

## 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<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for a dithioperylene individual nanoribbon make it particularly attractive for electronic applications.

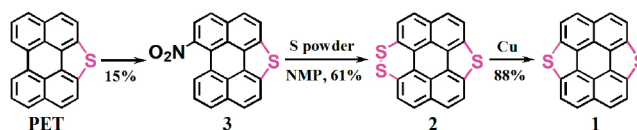
One-dimensional (1D) organic nano- or microstructures have been intensively developed in recent years for their high crystallinity, good processability, flexibility, and large area fabrication.<sup>1</sup> High performance transistors for both holes and electrons based on organic 1D structures were reported.<sup>2</sup> Remarkably, fabricating such structures with mobilities higher than 1.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was even achieved via solution process.<sup>3</sup> 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”.<sup>4</sup>

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).<sup>5</sup> 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<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratio up to 10<sup>6</sup> were easily fabricated utilizing this molecule by solution process.

Stimulated by the practical synthesis of PET from 1-nitroperylene,<sup>6</sup> 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<sub>3</sub>/H<sub>2</sub>O reagent in almost 15% yield. And the desired product was synthesized as bright yellow needle-like crystals by copper-mediated dechalcogenation<sup>7</sup> 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*<sub>d</sub>) at 343 °C for **1** (Figure S1). Both values indicate an exceptional thermal and chemical stability of this material.

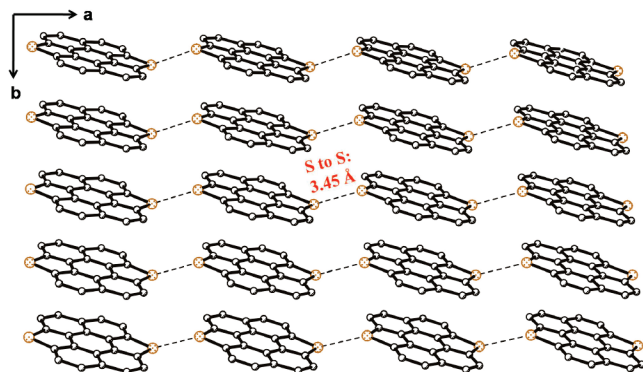
Crystals suitable for single-crystal X-ray analysis are obtained by slow cooling of a solution of **1** in hot toluene. The crystals packed into columns along the *b*-axis direction (Figure 1). Intermolecular  $\pi$ - $\pi$  interactions could be observed in the stacked column with the interplane distance 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°).<sup>8</sup> 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.<sup>3a</sup> 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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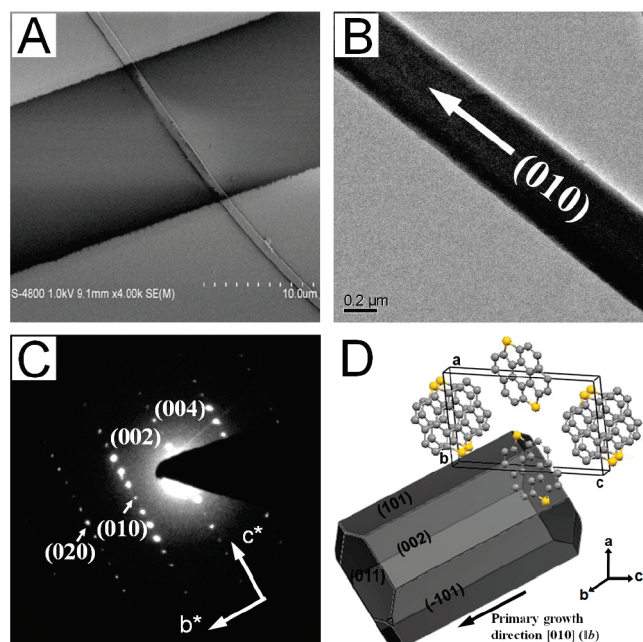
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**Figure 1.** Packing arrangement of dithiopyrene (**1**) illustrating the ideal  $\pi$ - $\pi$  molecular stacking along the  $b$  axis, and a compressed highly ordered packing mode induced by marked intercolumnar S $\cdots$ S interactions within 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

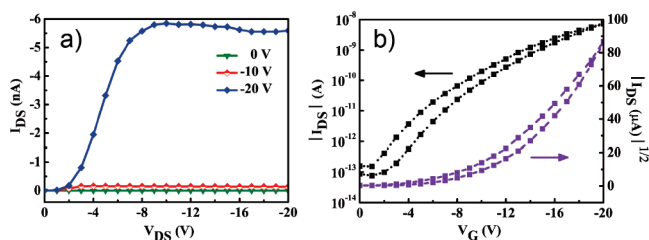


**Figure 2.** (A) The SEM image of the individual ribbon OFET by a plastic microfiber mask. (B) The TEM image of an individual ribbon, showing a preferential growth along the [010] direction. (C) Its corresponding SAED pattern. (D) Theoretically predicted growth morphology of a single crystal of **1**.

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,  $\beta = 98.37(3)^\circ$ . 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 dithiopyrene molecules (Figure 2D).

The suspension in THF/methanol solution was directly spin-coated onto the  $n$ -octadecyltrimethoxysilane (OTS)-treated SiO<sub>2</sub>/Si substrate,<sup>9</sup> and then, the nanoribbons were assembled onto the

substrate surface. The plastic microfiber mask was employed here to fabricate the single nanoribbon transistors.<sup>2c</sup> 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<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with on/off ratio of 10<sup>6</sup> was achieved, the average mobility of 18 devices was 0.45 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and the average threshold was -14 V. The value is almost 3 times higher than that of PET (0.8 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>),<sup>5a</sup> even though the vapor-phase deposited organic single crystals generally exhibit higher quality and thus higher performance than the solution-processed crystals.<sup>10</sup> In addition, we have carried out a first-principles calculation based on hopping model coupled with a Random Walk simulation.<sup>11</sup> We found that the room temperature hole mobility for crystal of **1** can reach 29.52 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, 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 $\cdots$ S interactions for two-dimensional hole transport. Employing this molecule in the OFETs produced mobilities as high as 2.13 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratios up to 10<sup>6</sup> 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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