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Synthesis of Heterocyclic Core-Expanded Bis-Naphthalene Tetracarboxylic Diimides

Hewei Luo,^{*,†} Dongdong He,[†] Yong Zhang,[†] Shiwen Wang,[†] Haili Gao,[†] Ji Yan,[†] Yang Cao,[†] Zhengxu Cai,[§][®] Luxi Tan,^{||}[®] Shide Wu,^{*,†} Lizhen Wang,^{*,†} and Zitong Liu^{*,‡}[®]

[†]School of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, China [‡]Beijing National Laboratories for Molecular Sciences, CAS Key Laboratories of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[§]School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

S Supporting Information

ABSTRACT: A highly reactive bis-naphthalene tetracarboxylic diimide (bis-NDI) intermediate, **TBrDNDI**, was designed and synthesized for core-expanded NDIs. Based on this intermediate, we achieved 9- and 11-membered coreexpanded bis-NDI derivatives. Through expanding the NDI core and introducing electron-donor or electron-acceptor groups, the frontier energy orbitals, optical and electrical properties of these bis-NDIs can be finely tuned to obtain airstable ambipolar or *n*-type materials.

N aphthalene tetracarboxylic diimide (NDI) is an important core for electron-transporting materials, because of its high electron-withdrawing property.¹ Recently, the core-expanded derivatives based on NDI have received more and more attention, because of their fascinating electro-optical properties² and potential applications as organic semiconductors.³ A majority of high-mobility organic semiconductors have been developed by expanding the π -conjugation of NDI core.^{4–7} Most of them are based on the intermediate 2,3,6,7-tetrabromonaphthalene diimide (TBrNDI; see Scheme 1) with different side chains.^{5,6} For instance, Wang et al. have synthesized a hexacene diimide utilizing TBrNDI.⁶ Single-crystal microribbon-based organic







field-effect transistors (OFETs) exhibited outstanding ambipolar properties with maximum electron and hole mobilities of 2.17 and 0.30 cm² V⁻¹ s⁻¹, respectively.

In addition to the acene-type,^{6,7} various core-expanding NDIs with heterocyclic rings containing sulfur,⁸ oxygen,⁹ and nitrogen^{5e,10} are also constructed using nucleophilic aromatic substitution through TBrNDI. The heterocyclic ring endows NDI with unique optical and electrical properties caused by heteroatom effect and hybrid electron-donor (D) or electronacceptor (A) interactions. Among them, bis-NDI with heterocyclic rings can further extend the π -conjugation, which can effectively obtain mixing D-A structures and modulate the HOMO/LUMO levels. However, bis-NDIs with core-expanded heterocyclic rings are seldom reported, because of the synthetic limitation.¹¹ For instance, Zhao et al. reported nitrogen-containing seven-ring expanded bis-NDI derivatives with red to NIR absorptions, and exhibited well-defined solution and thin-film J-aggregation behaviors. However, it is difficult to further expand the ring, because of weak reactivity of C–Br for nucleophilic groups.¹

Herein, we reported a new intermediate **TBrDNDI** with four Br atoms as reactive sites (see Scheme 1). **TBrDNDI** can be easily synthesized through the condensation of alkyl chain attached 2,3,6,7-tetrabromonaphthalene diimide (**TBrNDI**) and benzene-1,2,4,5-tetrathiol in good yield. Because of weak

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electron-donating S atoms in the structure, **TBrDNDI** exhibits high reactivity to expand the conjugation length. Moreover, **TBrDNDI** itself has a 7-membered ring A–D–A structure showing a narrow HOMO–LUMO gap (0.96 eV). All of these make **TBrDNDI** an excellent intermediate for the synthesis of core-expanded bis-NDI derivatives. As an example, we synthesized a 9-membered ring (**TCNDNDI**) and an 11membered ring (**DBDNDI**) by attaching electron-accepting groups (2,2-dicyanoethene-1,1-bis(thiolate)) and electrondonating groups (benzene-1,2-bis(thiolate)), respectively (see Scheme 1). These sulfur-heterocyclic ring expanded bis-NDIs can effectively tune the optical and electrical properties to be appropriate for potential application in organic semiconducting materials.

The synthetic routes of sulfur-heterocyclic expanded bis-NDI derivatives are shown in Scheme 2. Benzene-1,2,4,5-

Scheme 2. Synthetic Routes



tetrathiol was synthesized according to a known procedure.¹³ Using Birch reduction through sodium in $NH_3(l)$, four isopropyl groups can be removed from 1,2,4,5-tetrakis-(isopropylthio)benzene, then neutralizing reaction solution with HCl (10% aqueous), extracting product with dichloromethane (DCM). Benzene-1,2,4,5-tetrathiol was obtained as a light green solid after solvent was removed in vacuo. Because benzene-1,2,4,5-tetrathiol is sensitive to air, we used it for next reaction without other purified procedure (see the Supporting Information).

TBrDNDI was synthesized through the condensation of bis(2-octyldodecyl) attached 2,3,6,7-tetrabromonaphthalene diimide (**TBrNDI**)¹⁴ and benzene-1,2,4,5-tetrathiol in good yield. As shown in Scheme 2, when we treated **TBrNDI** (2 equiv) with benzene-1,2,4,5-tetrathiol (1 equiv) in tetrahydrofuran (THF) with Aliquat 336 (Starks' catalyst) and potassium carbonate for 1 h at room temperature, **TBrDNDI** was obtained in good yield (67%). Further reaction to the polymer can be avoided by controlling the feed ratio. Potassium carbonate and Aliquat 336 (phase transfer catalyst) made the mixture react at room temperature and shortened the

reaction time. Without them, the reaction time was extended to 5 h with 50 °C exhibiting low yield of 40%. To examine the reactivity of the sulfur-heterocyclic expanded bis-NDI intermediate (**TBrDNDI**), we also synthesized **DBDNDI** and **TCNDNDI** by using benzene-1,2-dithiol and sodium 2,2dicyanoethene-1,1-bis(thiolate), respectively, to react with **TBrDNDI** (Scheme 2). **DBDNDI** and **TCNDNDI** were obtained under similar reaction conditions for 2 h at room temperature in 95% and 90% yield. These high yields indicate that **TBrDNDI** can be a good intermediate for the synthesis of core-expanded bis-NDI derivatives.

All three compounds show very good solubility above ~20 mg/mL in usual organic solvents such as DCM, THF, chloroform, and methylbenzene. The better solubility, compared other planar NDI derivatives, results from their V-shaped geometries, because of symmetric S atoms in the structures, as discussed below. The UV-vis absorption spectra of **TBrDNDI**, **DBDNDI**, **TCNDNDI**, and **TBrNDI** in chloroform are shown in Figure 1a. Three sulfur-heterocyclic



Figure 1. (a) Absorption spectra of TBrDNDI, DBDNDI, TCNDNDI, and TBrNDI in 10^{-5} M chloroform. (b–d) Normalized solution (in chloroform) and film (spin-coated on quartz wafer) absorption spectra of TBrDNDI, DBDNDI, and TCNDNDI.

expanded bis-NDI derivatives exhibit a broad absorption band at 450-800 nm, and TBrNDI shows a narrow absorption band at 350-450 nm. Maximum absorption wavelength of TBrDNDI, DBDNDI, TCNDNDI, and TBrNDI emerged at 557, 592, 611, and 401 nm, respectively (see Table 1). There is a clearly red-shifted absorption of TBrDNDI, compared to TBrNDI. In addition, DBDNDI and TCNDNDI show more red shifts and broad absorption bands as more D/A moieties attached to the NDI core position. Besides, DBDNDI and **TCNDNDI** show higher absorptivity (Figure 2a and Table 1) than TBrDNDI. The molar extinction coefficient for TBrDNDI, DBDNDI, TCNDNDI, and TBrNDI were 24 240, 37 200, 38 910, and 9915 L M⁻¹ cm⁻¹, respectively, indicating effective donor-acceptor interactions. Film absorption spectra of three compounds were also measured to further investigate their packing in the solid state (Figures 1b-d). Interestingly, compared to TBrDNDI in chloroform solution, the maximum absorption wavelength of film shows blue-shifted from 557 nm to 539 nm, which may be due to the Haggregation in solid state. In contrast, DBDNDI film shows a red shift from 592 nm to 608 nm, compared to that in

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Table 1. Absorption and Electrochemical Properties

compound	λ_{\max}^{a} (nm)	ε^{b} (L M ⁻¹ cm ⁻¹)	LUMO (eV)	HOMO (eV)	HOMO-LUMO gap (eV)
TBrDNDI	557	24 240	-4.15°	-5.11^{d}	0.96 ^e
DBDNDI	592	37 200	-4.05^{c}	-5.08^{d}	1.03 ^e
TCNDNDI	611	38 910	-4.49^{c}	-5.10^{d}	0.61 ^e
TBrNDI	401	9915	-4.12^{f}	-6.91^{f}	2.79 ^f

^{*a*}Wavelength at maximum absorption in chloroform. ^{*b*}Molar extinction coefficient at λ_{max} . ^{*c*}Estimated from the first onset reduction wave in CV. ^{*d*}Estimated from the first onset oxidation wave. ^{*e*}Estimated from $E_{LUMO} - E_{HOMO}$. ^{*f*}According to literature reported in ref 14.



Figure 2. Cyclic voltammogram (CV) of TBrDNDI, DBDBDI, and TCNDNDI in dichloromethane (DCM).

chloroform solution. Moreover, **TCNDNDI** film exhibits a strong red shift from 611 nm to 689 nm, and a new shoulder absorption at 746 nm is observed in Figure 1d. The different UV–vis absorption phenomena may be related to their unique mixing D–A structures and diverse molecular packing in the solid state.

The electrochemical properties of three sulfur-heterocyclic expanded bis-NDIs were also examined by cyclic voltammetry (Figure 2), and their LUMO and HOMO levels, as well as HOMO–LUMO gaps are listed in Table 1. Multiple reversible reduction and one irreversible oxidation waves were observed for three compounds. Based on their onset reduction and oxidation waves, the LUMO/HOMO levels of TBrDNDI, DBDNDI, and TCNDNDI were estimated to be -4.15/-5.11 eV, -4.05/-5.08 eV, and -4.49/-5.10 eV. Note that TCNDNDI has a very low LUMO level and a narrow HOMO–LUMO gap (0.61 eV), because of the presence of electron-accepting groups 2,2-dicyanoethene-1,1-bis(thiolate). Such appropriate LUMO and HOMO levels suggest their potential application as electron-transporting or ambipolar molecules.

Density functional theory (DFT) calculations were performed to help further investigate the geometries and frontier orbitals of the molecules. To be simplified, octyldodecyl-alkyl chains were replaced by methyl. As depicted in Figure 3, all three molecules exhibit a zigzag structure. Through a five-membered ring containing two S atoms as a bridge, the 2-(1,3-dithiol-2-ylidene) malonitrile group in **TCNDNDI** is coplanar to the NDI core. However, through a six-membered ring containing two S atoms as a bridge, the phenyl moieties in **TBrDNDI** and **DBDNDI** and NDI core are not coplanar. **TBrDNDI** and **TCNDNDI** form two dihedral angles of 136.3° and 138.2°, respectively. **DBDNDI** forms four dihedral angles of 136.8° for the two bilateral components, and



Figure 3. Optimized geometries and frontier orbitals of TBrDNDI, DBDNDI, and TCNDNDI, based on calculated density functional theory (DFT).

136.6° for the two medial components. HOMO orbitals of three compounds are localized on phenyl, the bridging S atoms, and 2-(1,3-dithiol-2-ylidene) malonitrile moieties. LUMO orbitals are primary contributed by the NDI core and slightly by bridging S atoms. The HOMO and LUMO energies of three compounds were also calculated and summarized in Table S1 in the Supporting Information. These calculating results also indicate that introducting donor and acceptor functional groups onto the NDI core can efficiently tune HOMO/LUMO levels.

To explore the viability of our concept, BGBC architecture OFETs were fabricated (see the Supporting Information). Because of their good solubility, thin-film devices were made by spin-coating their solutions in nonhalogen solvent THF. The transfer and output characteristics of thin film devices were measured under ambient conditions. As shown in Figure S1 in the Supporting Information, DBDNDI exhibits ambipolar semiconducting behaviors. The highest electron/ hole mobility was 0.02/0.01 cm² V⁻¹ s⁻¹ (see Table S2 in the Supporting Information). TCNDNDI shows unipolar election mobility of 0.0002 cm² V⁻¹ s⁻¹ (see Table S2 and Figure S1). Notably, they all exhibit *n*-type or ambipolar behaviors under ambient conditions, indicating the successful modulation of the HOMO/LUMO energy levels. Further optimizing the device may further increase their semiconducting properties. Noting the extended absorption of TCNDNDI, it may be suitable for use as an electron acceptor in organic solar cells.

In conclusion, new intermediate **TBrDNDI** was developed to build up multimembered heterocyclic ring-expanded bis-NDIs. By using it, we achieved 9- and 11-ring expanded heterocyclic structures. Through expanding NDI core and introducing D or A groups, the frontier energy orbitals, optical and electrical properties of these sulfur-heterocyclic expanded bis-NDIs can be tuned to obtain air-stable ambipolar or n-type materials. Further studies of other bis-NDI materials including oligomers and polymers with nitrogen or other heteroatoms through **TBrDNDI** are underway.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b03891.

Experimental details and characterization of new compounds (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: luohw@zzuli.edu.cn (H. Luo).

*E-mail: drzitong@gmail.com (Z. Liu).

*E-mail: wushide@zzuli.edu.cn (S. Wu).

*E-mail: wlz@zzuli.edu.cn (L. Wang).

ORCID ®

Zhengxu Cai: 0000-0003-0239-9601 Luxi Tan: 0000-0003-0587-4607 Zitong Liu: 0000-0003-1185-9219

Notes

The authors declare no competing financial interest.

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