

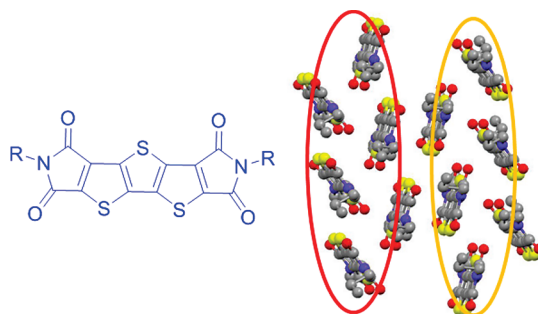
Linear Fused Dithieno[2,3-*b*:3'2'-*d*]-
thiophene DiimidesWei Hong,[†] Haihong Yuan,[†] Hongxiang Li,^{*,†} Xiaodi Yang,[§] Xike Gao,[†] and
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ABSTRACT



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 (**ADIs**, Scheme 1) display electron transport properties.⁴ In contrast, linear dibenzotetrathiafulvalene diimide derivatives (**DBTTFDIs**, Scheme 1) exhibit hole transport characteristics.⁵ Until now, aromatic imide studies are primarily focused on fused phenyl imides, such as naphthalene⁶ and perylene diimides⁷ (**NDIs** and **PDIs**,

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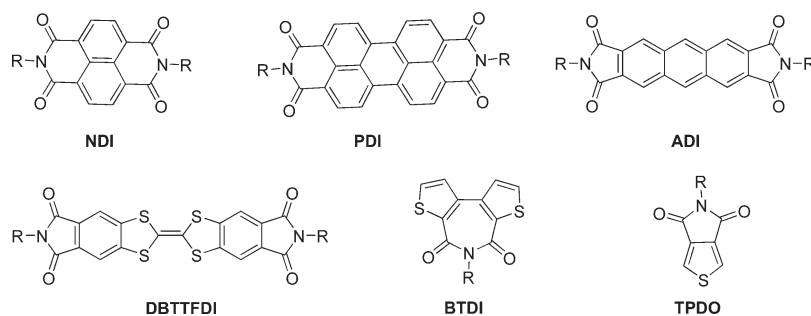
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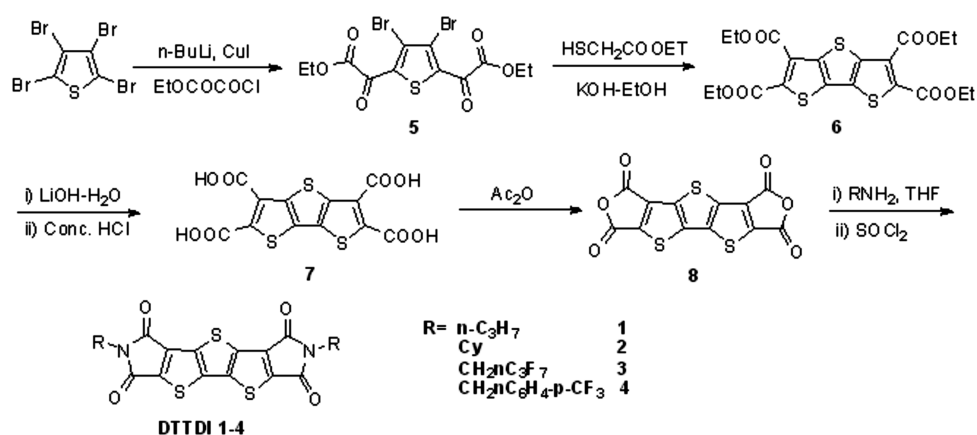
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Scheme 1. Chemical Structures of Some Aromatic Imides



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 (DTTDIs, 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 DTTDIs 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 co-workers.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 **DTTDIs** ($\lambda_{\text{max}} \approx 405\text{--}410\text{ nm}$) were significantly red-shifted, compared to that of the **DTT** ($\lambda_{\text{max}} \approx 300\text{ nm}$).¹⁸ Minor red shifts of 2–15 nm were also exhibited, compared to those of the α,α -dicarbonyl substituted **DTTs**,¹⁹

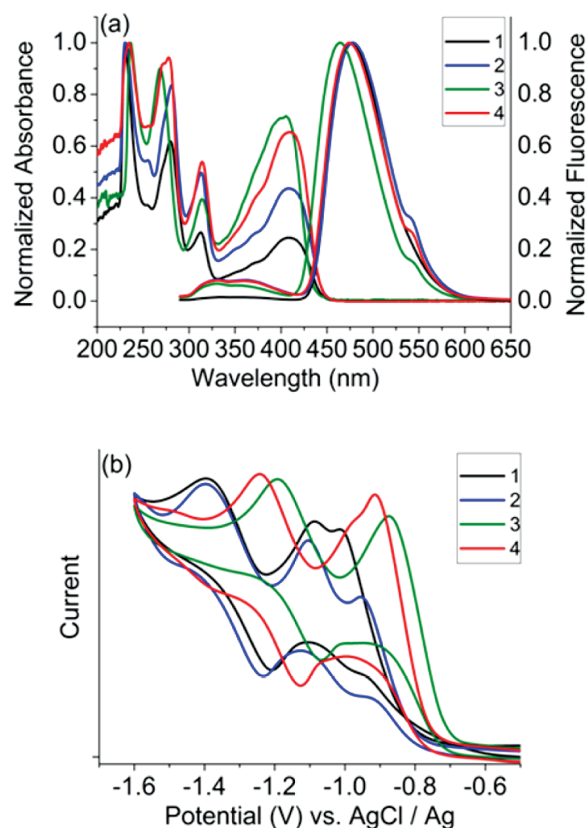


Figure 1. (a) Absorption (left) and emission spectra (right) of **DTTDIs 1–4** in diluted CH_2Cl_2 ($10^{-5}\text{ mol L}^{-1}$). (b) Cyclic voltammograms of **DTTDIs 1–4** in CH_2Cl_2 solutions with the following condition: 0.1 M Bu_4NPF_6 , supporting electrolyte; AgCl/Ag, reference electrode; Pt disk,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

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 $3 < 1 < 2 \approx 4$. 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.

The electrochemical properties of **DTTDIs 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 **DTTDIs** upon oxidation up to 1.8 V, indicating that the substitution of the imide groups remarkably enhanced the electron affinity of the **DTT** core ($E_{1/2}^{\text{ox}} = +0.98\text{ V}$).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** ($E_{1/2}^{\text{red1}}$ of -0.78 and -0.82 V for **3** and **4**, respectively) were shifted to positive values, compared with those of **1** and **2** ($E_{1/2}^{\text{red1}}$ 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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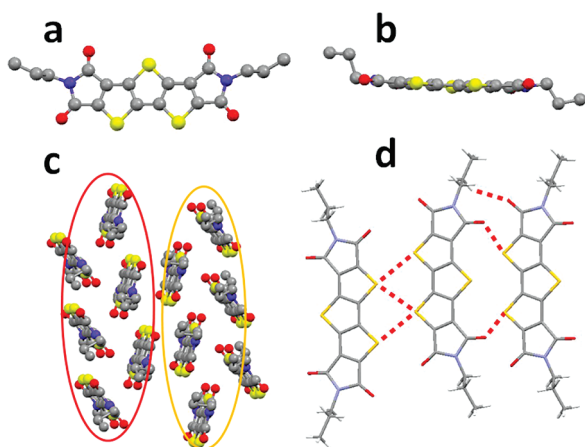


Figure 2. X-ray crystal structure of **DTTDI 1**. (a,b) The molecular structure of **1** is represented. (c) The molecular packing of **1** in crystals with layered herringbone structures is shown. (d) The short interactions existing between adjacent herringbone packages are depicted. H atoms were omitted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

alkyl chain substituents. The reduction potentials of the **DTTDIs** were larger than those of the unsubstituted **ADIs** ($E_{1/2}^{\text{red1}}$ of -1.17 V for **ADI-Cy**)⁴ but were smaller than those of the **NDIs** ($E_{1/2}^{\text{red1}}$ of -0.67 V for **NDI-Cy**).²⁰ The LUMO energy levels of **1–4** were estimated by the reduction potentials ($E_{\text{LUMO}} = -(E_{1/2}^{\text{red1}} + 4.44)$ eV),^{1a} -3.52 , -3.56 , -3.66 , and -3.62 V for **1–4**, respectively. The low-lying LUMO levels indicated that the **DTTDIs** might serve as n-type semiconductor candidates. The frontier orbitals of the **DTTDIs** 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.

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By slow evaporation of a chloroform solution, large area (> 0.3 cm²), 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). $\text{S} \cdots \pi$ and $\text{C}-\text{O} \cdots \pi$ interactions were observed in each herringbone packing, with a herringbone angle of $\sim 55.7^\circ$. Between the two differently orientated herringbone packages, $\pi-\pi$, $\text{C}-\text{O} \cdots \text{S}$, and $\text{S} \cdots \text{S}$ 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 **DTTs**.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 **DTTDIs**. 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 **DTTDIs**, 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 **DTTDIs**, 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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