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Hexathiapentacene: Structure, Molecular Packing, and Thin-Film Transistors

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The past decade witnessed a tremendous development of organic molecules for use in electronic and optoelectronic devices.[1] Oligoacenes, tetrathiafulvalene (TTF), and their derivatives have been extensively studied as fundamental building blocks for organic electronics.[2] As an example of oligo-acenes, pentacene has led organic semiconductors with the highest field-effect mobility in thin film transistors.[3] Most recently, several neutral TTF derivatives have been applied as organic semiconductors in field-effect transistors.[4] The molecular packing of TTF derivatives is characteristic of $\pi-\pi$ interactions and the S···S interactions, both of which are responsible for intermolecular charge transport.[4a] Inspired from studies on TTF derivatives, we became interested in introducing S···S interactions to oligo-acenes to provide an alternative charge transport pathway other than $\pi-\pi$ interactions, which are well-known in herringbone packing for oligo-acenes.[2] In this communication we report on the electrical characteristics of hexathiapentacene (**HTP**), emphasizing the unusual chemical structure and molecular packing. We report field-effect mobilities as high as 0.04 cm^2 V^{-1} s^{-1} and current on/off ratios of $>10^5$. Although **HTP** was first described over 30 years ago,[5] only minimal characterization has been reported. This work is the first to determine its molecular structure/packing mode and to study its application in organic transistors.[6]

HTP was prepared in one step from pentacene and sulfur as previously reported.[5] The product was purified by vacuum sublimation, which produced dark-green, needle-like crystals (Figure S-1). **HTP** was characterized by UV−vis spectroscopy, elemental analysis, TGA, cyclic voltammetry, high-resolution mass spectrometry, XRD, X-ray crystallography, and AFM. **HTP** is slightly soluble in hot trichlorobenzene and remains very stable in solution without any indications of bleaching such as that exhibited from solutions of pentacene and other derivatives.[7] Thermal gravimetric analysis was performed under nitrogen, and the onset of weight loss begins at well over 400 °C, suggesting a high thermal stability of the material. Cyclic voltammograms of **HTP** in hot trichlorobenzene/n-Bu$_4$NPF$_6$ showed quasi-reversible oxidation and reduction onset potentials at $+0.91$ V and -0.72 V vs SCE, respectively. The estimated energy levels (Figure S-2) are -5.35 eV (HOMO) and -3.72 eV (LUMO). A band gap of 1.63 eV is determined, which correlates well with an optical band gap of 1.61 eV as determined from an onset absorption of ∼769 nm measured from UV−vis. This value is significantly narrower than that of pentacene (1.7−2.2 eV)[1c,2] and absorbs well into the low-frequency region of red, almost in the near-IR region.

A quinoid structure was assigned for **HTP** with C═S double bonds on the central ring when **HTP** was first reported (Figure 1b).[5] However this molecular structure has not been confirmed, apparently due to lack of spectroscopic characterization, such as NMR, which is limited by the low solubility of **HTP**. In order to unambiguously determine the structure of **HTP**, a single-crystal grown by vacuum sublimation was analyzed using X-ray crystallography. **HTP** forms a triclinic unit cell, space group P$\bar{1}$, and unit cell dimensions $a = 3.8941$ Å, $b = 14.334$ Å, $c = 16.551$ Å, $\alpha = 72.458°$, $\beta = 88.886°$, $\gamma = 84.169°$. As shown in Figure 1a (**HTPcr**), X-ray crystallographic analysis revealed a structure in which all of the S−C bonds have nearly equal averaged bond lengths, with the central ring (bond length = 1.73 Å) slightly longer than the other two (bond length = 1.70−1.71 Å). Additionally the S−S bonds are much longer than normal S−S single bonds, even those with ring strain (such as the S−S bonds in tetrathiatetracene).[8] The observed bond lengths are not consistent with the structure that was previously proposed (shown as **HTP** in Figure 1b) and cannot be represented by a single Kekulé structure. In the valence bond formalism, the correct structure of **HTP** should be represented by a number of resonance contributors shown in Figure 1b. While the resonance contributor **HTPc** could be intuitively (assuming a traditional view) considered the most important, a more likely charge distribution based on high-level calculations[9] is represented in the hypervalent contributor **HTPd**. This resonance contributor is also in agreement with more recent accepted values of electronegativity (S > C). Furthermore, zwitterionic structures, where aromaticity is sacrificed, are also possible.[10] In the report by Hutchison et al.,[10] the transannular bonds are relatively long (1.439 Å average); the corresponding bond lengths in **HTPcr**, C2−C15 and C4−C13, are 1.441 Å, average (Figure S-6). The equality of each of the S−S and C−S bond lengths is similar to that of 1,6,6aλ^4-trithiapentalene.[11] In this recent publication, Perrin et al.[11a] did not consider the 1,6,6aλ^4-trithiapentalene equivalent of **HTPc** or **HTPd** that would give the same NMR characteristics.

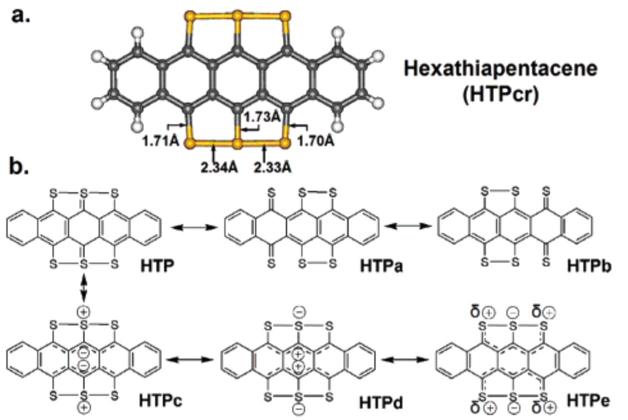

Figure 1. (a) Crystal structure of hexathiapentacene (**HTPcr**); (b) **HTPa**−**HTPc**, possible resonance contributors to the overall structure.

As shown in Figure 2, X-ray crystallographic analysis has revealed the molecular packing of **HTP**, which is characteristic of $\pi-\pi$ stacking in two directions with very short intermolecular

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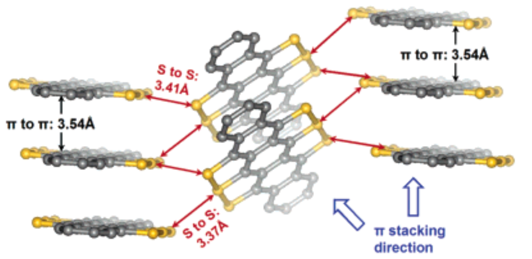

Figure 2. Molecular packing of hexathiapentacene (**HTP**) illustrating the two $\pi-\pi$ stacking directions and intermolecular S-to-S distances.

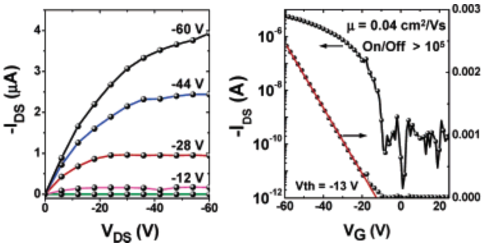

Figure 3. Electrical characteristics of a top-contact **HTP** OTFT device for a deposition temperature of 60 °C. $V_{DS} = -60$ V, $Vt_{sub} = 2.6$ V/dec, $W = 400$ μm, $L = 40$ μm.

contacts between neighboring sulfur atoms. **HTP** molecules stack face-to-face along the *a*-axis with π-to-π distances of 3.54 Å directly through the center of inversion of the **HTP** molecule. The π-stacking may be due to the chalcogen atoms located on the peripheral of pentacene's backbone, which blocks the edge-to-face interactions in the herringbone structure of pentacene. It is known that face-to-face stacking is favored with added peripheral substituents[12,13,14] as well as with an increase of π-surface-to-circumference ratios.[15] This face-to-face π-stacking structure is believed to be more efficient for charge transport than in herringbone packing.[12,14,16] A distance of 3.37−3.41 Å, which is smaller than twice the Van der Waals radius of S atom (3.70 Å), is observed between the central S atom and the outermost S atom of a neighboring **HTP** molecule. By all accounts, this unusually short intermolecular S···S distance appears to be one of the shortest distances reported for a sulfur-containing semiconductor/conductor.[8] This short intermolecular S-to-S distance may be attributed to the partial positive charge on the outer S atoms, which is shown in the resonance forms of **HTPe** in Figure 1b. The partial positive charge on the outer S atoms allows electrostatic intermolecular attraction with the negative central S atoms of neighboring molecules. In addition to $\pi-\pi$ stacking, the short intermolecular S···S distances may possibly provide another pathway for charge transport.

Thin-film transistors were fabricated in a top-contact configuration using gold as the source and drain electrodes. The carrier mobility of **HTP** was found to be dependent on the substrate deposition temperatures, and studies were carried out in ranges of 20−180 °C. Mobilities in the range of 0.005−0.04 cm^2 V^{-1} s^{-1} were measured with the highest mobility observed at a substrate deposition temperature of 60 °C. At this temperature, we observed on/off ratios as large as 10^7 and threshold voltages as small as −1.4 V. Table S-1 (Supporting Information) provides a summary of the electrical characteristics of **HTP** devices at all temperature ranges. Figure 3 shows the well-resolved output and transfer characteristics of a representative **HTP** device. While a long-term stability analysis of the devices is still in progress, preliminary results indicate the devices remain functional 8 months after fabrication and storage in ambient conditions.

One could speculate that the relatively low mobility of **HTP** (e.g., compared to that of pentacene)[3] measured in our devices may be due to charge carriers being trapped in the dipolar field of the zwitterions; this hypothesis of course is based on the presumption that the proposed zwitterionic structure is predominant. Nevertheless, the unique structure and molecular packing of **HTP** may find practical applications in areas such as sensors and charge-transport mechanistic studies. Moreover, the narrow band gap (∼1.63 eV) and long wavelength absorption are ideal parameters for solar cell applications.

In summary, we have determined the crystal structure and measured the electronic characteristics of hexathiapentacene. We report respectable mobilities on the order of 10^{-2} cm^2 V^{-1} s^{-1} with large current on/off ratios and small threshold voltages for top-contact devices. With crystallographic evidence of unusually long S−S bonds compared to normal S−S bonds, we have suggested a unique resonance structure similar to trithiapentalene,[9b,11] which well explains the bonding characteristics of **HTP** and the unusually short intermolecular S-to-S distances.

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Supporting Information Available: Additional data and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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