terminated with Dicyanomethylenes as n-Type Semiconductors for High-Performance Organic Thin-Film Transistors. J. Am. Chem. Soc. 2014, 136, 16176–16184.

(24) Uemura, T.; Hirose, Y.; Uno, M.; Takimiya, K.; Takeya, J. Very High Mobility in Solution-Processed Organic Thin-Film Transistors of Highly Ordered [1]Benzothieno[32-b]Benzothiophene Derivatives. *Appl. Phys. Express* **2009**, *2*, 111501.

(25) Kalita, A.; Dey, A.; Iyer, P. K. The Effect of Inorganic/Organic Dual Dielectric Layers on the Morphology and Performance of n-Channel OFETs. *Phys. Chem. Chem. Phys.* **2016**, *18*, 12163–12168.

(26) Bittle, E. G.; Basham, J. I.; Jackson, T. N.; Jurchescu, O. D.; Gundlach, D. J. Mobility Overestimation Due to Gated Contacts in Organic Field-Effect Transistors. *Nat. Commun.* **2016**, *7*, 1–7.

(27) Choi, H. H.; Cho, K.; Frisbie, C. D.; Sirringhaus, H.; Podzorov, V. Critical Assessment of Charge Mobility Extraction in FETs. *Nat. Mater.* **2018**, *17*, 2–7.