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# Solution-Processed, High-Performance Nanoribbon Transistors Based on Dithioperylene

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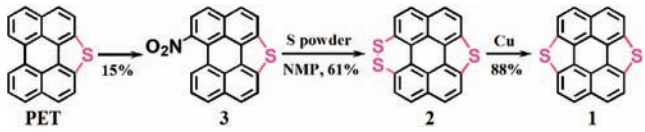
***Abstract:*** Solution-processed, high-performance 1D single-crystalline nanoribbon transistors fabricated from dithioperylene are described. The integration of two sulfur atoms into the perylene skeleton induces a compressed highly ordered packing mode directed by S···S interactions. The mobilities of up to 2.13 $cm^2\ V^{-1}\ s^{-1}$ for a dithioperylene individual nanoribbon make it particularly attractive for electronic applications.

One-dimensional (1D) organic nano- or microstructures have been intensively developed in recent years for their high crystallinity, good processability, flexibility, and large area fabrication.[1] High performance transistors for both holes and electrons based on organic 1D structures were reported.[2] Remarkably, fabricating such structures with mobilities higher than 1.0 $cm^2\ V^{-1}\ s^{-1}$ was even achieved via solution process.[3] Moreover, the chemical versatility of semiconductor molecules can be controlled by means of incorporating functionalities through rational molecular design ("molecular engineering"), which can fine-tune the molecular packing structures and thus improve the charge-carrier mobility for applications in OFETs ("crystal engineering"). However, only a few reports were focused on the device performance of the film instead of the "engineered crystals".[4]

We present here a crystal engineering strategy to control the organization of heteroatom-annulated perylenes in the solid state that enforces cofacial $\pi$-stacking with channels for hole transport directed by chalcogen−chalcogen interactions. In our earlier work, we have demonstrated that the double-channel 1D charge transport superstructures have been successfully achieved involving perylo[1,12-*b*,*c*,*d*]thiophene (PET) and its selenophene analogue (PESE).[5] In view of the unique structure of perylene, we would like to design and synthesize a symmetric derivative dithioperylene (**1**) with two sulfur atoms annulated on its two bay positions that will facilitate more effective charge transporting. As expected, marked S···S intercolumnar interactions of 3.45 Å were found in the solid state, and thus, a compressed highly ordered packing mode was formed. The individual nanoribbon transistors with carrier mobility as high as 2.13 $cm^2\ V^{-1}\ s^{-1}$ and an on/off ratio up to $10^6$ were easily fabricated utilizing this molecule by solution process.

Stimulated by the practical synthesis of PET from 1-nitroperylene,[6] dithioperylene (**1**) was obtained via three-step reactions in about 8% overall yield. The key step in our approach involved effective regiospecific mononitration of PET at the free bay region with an excess of $HNO_3/H_2O$ reagent in almost 15% yield. And the desired product was synthesized as bright yellow needle-like crystals by cooper-mediated dechalcogenation[7] since the intermediate 1,2-dithiin (**2**) is preferentially produced (Scheme 1, for details see the Supporting Information).

***Scheme 1.*** Synthesis of Dithioperylene




Considering the very limited solubility of the studied molecules in common solvents at ambient temperature, solution electrochemistry measurement of dithioperylene **1** to corroborate the HOMO values was not possible. Electronics structure has been calculated at B3LYP/6-31G(d) level by Gaussian03 software; the energy levels are −5.30 eV (HOMO) and −1.82 eV (LUMO), and hence, a very large gap of 3.48 eV is estimated. And an optical band gap of 3.12 eV is determined from an onset absorption of ∼398 nm measured from UV−vis spectra (Figure S2) comparable to the above theoretical calculations. Thermogravimetric analysis (TGA) performed under nitrogen showed the onset decomposition temperature ($T_d$) at 343 °C for **1** (Figure S1). Both values indicate an exceptional thermal and chemical stability of this material.

Crystals suitable for single-crystal X-ray analysis are obtained by slow cooling of a solution of **1** in hot toluene. The crystals packed into columns along the *b*-axis direction (Figure 1). Intermolecular $\pi-\pi$ interactions could be observed in the stacked column with the interplane distance of about 3.42 Å and the tilt angle of about 38.5°, revealing the more compressed packing and slightly more overlap of $\pi$ stacks than that of PET molecules (3.47 Å and 39.8°).[8] Most importantly, these columns were linked through S···S nonbonding interactions (3.45 Å) to form a compressed highly ordered packing mode, which makes **1** an attractive candidate for device applications.

Single-crystalline nanoribbons were fabricated by solution process in which the crystallization process was sped up to form nanosized crystals by methanol injection.[3a] A total of 0.5 mg of powder of the compound **1** was dissolved in 1 mL of boiling tetrahydrofuran (THF) in the glove box, while 200 $\mu$L of methanol was injected into the hot solution. The light yellow precipitations were formed within 1 h. During the process, the molecules of compound **1** self-assembled into 1D nanostructure due to the optimized $\pi-\pi$ stacking of the aromatic plane. To elucidate the

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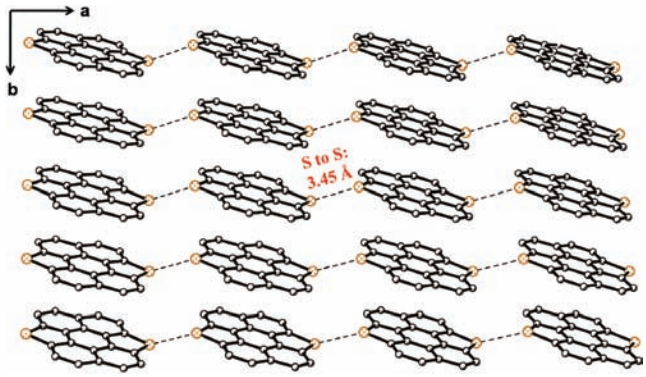


***Figure 1.*** Packing arrangement of dithioperylene (**1**) illustrating the ideal $\pi-\pi$ molecular stacking along the *b* axis, and a compressed highly ordered packing mode induced by marked intercolumnar S···S interactions within the $a-b$ plane (hydrogen atoms were omitted for clarity).

structure of **1**, a typical transmission electron microscopy (TEM) image of a representative nanoribbon is given in Figure 2B, and

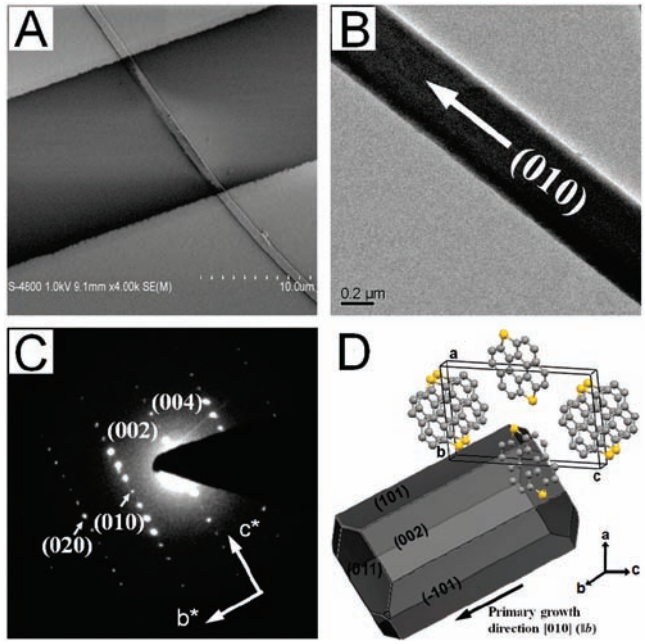


***Figure 2.*** (A) The SEM image of the individual ribbon OFET by a plastic microfiber mask. (B) The TEM image of an individual ribbon, showing a preferential growth along the [010] direction. (C) Its corresponding SAED pattern. (D) Theoretically predicted growth morphology of a single crystal of **1**.

its corresponding selected-area electron diffraction (SAED) pattern (Figure 2C) is indexed with lattice constants obtained from the single-crystalline XRD diffraction data: $a = 9.6585(19)$ Å, $b = 4.3731(9)$ Å, $c = 15.436(3)$ Å, $\beta = 98.37(3)°$. No change of the SAED pattern was observed for different parts of the same ribbon, indicating the single crystallinity of the 1D nanostructure. The diffraction spots suggest that the single-crystalline **1** nanoribbons grew along the [010] direction (i.e., *b*-axis). The morphology theoretically predicted by the Bravais−Friedel−Donnay−Harker (BFDH) method agreed well with the electron diffraction data, which coincided with the $\pi-\pi$ stacking direction of dithioperylene molecules (Figure 2D).

The suspension in THF/methanol solution was directly spin-coated onto the *n*-octadecyltrimethoxylsilane (OTS)-treated $SiO_2$/Si substrate,[9] and then, the nanoribbons were assembled onto the substrate surface. The plastic microfiber mask was employed here to fabricate the single nanoribbon transistors.[2c] Typical output and transfer characteristics of representative OFETs based on 1D single-crystalline nanoribbons are shown in Figure 3. All devices exhibited

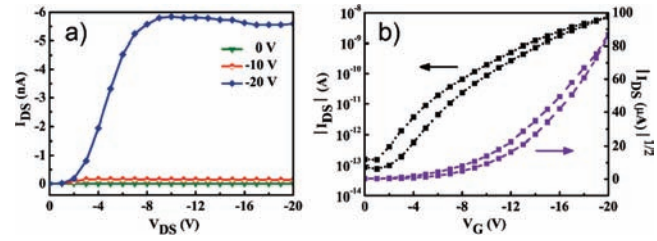


***Figure 3.*** The electrical characteristics of the transistor based on individual microribbon of **1**: (a) output, (b) transfer characteristics of the device.

typical p-channel FET characteristics. The mobility as high as 2.13 $cm^2\ V^{-1}\ s^{-1}$ with on/off ratio of $10^6$ was achieved, the average mobility of 18 devices was 0.45 $cm^2\ V^{-1}\ s^{-1}$, and the average threshold was −14 V. The value is almost 3 times higher than that of PET (0.8 $cm^2\ V^{-1}\ s^{-1}$),[5a] even though the vapor-phase deposited organic single crystals generally exhibit higher quality and thus higher performance than the solution-processed crystals.[10] In addition, we have carried out a first-principles calculation based on hopping model coupled with a Random Walk simulation.[11] We found that the room temperature hole mobility for crystal of **1** can reach 29.52 $cm^2\ V^{-1}\ s^{-1}$, which is a defect or disorder free limit (see Supporting Information).

In summary, we have demonstrated a molecular and crystal engineering strategy toward high-performance p-channel 1D single-crystalline nanoribbon transistors based on heteroatom-annulated perylenes. The integration of two sulfur atoms instead of one into the perylene skeleton enforces a compressed highly ordered packing mode directed by S···S interactions for two-dimensional hole transport. Employing this molecule in the OFETs produced mobilities as high as 2.13 $cm^2\ V^{-1}\ s^{-1}$ and an on/off ratios up to $10^6$ for single-crystalline nanoribbons by solution process as a consequence of more uniform symmetric molecular design. Further exploration of crystal growth and device fabrication are currently underway.

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**Supporting Information Available:** Further experimental details, characterization data of all new compounds, information of device fabrication, as well as crystallographic data for **1** and **2** presented in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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