

Manipulation of crystal structures of pyrene-based organic semiconductors enabling ultrahigh mobility

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ABSTRACT

Although the importance of molecular arrangement in the solid state of organic semiconductors has been widely recognized, the control of crystal structure has been a formidable task. We have recently realized that methylthiolation is a potential way to control the crystal structure of organic semiconductors, and in the present work, we take pyrene, which is known to crystallize into a sandwich herringbone structure. The four-fold methylthiolated derivative of pyrene (MT-pyrene) was turned out to have a new type of brickwork structure. Single-crystal field-effect transistors (SC-FETs) of MT-pyrene showed excellent transport properties with impressively high mobility of $32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

1 Introduction

Carrier transport in molecular semiconductors is governed by both the molecular properties and crystal structure of molecular semiconductors, which determine the electronic structure of molecular solid. Thus, both of them must be considered for developing superior molecular semiconductors. Prediction and simulation of molecular properties by theoretical calculations are now routinely carried out, and nowadays such theoretical calculations at the molecular level are indispensable tools in the design of new molecular semiconductors. In contrast, prediction and control of the crystal structure of a given molecular semiconductor are difficult challenges to overcome. For this reason, molecular semiconductors have been developed by just considering the predictable molecular properties and/or by mimicking the molecular structures of already-known superior semiconducting molecules.

We have recently found that introduction of methylthio groups (i.e., methylthiolation) is a useful way to control the crystal structure of molecular semiconductors; the packing structure of a series of acenedithiophenes can be predictably altered from the herringbone structure to rubrene-like pitched π -stack by methylthiolation. [1,2] In the present work, we demonstrate the possibility of crystal-

structure control by methylthiolation on pyrene, a *peri*-condensed polyaromatic hydrocarbon (PAH), from the sandwich herringbone in the parent compound to the brickwork structure in 1,3,6,8-tetrakis(methylthio)pyrene (MT-pyrene) (Fig. 1). [3]

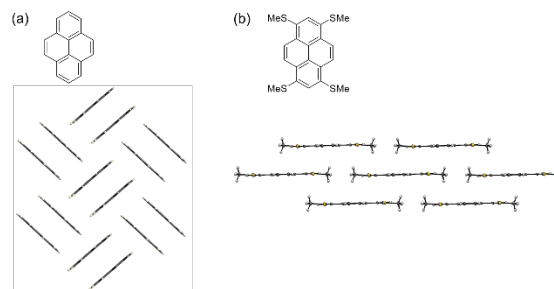


Fig. 1. Molecular and packing structure of pyrene (a) and MT-pyrene (b).

2 Experiment

2.1 Synthesis and preparation of single crystals of MT-pyrene

MT-pyrene was synthesized from 1,3,6,8-tetrabromopyrene and sodium methanethiolate according to the reported procedure [3]. The crude product was purified by multiple train-sublimation under vacuum. With the purified powder sample, single crystals were grown by the physical vapor transport (PVT) technique under a flow of nitrogen carrier gas. The temperatures of the source and crystallization zone were set to 240 and 130 °C, respectively.

2.2 Single crystal X-ray analysis

Single-crystal X-ray analysis of MT-pyrene was carried out with relatively thick crystals (1~10 μm) obtained by the PVT technique on a Rigaku Oxford Diffraction XtaLAB Synergy Custom DW system with a HyPix-6000HE detector (CuK α radiation, wavelength: 1.5418 Å, multilayer confocal optics). Crystal data: orange plate, *triclinic*, $P\bar{1}$, $a = 6.5536(7)$, $b = 7.9935(14)$, $c = 9.3715(10)$ Å, $a = 111.132(13)$, $b = 101.623(10)$, $g =$

98.940(11)°, $V = 434.34(11) \text{ \AA}^3$, $Z = 2$, $T = 293(2) \text{ K}$, $R = 0.0916$, $wR^2 = 0.2498$, $\text{GOF} = 1.083$.

2.3 Fabrication and evaluation of single-crystal field-effect transistors

Heavily doped n-type Si wafers with thermally grown SiO_2 layers were used as substrates. The cleaned substrates were spin-coated with 3 wt.% CYTOP (AGC) solution at 3000 rpm for 1 min, and then dried at 180 °C on a hot plate in air. On top of the substrate, the MT-pyrene crystals were laminated under the optical microscope. The top-contact FETs were completed by placing droplets of colloidal graphite (source and drain electrodes) on each side of the crystal and drying for more than 30 min at ambient conditions. All the FET measurements were performed with a probe station and a semiconductor parameter analyzer (Keithley 4200-SCS) in air. The carrier mobility μ , was determined from the forward swing of the transfer characteristics using equation (1):

$$|I_d| = \frac{W}{2L} C_i \mu (V_g - V_{th})^2 \quad (1)$$

where L and W are channel length and width of the OFETs, respectively, C_i is the gate capacitance per unit area, and V_{th} is the threshold voltage.

3 Results and discussion

The theoretical calculations assist to understand the structural change in the series of methylthiolated pyrene derivatives, i.e., 1,6-bis(methylthio)pyrene and MT-pyrene, the number and position of the group are the key to control the crystal structure. The resulting brickwork structure of MT-pyrene afforded very large orbital overlap ($> 100 \text{ meV}$) and functioned as an excellent FET channel showing very high hole mobility of $32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the single-crystal field-effect transistors operated at $V_d = V_g = -5 \text{ V}$. [4] The MT-pyrene SC-FETs were thus characterized by high mobility and low-voltage operation; the former was explained by the band-like transport confirmed by temperature dependence of mobility and the band calculations demonstrating the large bandwidth and small effective mass. On the other hand, the low trap density in the MT-pyrene SC-FETs estimated from the subthreshold properties rationalized the latter.

All these excellent device characteristics of MT-pyrene-based SC-FETs compare well with those of the best organic SC-FETs so far reported. This means that MT-pyrene, which is easily synthesized in only two steps from parent pyrene, is an excellent molecular semiconductor.

4 Conclusions

Through the present work, three important results were obtained; (i) methylthiolation is a powerful tool to manipulate crystal structure of *peri*-condensed PAHs. (ii) MT-pyrene afforded SC-FETs showing extremely high mobility of $> 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. (iii) The high mobility and bandlike transport of the MT-pyrene-based SC-FETs are rationalized by the electronic structure in the solid state, which is deeply rooted in the crystal structure of MT-pyrene.

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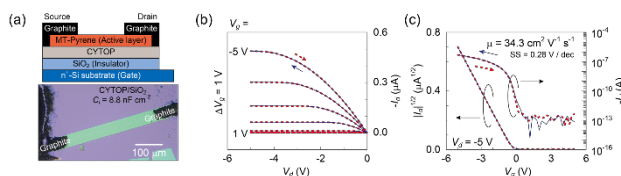


Fig. 2. Device structure (a), output (b) and transfer characteristics (c) of MT-pyrene-based SC-FET.