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Zitang Wei, Xiangchun Li, Fred Wudl, Yonghao Zheng



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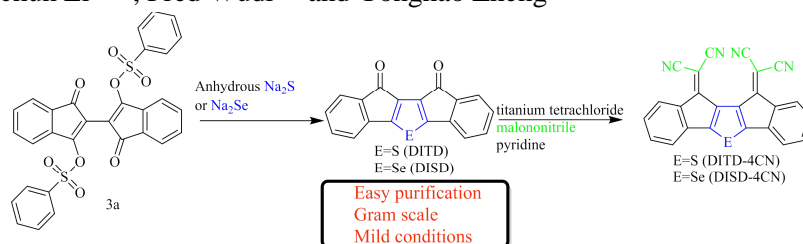
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## Graphical Abstract

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## Facile synthesis of thiophene/selenophene-fused acene and their optoelectronic properties

Zitang Wei<sup>a,§</sup>, Xiangchun Li<sup>a,c,§</sup>, Fred Wudl<sup>a,\*</sup> and Yonghao Zheng<sup>a,b,\*</sup>

<sup>a</sup> California NanoSystems Institute, University of California, Santa Barbara, CA 93106, USA.

<sup>b</sup> School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, China.

Center for Applied Chemistry, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, China.

<sup>c</sup> Key Laboratory for Organic Electronics and Information Displays (KLOEID) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM) Nanjing University of Posts & Telecommunications, Nanjing 210023, China

<sup>§</sup> These authors contributed equally.

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### ABSTRACT

Dibenzo thiophene- and selenophene are widely used in very different areas, ranging from biology to electronic engineering. However, their compounds require multiple synthetic steps. In this report, we introduce a two-step facile synthesis of a dibenzo thiophene/selenophene, namely diindeno[1,2-b:2', 1'-d]thiophene-10, 11-dione (**DITD**) and diindeno[1,2-b:2', 1'-d]selenophene-10, 11-dione (**DISD**). The compounds were further converted *via* a Knoevenagel condensation to dicyanovinylene derivatives. Their electronic and optoelectronic properties, backed by density functional theory (DFT) calculations are reported.

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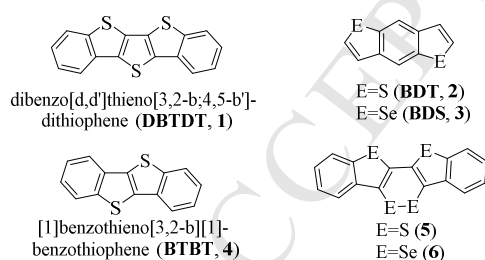
\* Corresponding author. E-mail address: wudl@chem.ucsb.edu (Fred Wudl)

\* Corresponding author. E-mail address: zhengyonghao@uestc.edu.cn (Yonghao Zheng)

## 1. Introduction

Heterocycles have been attracting a great deal of attention in materials science.<sup>1,2</sup> Thiophenes and selenophenes are widely distributed in nature and are treated as important classes of heterocycles due to their existence in a broad spectrum of natural and synthetic organic compounds with multiple biological and electronic properties.<sup>3</sup> Over the decades, Thiophene- and selenophene-containing compounds have drawn attention from medicinal<sup>4</sup> and synthetic chemists to explore different synthetic routes of thiophene and selenophene derivatives. Moreover, relatively easy access of functional thiophene and selenophene derivatives gives chemists opportunities to make use of appropriated functionalized derivatives in various applications. For example, the structural characteristic and substitution of thiophene ring-containing drugs have an important impact on the metabolic pathways utilized for that drug.<sup>5</sup> Also, thiophene-core estrogen receptors show interesting binding affinity patterns that may lead to significant superagonist activities.<sup>6</sup> Additionally, thiophene derivatives have huge applications as functional materials in discotic liquid crystals,<sup>7</sup> biosensors,<sup>8,9</sup> organic field effect transistors (OFETs),<sup>10-12</sup> organic light-emitting diodes (OLEDs),<sup>13,14</sup> and organic photovoltaics (OPVs).<sup>15-18</sup>

Several synthetic routes for thiophene- and selenophene-containing molecules have been reported with applications in different fields. Among them, heteroaromatic-incorporated acenes are frequently involved. Highly extended polyacenes have well-known applications in organic electronics,<sup>19,20</sup> but large polyacenes are not chemically stable under ambient conditions.<sup>19</sup> Therefore, the introduction of heteroatoms can help stabilize the backbone structures with effects on the system's electronic and solid-state structures. Most of the existing synthetic routes of dibenzo heterocycles require multiple, complicated steps. Several typical examples are shown in Figure. 1, including synthesis of dibenzo[d,d']thieno [3,2-b;4,5-b']-dithiophene (**DBTDT**, **1**),<sup>21</sup> synthesis of benzo [1,2-b:4,5-b']-dithiophene (**BDT**, **2**),<sup>22</sup> benzo[1,2-b:4,5-b']-diselenophene (**BDS**, **3**)<sup>22</sup> and [1]benzothieno[3,2-b][1] benzothiophene (**BTBT**, **4**),<sup>19</sup> and intramolecular cyclization of fused thiophene derivative **5** and selenophene derivative **6**.<sup>23</sup> But even today, the synthetic difficulties and cost are still issues that limit the development of heteroacenes.



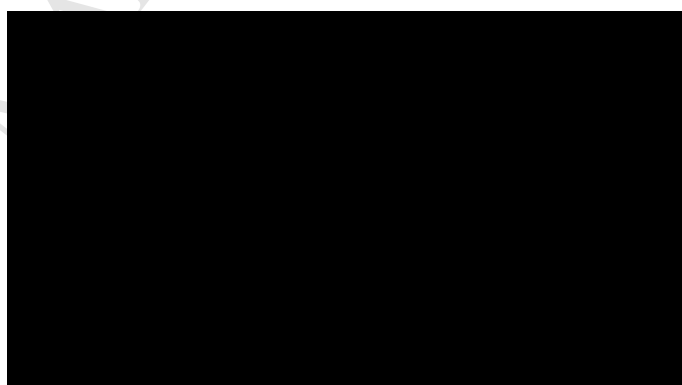
**Figure. 1.** Examples of thiophene/selenophene based acenes.

We reported a gram-scale and column-free synthetic approach for the thiophene- and selenophene-containing heteroacenes, namely diindeno[1,2-b:2',1'-d]thiophene-10,11-dione (**DITD**) and diindeno[1,2-b:2',1'-d]selenophene-10,11-dione (**DISD**) (Scheme 1), based on a new intramolecular cyclization starting with readily available [2,2'-Bi-1*H*-indene]-3,3'-dihydroxy-1,1'-dione (**BIT-OH<sub>2</sub>**) that was first synthesized and characterized over 100 years ago by Gabriel and Leupold.<sup>24</sup> Recently, **BIT-OH<sub>2</sub>** derivatives have been synthesized and characterized, such as BIT-zwitterion,<sup>25</sup> and BIT-diester that exhibited a highly efficient topochemical polymerization.<sup>26</sup> We further take advantage of the backbone of **BIT-OH<sub>2</sub>**, bridging the two indene units by sulfur or selenium atom to help establish the

co-planarity of the molecular system so that it can allow an efficient intermolecular  $\pi$ - $\pi$  stacking in the solid state. At the same time, the backbone is modified by adding the electron-withdrawing dicyanovinylene functionality to the core to remarkably depress the LUMO energy level without interrupting the  $\pi$ -conjugation.

## 2. Results and Discussion

The synthetic approach is shown in Scheme 1. **BIT-OH<sub>2</sub>** reacted with benzenesulfonyl chloride to yield compound **1** as a bright yellow solid at 0 °C. During the reaction workup, we found out that compound **1** starts decomposing before precipitating from the reaction mixture. Once in the solid form, compound **1** becomes stable. The essential step for this molecular system was the ring closure step to make the fused  $\pi$ -conjugated molecular systems **DITD** and **DISD**. After intensive exploration of method, solvent, temperature, reaction time, *etc.*, sodium sulfide was found to be the ideal sulfur source. The anhydrous sodium sulfide was generated reduction of sodium and sulfur under reflux for 2 days in tetrahydrofuran (THF) with naphthalene as catalyst. Compound **1** was dissolved in DCM, followed by a large excess of anhydrous sodium sulfide. The reaction was stirred at room temperature for 12 hours. A brown solid was collected and analyzed to be compound **DITD** in 62% yield. The synthesis of selenophene-based **DISD** followed the same steps as **DITD**, resulting in 65% yield. It is worth to mention that we have tried to introduce the sulfur/selenium source by using commercially available Lawrenson/Woolings reagent, but the yield of products from this approach were less than 20%.



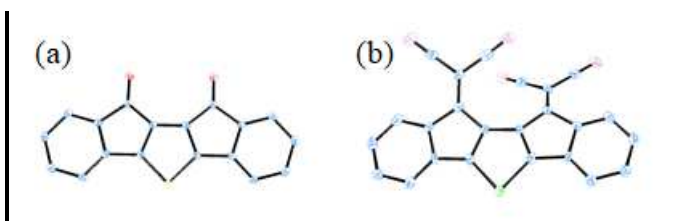
**Scheme 1.** Synthetic route for **DITD**, **DISD**, **DITD-4CN** and **DISD-4CN**: i: triethylamine, pyridine, benzenesulfonyl chloride, dichloromethane (DCM), 0 °C; ii: Anhydrous Na<sub>2</sub>S or Na<sub>2</sub>Se, DCM, room temperature; iii: titanium tetrachloride, pyridine, malononitrile.

After the **DITD** and **DISD** compounds were synthesized and characterized, the final step was to perform the Knoevenagel condensation to add two dicyanovinylene units on the molecule. However, the poor solubility of the **DITD** and **DISD** negatively influenced the efficiency of the Knoevenagel condensation (Scheme 1). Even though the same reactions have been performed for similar molecules, such as dihydroindeno[1,2-*b*]fluorenone by Marks *et al.*,<sup>27</sup> truxenone by Nielsen *et al.*,<sup>28</sup> diindenopyrazinedione by Yamashita *et al.*,<sup>29</sup> and pentaphenyleneone by Maxine *et al.*,<sup>30</sup> moderate to low yield reactions were reported because of either the steric hindrance of the carbonyl groups or low reactivity.

The condensation was performed with the aid of titanium tetrachloride, which is often used to activate the carbonyl units of sterically hindered molecules. Under relatively mild conditions, **DITD**, titanium tetrachloride, pyridine and large excess of malononitrile were stirred in chloroform at room temperature for

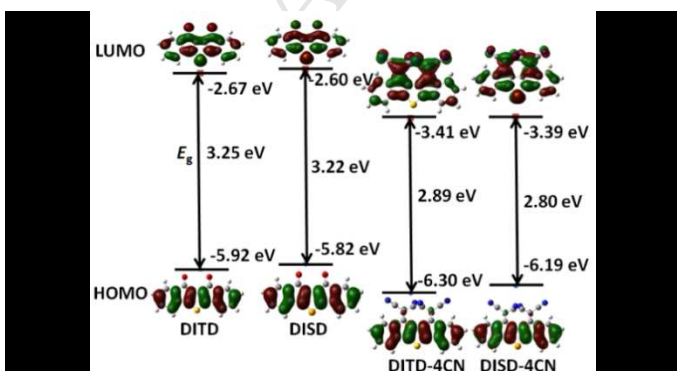
24 hours to obtain purple solid **DITD-4CN** 30% yield. On the other hand, the Knoevenagel condensation with **DISD** was slightly different from that of **DITD**, the reaction was refluxed in chloroform for 2 hours and afforded **DISD-4CN** in 35%. The structure of them has been adequately verified by MS,  $^1\text{H}$  NMR and elemental analysis. Unfortunately, we were not able to get the  $^{13}\text{C}$  NMR spectra of these four compounds due to their low solubility.

We obtained crystals of all the molecules by slow evaporation from DCM/ethanol solutions, but only those of **DITD** and **DISD-4CN** were suitable for single crystal X-ray diffraction (Figure. 2). **DITD** crystallizes in an orthorhombic unit cell, space group Pmn21, while **DISD-4CN** crystallizes in an orthorhombic unit cell, space group Pccn. **DITD** is a completely flat molecule. In contrast, the backbone of **DISD-4CN** remains almost coplanar. But the two dicyanovinyl groups are forced to be out of plane due to steric hindrance. Both systems showed a brick-wall arrangement that is very promising to achieve high mobility structures by increasing the dimensionality of charge transport and rendering the systems less sensitive to charge traps. According to the crystal structure of **DITD**, the  $\pi$ - $\pi$  distance between two molecules is 3.416 Å. On the other hand, the  $\pi$ - $\pi$  distance between two **DISD-4CN** molecules is 3.621 Å, which is due to the out of plane CN groups. The stacking structures of **DITD** and **DISD-4CN** are shown in Figure S1.



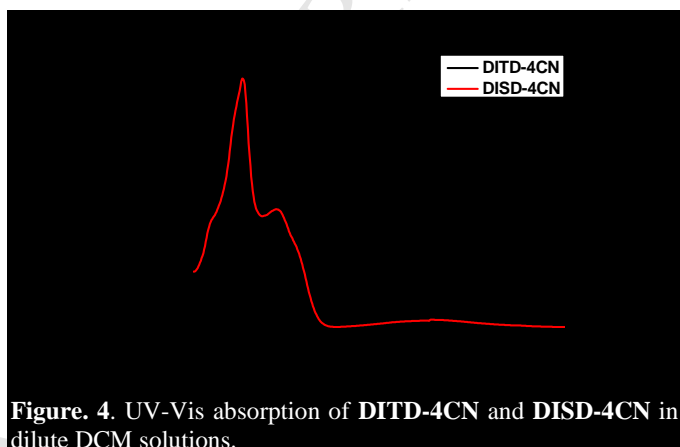
**Figure. 2.** Crystal structures of **DITD** (a) and **DISD-4CN** (b). Thermal ellipsoids are shown at 50% probability level (purple, red, yellow and green colors represent nitrogen, oxygen, sulfur and selenium atoms, respectively). The hydrogen atoms are omitted for clarity.

To better understand the role of S or Se-annulated compounds with and without dicyano-substitution, density functional theory (DFT) calculations and photophysical experiments were performed on all the molecules. Optimized geometries showed planar linear structure in **DITD**, **DISD**, **DITD-4CN** and **DISD-4CN** which are preferred for  $\pi$ - $\pi$  stacking. In all the molecules, the HOMO and LUMO frontier molecular orbitals were delocalized throughout the thiophene or selenophene conjugated skeleton, with the exception of **DITD-4CN** and **DISD-4CN**, where the LUMO orbitals are mainly localized on the dicyanovinylene-group (Figure. 3). The HOMO-LUMO energy gaps of **DITD-4CN** and **DISD-4CN** were found to be in the range of 2.89 eV and 2.80 eV, respectively.



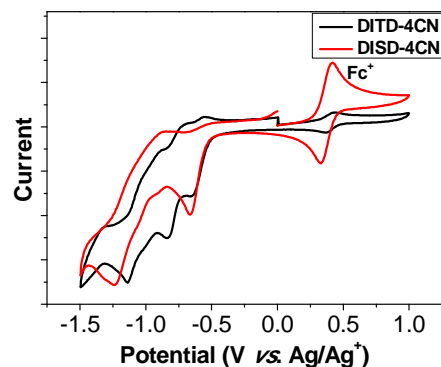
**Figure. 3.** Frontier molecular orbitals and HOMO-LUMO gaps.

The normalized absorption spectra of **DITD-4CN** and **DISD-4CN** in dilute DCM solutions are shown in Figure 4. The details of the photophysical properties of the compounds are summarized in Table 1. Their UV-vis spectra showed two strong absorption bands and one weak absorption band. The absorption band in the region of 250-332 nm is attributed to the  $\pi$ - $\pi^*$  local electron transition of the benzene ending group ring. The absorption band at longer wavelengths (332-400 nm) can be assigned to the delocalized  $\pi$ - $\pi^*$  excitation between the end group benzene and thiophene or selenophene conjugated system. The less pronounced band from 400 nm to 600 nm may be attributed to the intramolecular charge transfer from the conjugated skeleton to the electron-withdrawing cyano group. Moreover, the absorption edge is red-shifted about 5 nm on going from **DITD-4CN** to **DISD-4CN**. This assignment is also well-supported by our theoretical calculations. The absorption spectra of **DITD** and **DISD** were also obtained and are shown in Figure S2.



**Figure. 4.** UV-Vis absorption of **DITD-4CN** and **DISD-4CN** in dilute DCM solutions.

Electrochemical measurements revealed three pseudo reversible reduction waves for **DITD-4CN** and **DISD-4CN**, while no oxidation waves were observed in the solvent window. (Table 1 and Figure. 5). They exhibited rather closely spaced, reversible electron reduction processes with a low onset reduction potential that corresponds to a LUMO value of -3.81 eV, and -3.79 eV, respectively. The low onset reduction potential suggests good electron accepting properties of the resulting strong electron-withdrawing cyano groups, consistent with their electron-deficient nature. Such a redox behavior is reasonable considering the good electron-accepting ability for the S or Se-annulated skeleton, making the system more susceptible to reduction (*n*-doping) rather than oxidation (*p*-doping). Moreover, the solution optical band gaps were 2.03 and 2.01 eV, respectively. These trends are consistent with the results of theoretical calculations.



**Figure. 5.** Cyclic voltammetry of **DITD-4CN** and **DISD-4CN** (DCM/0.1 M TBAPF<sub>6</sub> vs. Ag/Ag<sup>+</sup> at 100 mV/s).

**Table 1.** Photophysical and electrochemical properties of **DITD**, **DISD**, **DITD-4CN** and **DISD-4CN**. Mp: >260 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 7.90 (dd, J = 8.0, 1.4 Hz, 4H), 7.41 (td, J = 7.4, 1.1 Hz, 2H), 7.35 (d, J = 6.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.25-7.19 (m, 8H). MS (m/z): Calcd for C<sub>30</sub>H<sub>18</sub>O<sub>8</sub>S<sub>2</sub>: C, 63.15; H, 3.18; S, 11.24. Found: C, 63.91; H, 2.81; S, 11.92.

	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{onset}}$ (nm) <sup>a</sup>	$E_{\text{g}}^{\text{opt}}$ (eV) <sup>b</sup>	$E_{\text{LUMO}}$ (eV) <sup>c</sup>	$E_{\text{HOMO}}$ (eV) <sup>d</sup>
<b>DITD</b>	276, 439	485	2.56	-3.49	-6.05
<b>DISD</b>	277, 293, 453	503	2.46	-3.37	-5.83
<b>DITD-4CN</b>	305, 349, 531	610	2.03	-3.81	-5.84
<b>DISD-4CN</b>	309, 354, 541	616	2.01	-3.79	-5.80

<sup>a</sup>  $\lambda_{\text{onset}}$  was the onset for the solution absorption spectra. <sup>b</sup>  $E_{\text{g}}$  (optical energy gap) calculated from the absorption onset of solution spectra. <sup>c</sup> Obtained from CV data. <sup>d</sup> Obtained from the  $E_{\text{LUMO}}$  (CV data) - optical band gap ( $E_{\text{g}}^{\text{opt}}$ ).

### 3. Conclusion

In summary, we have applied a facile and simple gram-scale synthetic procedure for a unique planar,  $\pi$ -extended S or Se-annulated building block. Based on the linear molecules, a novel series of tetracyano-substituted S and Se-annulated derivatives have thus been facilely constructed. The optical and electrochemical properties were investigated to understand the role of the structure on functional properties of the resultant molecules. The results showed unique optoelectronic characteristics with wide optical band gaps and redox-active properties. The interesting structural and electronic properties of the novel planar,  $\pi$ -extended S or Se-annulated building block as the skeleton reported herein hold promise for potential applications of in the field of molecular electronics.

### 4. Experimental

#### 4.1. General

Unless otherwise stated, all of the chemicals were purchased from Aldrich Chemical and used as received. When necessary, solvents and reagents were purified using standard procedures. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen. <sup>1</sup>H NMR spectra were recorded on a Varian Inova600 spectrometer. Absorption spectra were taken on a Varian Cary 50 ultraviolet-visible spectrometer. Single crystal X-ray diffraction was carried out using a Bruker Kappa Apex diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at a temperature of 100 K. Mercury software was used to process the raw data. Electrochemical measurements were performed with a Princeton Applied Research Potentiostat/Galvanostat model 263A. The electrochemical measurements were carried out in DCM solution containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, with a platinum disc, platinum wire, and silver wire as the working, counter, and pseudo-reference electrodes, respectively. A ferrocene-ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used as an internal standard (4.80 eV below the vacuum level).

#### 4.2. General Procedures

##### 4.2.1 General procedure for the preparation of compound **1**

**BIT-OH<sub>2</sub>** (2.00 g, 6.94 mmol) was suspended in a 2 L round-bottom flask in 250 mL of dry DCM and 2 mL of triethylamine under nitrogen atmosphere. The reaction mixture was cooled to 0 °C in a salt ice bath. Benzenesulfonyl chloride (3.5 mL, 27.43 mmol) was combined in a separate flask with 2 mL of DCM and 1 mL of pyridine. This mixture was added dropwise to the reaction solution, which turned dark yellow. After stirring for 10 minutes at 0 °C the reaction was quenched 100 mL of methanol and an orange precipitate was observed. The solids were filtered, washed with methanol multiple times, and dried under vacuum to yield 2.45 g of compound **1** (62% yield.)

Mp: >260 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 7.90 (dd, J = 8.0, 1.4 Hz, 4H), 7.41 (td, J = 7.4, 1.1 Hz, 2H), 7.35 (d, J = 6.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.25-7.19 (m, 8H). MS (m/z): Calcd for C<sub>30</sub>H<sub>18</sub>O<sub>8</sub>S<sub>2</sub>: C, 63.15; H, 3.18; S, 11.24. Found: C, 63.91; H, 2.81; S, 11.92.

##### 4.2.2 Synthesis of Na<sub>2</sub>S

All glassware and stir bars were dried in the oven at 140 °C for several hours. 14.0 g of sodium was added into 50 mL of dry THF with 3.0 g of naphthalene as catalyst. 9.6 g of sulfur was then added to the suspension and the mixture was heated to reflux for 12 hours under nitrogen gas protection. Thus a white solid, sodium sulfide was formed and washed with dry THF.

##### 4.2.3 Synthesis of diindeno[1,2-b:2',1'-d]thiophene-10,11-dione (**DITD**)

1.10 g (1.93 mmol) of compound **1** was added in a 500 mL round-bottom flask with 200 mL of DCM. 260 mg of sodium sulfide was added and the mixture was stirred for 12 h. Purple solid was formed and filtered, washed with methanol multiple times and dried with vacuum to yield 0.34g of **DITD** (62% yield). Mp: >260 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 7.53 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.0 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.3 Hz, 2H). MS (m/z): Calcd for MS: 288.02, Found: (M<sup>+</sup>). 289.48. Anal. Calcd for C<sub>18</sub>H<sub>8</sub>O<sub>2</sub>S: C, 74.99; H, 2.80; S, 11.12. Found: C, 75.78; H, 2.01; S, 12.01.

##### 4.2.4 Synthesis of **DITD-4CN**

0.50 g (1.74 mmol) of **DITD** was put into 160 mL of chloroform in a 500 mL round-bottom flask. 3.03 g of malononitrile and 8 mL of pyridine was added as well. Then 0.64 mL of titanium tetrachloride was added dropwise into the flask with stirring at room temperature for 24 hours and the precipitate was filtered and washed with methanol. The product **DITD-4CN** was formed as a dark purple solid (0.20 g, 30%). Mp: >260 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 8.17 (d, J = 7.7 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.31 (dd, J = 16.0, 7.8 Hz, 4H). MS (m/z): Calcd for MS: 384.05, Found: (M<sup>+</sup>). 384.93. Anal. Calcd for C<sub>24</sub>H<sub>8</sub>N<sub>4</sub>S: C, 74.99; H, 2.10; N, 14.57; S, 8.34. Found: C, 75.09; H, 2.18; N, 13.18; S, 7.03. UV-vis (DCM)  $\lambda_{\text{max}}$  nm ( $\epsilon$ ): 305 (277944), 349 (106890), and 531 (7508).

##### 4.2.5 Synthesis of Na<sub>2</sub>Se

All glassware and stir bars were dried in the oven at 140 °C for several hours. 14.0 g sodium was put into 50mL dry THF with 3.0 g naphthalene as catalyst. 23.7 g selenium was then added to the suspension and the mixture is heated to reflux for 9 hours under nitrogen gas protection. Thus, a white solid, sodium selenide was formed and washed with dry THF.

##### 4.2.6 Synthesis of diindeno[1,2-b:2',1'-d]selenophene-10,11-dione (**DISD**)

1.10 g (1.93 mmol) of compound **1** was added in a 500 mL round-bottom flask with 200 mL of DCM. 260 mg of sodium selenide was added and the mixture was stirred for 12 h. A dark purple solid was formed and filtered, washed with methanol multiple times and dried with vacuum to yield 0.42 g of **DISD** (yield 65%). Mp: >260 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 7.51 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H). MS (m/z): Calcd for MS: 335.97, Found: (M<sup>+</sup>). 336.96. Anal. Calcd for C<sub>18</sub>H<sub>8</sub>O<sub>2</sub>Se: C, 64.49; H, 2.41. Found: C, 65.04; H, 2.02.

##### 4.2.7 Synthesis of **DISD-4CN**

0.50 g (1.49 mmol) of **DISD** was put into 160 mL of chloroform in a 500 mL round-bottom flask. 3.03 g of malononitrile and 8 mL of pyridine was added as well. Then 0.64 mL of titanium tetrachloride was added dropwise into the flask with stirring. The mixture was heated in oil bath for 2 hours and the precipitate was filtered and washed with methanol. The product **DISD-4CN** was formed as a dark purple solid (0.23 g, 35%). Mp: >260 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 8.16 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.35-7.27 (m, 4H). MS (m/z): Calcd for MS: 431.99, Found: (M<sup>+</sup>). 432.04. Anal. Calcd for C<sub>24</sub>H<sub>8</sub>N<sub>4</sub>Se: C, 66.83; H, 1.87; N, 12.99. Found: C, 67.01; H, 1.02; N, 13.86. UV-vis (DCM) λ<sub>max</sub> nm (ε): 309 (296124), 354 (137502), and 541 (2994).

## 5. Crystal Structures

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 1571470 and 1571471. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk> or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223/336-033, Tel.: (+44) 1223/336-408.

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