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Linear Fused Dithieno[2,3-*b*:3′2′-*d*]thiophene Diimides

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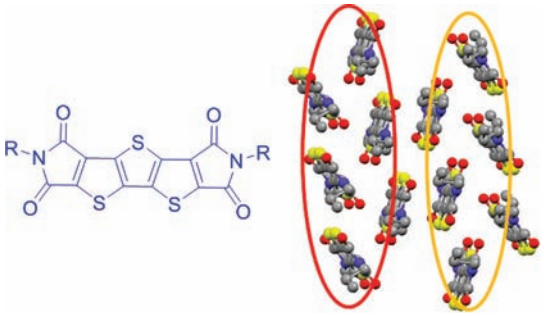
ABSTRACT



Linear fused dithieno[2,3-*b*:3′2′-*d*]thiophene diimides (DTTDIs, 1−4) were synthesized. Physicochemical investigations suggested that these diimides might be used as potential n-channel organic semiconductors. Single-crystal analysis of *N*-propyl DTTDI (1) revealed that molecules adopt a layered herringbone packing motif.

Aromatic imides are significant organic species that benefit a wide range of applications as flexible optoelectronic devices,[1] chemical sensors,[2] and supramolecular assemblies.[3] The properties of aromatic imides are strongly dependent on their π-conjugated cores. For example, as organic semiconductors of thin film transistors, anthracene diimide derivatives (**ADI**s, Scheme 1) display electron transport properties.[4] In contrast, linear dibenzotetrathiafulvalene diimide derivatives (**DBTTFDI**s, Scheme 1) exhibit hole transport characteristics.[5] Until now, aromatic imide studies are primarily focused on fused phenyl imides, such as naphthalene[6] and perylene diimides[7] (**NDI**s and **PDI**s,

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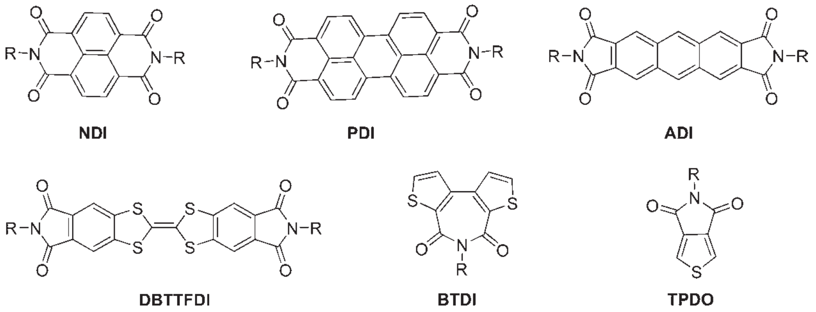
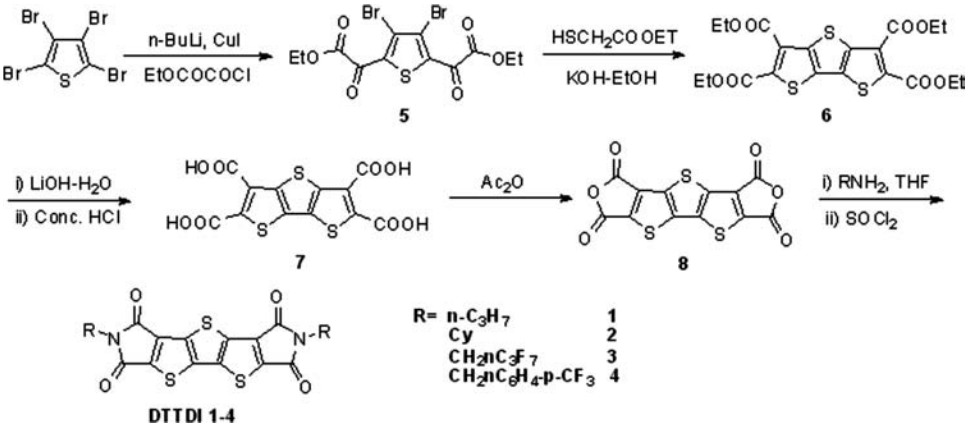
Scheme 1. Chemical Structures of Some Aromatic Imides



Scheme 2. Synthetic Route to Diimides **1**−**4**



respectively, Scheme 1). To broaden the applications and further understand the relationship between molecular structure and properties, it is necessary to synthesize novel types of aromatic imides with differently π-conjugated cores.

Thiophene-containing compounds are frequently used in organic electronics.[8] Among these molecules, linear ring-fused thiophenes have attracted particular attention because they exhibit rigid structures, strong intermolecular interactions, and usually high device performances.[9] Recently, several groups have reported the high power conversion efficiencies ($\leq$6.8%) of thieno[3,4-*c*]pyrrole-4,6-dione-based (**TPDO**, Scheme 1) copolymers in solar cells.[10] Facchetti et al. discovered that *N*-alkyl-2,2-bithiophene-3,3′-dicarboximides (**BTDI**, Scheme 1) were ideal π-conjugated units for the construction of electron-transporting organic semiconductors.[11] All of these results suggested that thiophene-based imides would offer more significant roles in organic electronics. However, to the best of our knowledge, there have been no precedents of imide groups directly attached to the 2,3-position of linear fused thiophenes. Such a desired structure would enlarge the π-conjugated system, lower the HOMO−LUMO energy levels, and improve solubility. Herein, we present the first examples of linear fused thiophene-based imides, dithieno[2,3-*b*:3′2′-*d*]thiophene diimides (**DTTDI**s, Scheme 2), and include their general accessible method and photophysical and electrochemical properties. The single crystal structure of *N*-propyl **DTTDI 1** is also reported.

The syntheses of **DTTDI**s **1**−**4** from commercially available tetrabromothiophene is outlined in Scheme 2. Previous approaches to prepare imides from anhydride have been described.[12] Additionally, the dehydration of the **DTT** tetracarboxylic acid, **7**, was assumed to lead to the formation of the corresponding anhydride, **DTTDA**

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8. Thus, compound **7** was the key intermediate in our synthetic route. We initially attempted to synthesize **7** via the hydrolysis of tetracyano-**DTT**, which was a cyanization product of tetrabromo-**DTT**. However, the full cyanization of tetrabromo-**DTT** was unsuccessful because both the starting materials and products were extremely insoluble in organic solvents. Our novel strategy to synthesize **7** included three steps. First, ethyloxoacetate groups were introduced to the two α positions of the tetrabromothiophene ring via an efficient CuI-catalyzed coupling reaction that we recently established.[13] Fortunately, product **5** could be separated in a satisfying yield (72%) through simple recrystallization from a solvent mixture composed of petroleum ether and dichloromethane (CH_2Cl_2). Next, the reaction of **5** with ethyl mercaptoacetate and potassium hydroxide in an ethanolic solution afforded **DTT** tetraethyl ester, **6** (32% yield). A similar reaction was first reported by Holmes and coworkers.[14] However, their reaction condition (potassium carbonate as a base suspension in DMF) only led to complicated byproducts for our reactants, probably due to the different reactivity of the ethyloxoacetate groups in **5**. Basic hydrolysis of **6**, followed by refluxing in excessive concentrated hydrochloric acid overnight, afforded **7** in high yield (88%).[15] Less drastic acidification conditions produced a mixture of **7** and its poorly water-soluble lithium salts, resulting in an unsuccessful dehydration, evident by elemental analysis. Tetracarboxylic acid **7** was easily dehydrated by refluxing acetic anhydride to afford **DTTDA 8** (75% yield).[16] The target diimides **1**−**4** were obtained in moderate yields (46−59%) via reacting **8** with different amines, followed by imidization in $SOCl_2$.[17,12] The chemical structures of all novel compounds are clearly supported by characterizations, such as ^1H NMR, ^{13}C NMR, MS, and elemental analysis (see Supporting Information, SI).

All linear fused thiophene-based diimides **1**−**4** were bright yellow crystals or powders and soluble in polar solvents, such as CH_2Cl_2, THF, and chlorobenzene. The absorption and emission spectra of **1**−**4** in diluted CH_2Cl_2 are shown in Figure 1a. The absorptions of the **DTTDI**s ($\lambda_{max} \approx$ 405−410 nm) were significantly red-shifted, compared to that of the **DTT** ($\lambda_{max} \approx$ 300 nm).[18] Minor red shifts of 2−15 nm were also exhibited, compared to those of the α,α-dicarbonyl substituted **DTT**s,[19] which indicated the strong electron-withdrawing property of diimide groups. The HOMO−LUMO energy gaps calculated from the on-set absorption were in the range 2.80 to 2.84 eV for **1**−**4** and slightly increased in the order **3** < **1** < **2** ≈ **4**. No absorption decay was observed for the solutions of **1**−**4** after storage in ambient conditions for one week, indicating the high environmental stability of these compounds.

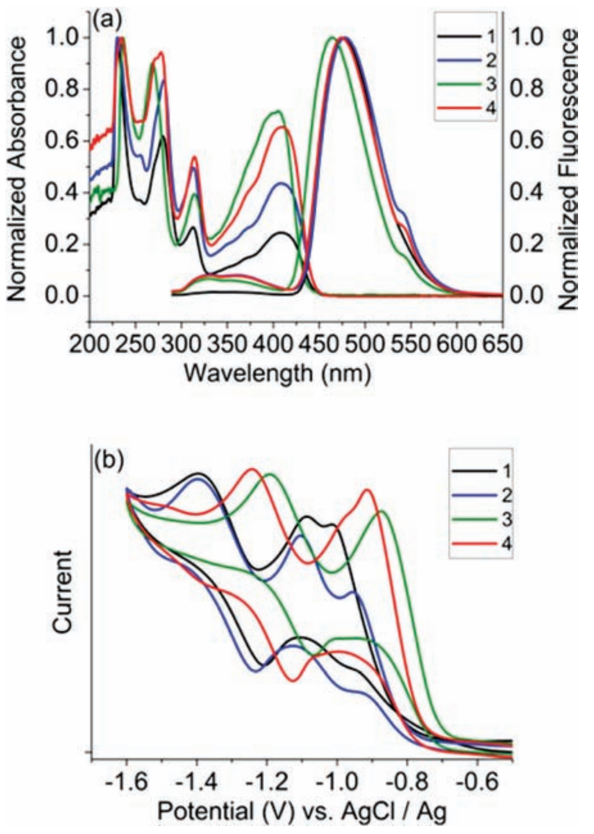

Figure 1. (a) Absorption (left) and emission spectra (right) of **DTTDI**s **1**−**4** in diluted CH_2Cl_2 (10^{-5} mol L^{-1}). (b) Cyclic voltammograms of **DTTDI**s **1**−**4** in CH_2Cl_2 solutions with the following condition: 0.1 M Bu_4NPF_6, supporting electrolyte; AgCl/Ag, reference electrode; Pt disk, working electrode; Pt wire, counter electrode; ferrocene, internal potential marker; and scan rate, 50 mV^{-1}.

The electrochemical properties of **DTTDI**s **1**−**4** were examined by cyclic voltammetry (CV). The measurements were performed in CH_2Cl_2, and the data are shown in Figure 1b. No obvious peaks were observed for **DTTDI**s upon oxidation up to 1.8 V, indicating that the substitution of the imide groups remarkably enhanced the electron affinity of the **DTT** core ($E_{1/2}^{ox}$ = +0.98 V).[18] A reversible and two irreversible reduction waves were observed for **1** and **2**, while only two reduction waves (one reversible, one irreversible) were seen for **3** and **4**. The initial reduction peaks of **3** and **4** ($E_{1/2}^{red1}$ of −0.78 and −0.82 V for **3** and **4**, respectively) were shifted to positive values, compared with those of **1** and **2** ($E_{1/2}^{red1}$ of −0.92 and −0.88 V for **1** and **2**, respectively). These results suggest that the fluoroalkyl substituents induced a stronger electron-accepting ability than that of the

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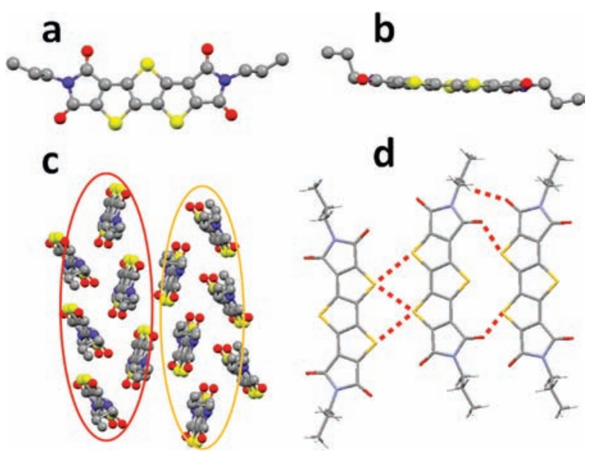

Figure 2. X-ray crystal structure of **DTTDI 1**. (a,b) The molecular structure of **1** is represented. (c) The molecular packing of **1** in crystals with layered herringbone structures is shown. (d) The short interactions existing between adjacent herringbone packages are depicted. H atoms were omitted for clarity in (a−c).

alkyl chain substituents. The reduction potentials of the **DTTDI**s were larger than those of the unsubstituted **ADI**s ($E_{1/2}{}^{\mathrm{red1}}$ of −1.17 V for ADI-Cy)[4] but were smaller than those of the **NDI**s ($E_{1/2}{}^{\mathrm{red1}}$ of −0.67 V for NDI-Cy).[20] The LUMO energy levels of **1**−**4** were estimated by the reduction potentials ($E_{\mathrm{LUMO}} = -(E_{1/2}{}^{\mathrm{red1}} + 4.44)$ eV),[1a] −3.52, −3.56, −3.66, and −3.62 V for **1**−**4**, respectively. The low-lying LUMO levels indicated that the **DTTDI**s might serve as n-type semiconductor candidates. The frontier orbitals of the **DTTDI**s were also estimated through density functional theory (DFT) calculations (using the Gaussian 03 program at the B3LYP/6-31G* level), using **3** and methyl diimides of **DTT** as models (see SI). The calculations showed that the extension of the **DTT** cores with diimides reduced both HOMO and LUMO levels, and the LUMO energy level of fluoroalkyl diimide **3** was 0.3 eV lower than that of the methyl diimides. This tendency was in good agreement with the experimental results.

By slow evaporation of a chloroform solution, large area (> 0.3 cm^2), single crystals of compound **1** could be obtained. The XRD patterns of **DTTDI** indicated that the core exhibited a planar structure, as expected (Figure 2a). The two terminal propyl chains were turned out of the plane, affording a chairlike configuration (Figure 2b). Compound **1** displayed a layered herringbone arrangement with two orientations in the crystals (Figure 2c). $S\cdots\pi$ and $C{-}O\cdots\pi$ interactions were observed in each herringbone packing, with a herringbone angle of ~55.7°. Between the two differently orientated herringbone packages, $\pi{-}\pi$, $C{-}O\cdots S$, and $S\cdots S$ interactions, as well as hydrogen bonds between the oxygen atom of the imides and the atoms in alkyl chains, existed (Figure 2d). The distance of the $\pi{-}\pi$ interaction was approximately 3.580 Å, which was comparable to that of the α,α-dicarbonyl substituted **DTT**s.[19] All of these intermolecular interactions would benefit the charge transport in single crystals.[9,21]

In summary, we report the synthesis and characterization of linear fused thiophene-based diimides, termed **DTTDI**s. The developed synthetic route was expected to be feasible for the preparation of novel types of fused thiophene-2,3-imides to present various functionalities around the imide rings. The optical, electrochemical, and thermal properties of the **DTTDI**s, as well as the single crystal XRD diffraction pattern results, suggest that these molecules may have various potential applications in organic electronics. Further studies on these avenues are currently underway.

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Supporting Information Available. Synthetic procedures, characterization data for all compounds **1**−**8**, density functional theory (DFT) calculations of **DTTDI**s, and X-ray crystallographic data of compound **1** in CIF format are presented here. The material is available free of charge via Internet at http://pubs.acs.org.

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