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H-Shaped Oligothiophenes with Low Band Gaps and Amphoteric Redox Properties

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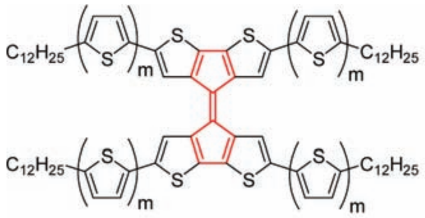
ABSTRACT



HT-1 (m = 1), E_g = 1.41 eV
HT-2 (m = 2), E_g = 1.37 eV

H-shaped bridged oligothiophenes HT-1 and HT-2 were synthesized by two different approaches. Different from normal oligothiophenes, HT-1 and HT-2 showed low band gaps and amphoteric redox behaviors due to intramolecular charge transfer, which is further supported by time-dependent DFT calculations.

Thiophene-based linear oligomers and polymers have been among the most promising functional materials for organic optoelectronic devices due to their excellent optical and electronic properties.[1] In the last 5−10 years, higher order, multidimensional oligothiophene systems with novel architectures and sophisticated topologies other than linear systems have emerged as a consequence of increased versatility of thiophene chemistry.[2] Recent representative examples include star-shaped,[3] X-shaped,[4] swivel cruciform,[5] spider-like,[6] macrocyclic,[7] dendritic,[8] and tetrahedral oligothiophenes.[9] These new π-conjugated materials have greatly broadened the scope of molecular candidates for organic field effect

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transistors,[3a,5b,7a] solar cells,[3b,e,4a,b,8a,e,9a] light-emitting diodes,[8c] and optical sensors.[8b]

Our particular interest in this work is to build up a new type of H-shaped oligothiophene such as **HT-1** and **HT-2** (Figure 1). The molecular design is based on the following considerations: (1) The two oligothiophene arms are bridged by a rigid C═C double bond that is different from the C−C single bond present in the swivel cruciform oligthiophenes and other branched oligothiophenes, thus the free rotation of the two arms is forbidden and this also allows efficient electronic coupling between the two oligothiophene units. The increased molecular planarity and rigidity also enhance the intermolecular $\pi-\pi$ interactions.[10] (2) The structure can also be regarded as two oligothiophenes fused together with a pentafulvalene unit. Pentafulvalene is a nonbenzenoid conjugated hydrocarbon that is extremely unstable.[11] However, fusion of aromatic rings such as benzene or thiophene can improve its stability. In fact, the $\Delta^{4,4'}$-dicyclopenta[2,1-*b*:3,4-*b*′]-dithiophene (**DCPT**, Figure 1)[12] that is constructed by fusing the pentafulvalene with two bithiophene units is stable. The existence of two five-membered rings in **HT-1** and **HT-2** also makes it possible that the molecule accepts electrons and becomes stable aromatic cyclopentadienyl anions. Thus, they are expected to show amphoteric redox behavior, i.e., the electron-rich oligothiophene can be oxidized into positively charged species and the fused pentafulvalene unit can also be reduced into stable negatively charged species. As a consequence, small band gap materials will be obtained. To test this concept, the H-shaped, pentafulvalene-fused oligothiophenes such as **HT-1** and **HT-2** were synthesized and investigated. So far, although the simple **DCPT** molecule and its electropolymerized polymers have been synthesized,[12] the well-defined oligomer systems have never been reported.

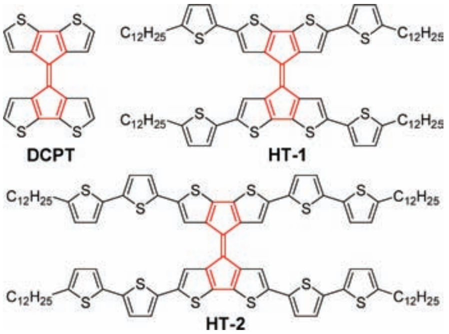
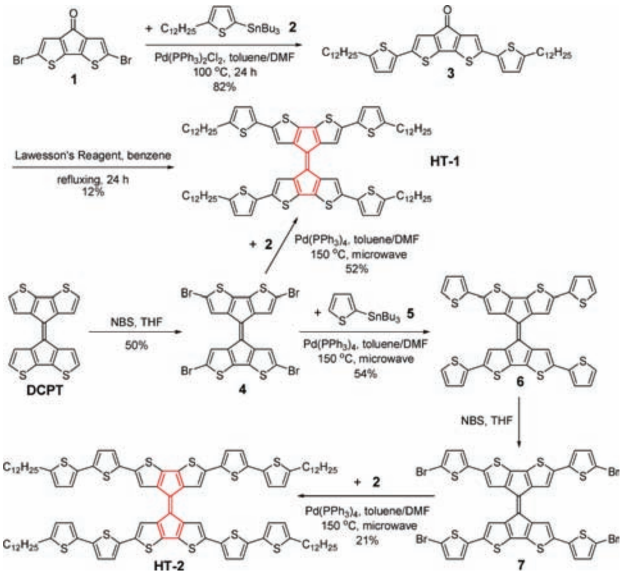


Figure 1. Chemical structures of **DCPT**, **HT-1**, and **HT-2**.

The synthesis of **HT-1** and **HT-2** is not trivial. As shown in Scheme 1, our first strategy is to prepare thiophene-substituted cyclopentabithiophene-4-one such as compound **3** followed by dimerization of the ketone. Compound **3** was prepared by Pd-catalyzed Stille coupling reaction between 2,6-dibromocyclopenta[2,1-*b*:3,4-*b*′]-dithiophene-4-one (**1**)[13] and 5-dodecyl-2-(tributylstannyl)thiophene (**2**).[14] It was found that the use of $Pd(PPh_3)_4$ as catalyst led to the title product in only a 15% yield, whereas a high yield of 82% was achieved by using $Pd(PPh_3)_2Cl_2$ as catalyst. The target compound **HT-1** was then prepared in a 12% yield by treating **3** with 3 equiv of Lawesson's reagent in refluxing benzene for 24 h. Toluene was also tested as solvent with an intention to improve the yield at higher reaction temperature, but unfortunately no title product could be obtained. The same strategy was also applied for the synthesis of **HT-2**. For that, the 2,6-bis(5′-dodecyl-2′,2″-bithienyl)cyclopentabithiophene-4-one was prepared by a similar approach to **3**; however, subsequent treatment with Lawesson's reagent in refluxing benzene gave no product. Different experimental conditions have been attempted including prolonging the

Scheme 1



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reaction time and increasing the amount of Lawesson's reagent, but all in vain, only the starting materials and some partially reduced compounds were obtained. This failure may be due to the decreased activity and increased steric hindrance arising from the prolonged oligothiophene arms.

To overcome this problem and to improve the yield of **HT-1**, we adopted an alternative synthetic strategy to prepare these two compounds. The new synthesis commenced with the **DCPT** (Scheme 1). According to Pickup's report,[12] **DCPT** was obtained in a 22% yield by treating cyclopentadithiophene-4-one with Lawesson's reagent in refluxing benzene for 12 h. In our experiment, the yield was increased to 51% by prolonging the reaction time to 24 h. The key reactive intermediate **4** was then prepared in a 50% yield by treatment of compound **DCPT** with 5 equiv of *N*-bromosuccinimide (NBS) in THF for 3 days. The target compound **HT-1** was obtained in a 52% yield by 4-fold Stille couplings between **4** and **2** under a microwave condition.[15] In contrast, under conventional thermal heating conditions **HT-1** can only be obtained in a 21% yield. Therefore, microwave condition is more effective for the multiple Stille coupling reactions. For **HT-2**, similar 4-fold Stille couplings between the dithiophene stannyl derivative and **4** only gave an incomplete coupling mixture under various conditions and this failure might be due to the decreased activity and increased steric hindrance arising from the larger dithiophene substituents. So, an alternative synthetic route has to be used: first, compound **6** was prepared in a 54% yield by the Stille coupling between **4** and 2-tributylstannylthiophene (**5**) and followed by 4-fold bromination with NBS in THF to provide **7**. The target compound **HT-2** was finally synthesized by 4-fold Stille coupling between **7** and **2** in a 21% yield. The final compounds **HT-1** and **HT-2** are readily dissolved in common organic solvents and this allows us to easily purify them by column chromatography and to conduct full characterizations in solution (see the Supporting Information (SI)).

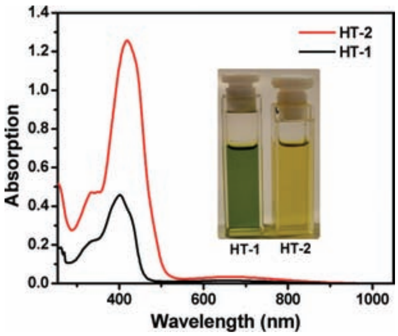

Figure 2. UV−vis−NIR absorption spectra of **HT-1** and **HT-2** in chloroform ($c = 1.0 \times 10^{-5}$ M). Insert: Photos for the dilute solutions of **HT-1** and **HT-2**.

The absorption spectra of **HT-1** and **HT-2** in dilute chloroform solutions are shown in Figure 2 and the photophysical data are summarized in Table S1 (see the SI). **HT-1** and **HT-2** exhibit a strong $\pi-\pi^*$ transition absorption with a maximum at 401 and 420 nm, respectively. In comparison to the maximum absorption at 380 nm for **DCPT**,[12] the redshift is attributed to the extended π conjugation with increasing the peripheral thiophene number. Moreover, the absorption maxima are substantially red-shifted relative to bithiophene (302 nm) and tetrathiophene (392 nm),[16] suggesting the formation of a highly delocalized system through the DCPT core. In addition to the strong absorption band at around 400 nm, there is a weak broad absorption band between 500 and 850 nm with absorption maximum at 658 nm (molar extinction coefficient $\varepsilon = 1580$ M^{-1}cm^{-1}) and 673 nm ($\varepsilon = 3450$ M^{-1} cm^{-1}) for **HT-1** and **HT-2**, respectively. Accordingly, the solutions of **HT-1** and **HT-2** are in green and yellow green (Figure 2). From the onsets of the long wavelength absorption bands the optical energy gaps (E_g) are calculated to be 1.41 and 1.37 eV for **HT-1** and **HT-2**, respectively.

To elucidate this unique absorption spectral property, time-dependent density function theory (TDDFT) calculations (B3LYP/6-31G**) were carried out. The calculations predict that **HT-1** and **HT-2** will show intense absorptions at 394 and 462 nm, as well as weak absorptions at the longer wavelength with maximum at 858 (oscillator strength $f = 0.0814$) and 918 nm ($f = 0.1571$), respectively (see the SI). The small oscillator strengths are consistent with the low absorption intensity. The whole shape of the absorption spectra and the tendency agree well with our experimental results. The calculated molecular structures and frontier molecular orbital (FMO) profiles of **HT-1** and **HT-2** are shown in Figure 3. Both compounds show a quasi-coplanar "H" shape. **HT-1** has a distorted DCPT core with an out-of-plane distortion angle of about 4.5° and the four branch

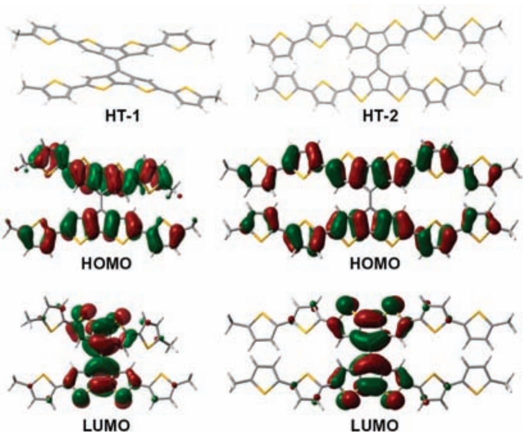

Figure 3. Calculated molecular structures and frontier molecular orbital profiles for **HT-1** and **HT-2**.

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thiophenes are almost coplanar with the DCPT core. **HT-2** shows a higher degree of distortion presumably due to the larger steric hindrance of the longer conjugated arms. Interestingly, both **HT-1** and **HT-2** adopt a disjoint FMO profile, i.e., spatially separated HOMO and LUMO. The HOMO resides wholly at the two parallel oligothiophene arms, while the LUMO is mainly localized on the central DCPT unit. Organic chromophores with a disjoint FMO structure are rare and have been found in donor- and acceptor-substituted cruciform molecules.[17] It is therefore reasonable to predict that the oligothiophene arms serve as the electron donor and the central pentafulvalene unit behaves as the electron acceptor, and intramolecular charge transfer (ICT) could happen. TDDFT calculations also suggest that the long wavelength absorption bands are mainly due to the electronic transitions from HOMO to LUMO. The UV−vis absorption and emission spectra of **HT-1** and **HT-2** recorded in different solvents with different polarities showed positive solvatochromic effect (Figure S3 and Table S3, SI) and low fluorescence quantum yields of 2.4% and 8.4% were determined for **HT-1** and **HT-2**, respectively, in chloroform. These observations support the ICT character of both compounds.

The electrochemical properties of **HT-1** and **HT-2** were investigated by cyclic voltammetry in dry chlorobenzene and the potentials are calibrated to Fc/Fc$^+$ (Figure 4 and Table S2 in the SI). **HT-1** exhibits three reversible oxidation waves with half-wave potentials $E_{1/2}^{ox}$ at 0.24, 0.48, and 0.70 V and two reversible reduction waves with $E_{1/2}^{red}$ at −1.45 and −1.72 V. Compared with **DCPT**,[12] the first oxidation potential of **HT-1** is shifted to a much more negative value by 0.2 V, which should be attributed to the extended π-conjugation in **HT-1**. **HT-2** exhibits one quasireversible oxidation wave with $E_{1/2}^{ox}$ at 0.08, one reversible oxidation wave with $E_{1/2}^{ox}$ at 0.47 V, and two reversible reduction waves with $E_{1/2}^{red}$ at −1.45 and −1.70 V, i.e., the first oxidation potential is further negatively shifted compared to **HT-1** whereas the reduction potentials are almost identical. From the difference of the onset potentials of oxidation and reduction, the electrochemical energy gaps of **HT-1** and **HT-2** are calculated as 1.40 and 1.29 eV, respectively, which are quite similar to the optical band gaps determined from their absorption spectra. So the HOMO levels of **HT-1** and **HT-2** show a slight increase as the number of thiophene rings increases, whereas the LUMO levels are almost unaffected. This feature can be ascribed to the disjoint FMO profile, which permits the independent tuning of the HOMO and LUMO level of the two compounds. The observed two reduction waves also suggest that both compounds can be reversibly reduced into stable radical anion and dianion, which are stable due to the aromatic character of the as-generated cyclopentadienyl anion and electron delocalization in the DCPT unit. As a result of the amphoteric redox behavior, small band gaps with long wavelength absorption were observed for both **HT-1** and **HT-2**.

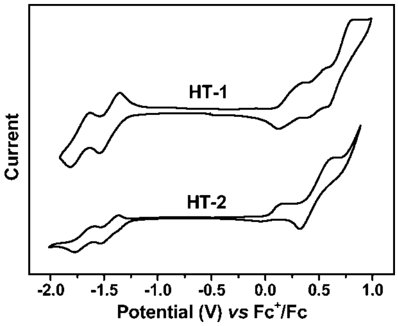

Figure 4. Cyclic voltammograms of **HT-1** and **HT-2** in dry chlorobenzene with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and a scan rate at 20 mV/s. Fc/Fc$^+$ was used as external reference.

In conclusion, two new two-dimensional H-shaped pentafulvalene-fused oligothiophenes were successfully synthesized. Both **HT-1** and **HT-2** can be regarded as a special donor−acceptor system with oligothiophene arms serving as donor unit and the central DCPT unit serving as acceptor unit, and this feature results in small band gaps, amphotetic redox behavior, and long wavelength absorption. Given these unique properties, the materials have potential applications for ambipolar OFETs and organic solar cells. Our preliminary results showed that both compounds had a strong tendency to aggregate in solution and in thin films as evidenced from the concentration-dependent fluorescence spectral measurements (Figure S2, SI) and the broadened absorption spectrum in thin films (Figure S1, SI). More detailed studies on their thermal behavior, molecular packing, and applications in electronic devices are underway in our laboratories.

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Supporting Information Available: Experimental procedures and characterizations of all new compounds, absorption spectra in films, fluorescence spectra, and theoretical calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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