# Novel highly stable semiconductors based on phenanthrene for organic field-effect transistors†

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*Received (in Cambridge, UK) 12th May 2006, Accepted 26th June 2006*
*First published as an Advance Article on the web 13th July 2006*
**DOI: 10.1039/b606759j**

**Two novel phenanthrene-based conjugated oligomers were synthesized and used as p-channel semiconductors in field-effect transistors; they exhibit high mobility and excellent stability during long-time ambient storage and under UV irradiation.**

Organic field-effect transistors (OFETs) have received considerable attention in recent years due to their potential applications in optoelectronics, such as displays and integrated circuits (ICs).[1] Organic semiconducting materials with high field-effect mobility ($\mu_{FET}$) and remarkable environmental stability are critical for fabrication of OFETs. Currently, most researches on p-channel organic semiconductors are devoted on two classes of materials, *i.e.* acenes and thiophene-based oligomers/polymers. In particular, with acene-type molecules, $\mu_{FET}$ values up to 5 cm$^2$ V$^{-1}$ s$^{-1}$ from vacuum deposited pentacene films[2] and 15.4 cm$^2$ V$^{-1}$ s$^{-1}$ from rubrene single crystals[3] have been reported. Recently, Ito *et al.* also reported anthracene oligomers with $\mu_{FET}$ in the range of 0.01–0.22 cm$^2$ V$^{-1}$ s$^{-1}$.[4] In contrast to their promising charge-carriers transporting properties, acene-type molecules are very reactive and environmentally unstable, especially in the presence of light.[5] The previous studies have revealed that pentacene devices underwent current degradation while stored in air[6] and threshold voltage ($V_T$) shift upon ultraviolet illumination.[7] As an isomer of anthracene, phenanthrene is also one of the most important fused aromatic compounds. It has higher resonance energy, and therefore is more stable,[8] especially less sensitive to photons. On the other hand, although thiophene oligomers are easily oxidized due to the relatively high-lying energy level of the highest occupied molecular orbital (HOMO) and relatively narrow band gap, appropriately substituted thiophene-based semiconductors[9] have shown good stability under ambient conditions with reasonably high mobility. In the current paper, we have synthesized two phenanthrene-based conjugated oligomers. Their optical properties, thermal properties, field-effect charge carrier transporting properties and device stability were studied.

The structures of oligomers, *i.e.* 2,2′;7′,2″-terphenanthrenyl (**Ph3**)[10] and 5,5′-bis(phenanthren-2-yl)-2,2′-bithiophene (**PhT2**), are depicted in Fig. 1. **Ph3** and **PhT2** were synthesized by means of Suzuki and Stille coupling reactions[11] in a yield of 54 and 50%, respectively, after double vacuum sublimation. The molecular structures were confirmed by $^1$H NMR spectroscopy and elemental analysis.

**Ph3** and **PhT2** show well-resolved absorption spectra in the film state, indicating the rigid characteristics of the molecules in the solid state (ESI†). The optical band gap ($E_g$), derived from the thin-film absorption edge, is 3.11 eV for **Ph3** and 2.55 eV for **PhT2**. These values are larger than that of pentacene (2.20 eV)[9b] and most thiophene-based oligomers/polymers (2.30–2.42 eV).[12] From cyclic voltammetry (CV) measurements, the HOMO energy level of **Ph3** and **PhT2** was estimated to be −5.85 and −5.40 eV, respectively, which are lower than pentacene and most oligothiophenes, indicative of better environmental stability.[13]

**Ph3** and **PhT2** are quite stable under ambient conditions. The absorption spectra of 100 nm-thick films after exposure to air and room light for two months are identical to those of the fresh films. Especially, they exhibit high photo-stability. The absorption spectra were almost unchanged after UV-irradiation when excited at 333 and 356 nm, respectively. In contrast, acene-type molecules are quite sensitive to light in both solution and film states.[5,14]

Thermogravimetric analysis (TGA) reveals that **Ph3** and **PhT2** are highly stable and exhibit a two-step degradation process with the first decomposition onset of 443 and 402 °C, respectively. Differential scanning calorimetry (DSC) measurements show a sharp melting endotherm peak at 434 °C for **Ph3** and 393 °C for **PhT2**, respectively.

OFETs of **Ph3** and **PhT2** were constructed on Si/SiO$_2$ substrates with top-contact geometry (ESI†). Both OFETs showed p-channel characteristics. The performance of the devices depended on the fabrication conditions, *e.g.* substrate temperature ($T_S$). On bare Si/SiO$_2$ substrate, the device of **Ph3** fabricated at $T_S$ of 150 °C exhibits a highest saturation region mobility $\mu_{FET}$ of 1.1 × 10$^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ along with a current on/off ratio of 2 × 10$^5$.

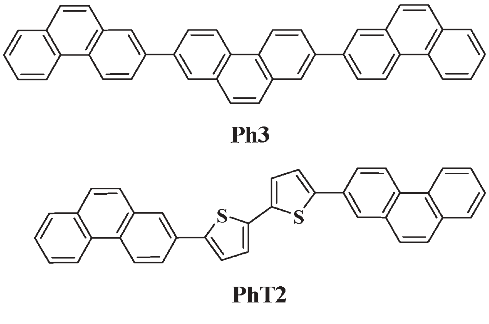

**Fig. 1** Chemical structures of **Ph3** and **PhT2**.

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† Electronic supplementary information (ESI) available: Complete synthetic and experimental data, UV-vis absorption data, and devices performance data. See DOI: 10.1039/b606759j

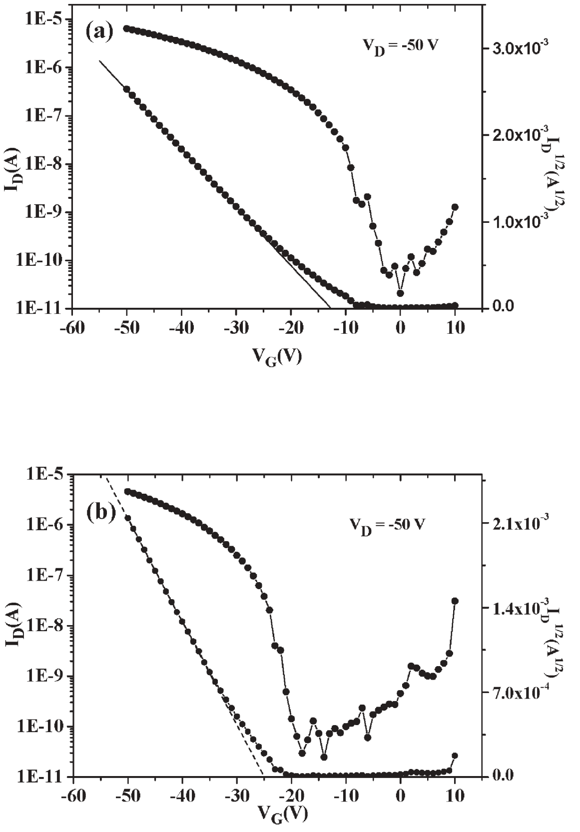

**Fig. 2** Transfer characteristics of OFETs based on **PhT2** at $T_S$ = 100 °C, without (a) and with OTS substrate treatment (b).

Similarly to anthracene oligomers,[4] it shows a threshold voltage as high as −46 V. **PhT2** shows a much better OFET performance. The typical transfer characteristics of **PhT2** devices are shown in Fig. 2(a). With identical device geometry, **PhT2** shows $\mu_{FET}$ of 1.9 × $10^{-2}$, 4.4 × $10^{-2}$ and 2.5 × $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ at $T_S$ of 50, 100 and 150 °C, respectively, with current on/off ratio of 4–30 × $10^4$. We attribute the improvement of device performance to better film quality and better-matched HOMO level of **PhT2** (−5.40 eV) with the work function of metallic gold (−5.20 eV), which results in less traps and reduced contact-resistance and hence enhancement of the hole-injection between the electrode and semiconductor layer.[15] In fact, atomic-force microscopy (AFM) characterizations show that **PhT2** forms dense and continuous films at $T_S$ of 50 and 100 °C. At $T_S$ of 100 °C, the size of crystalline domains is about 500 nm. Further increasing $T_S$ to 150 °C results in poorer continuity than that at lower temperature, even the size of crystalline domains increased to 1–2 μm. These observations are consistent with the highest $\mu_{FET}$ at $T_S$ of 100 °C. Modification of substrate with a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS)[16] was found to greatly improve the device performance. The transfer characteristics of the device are shown in Fig. 2(b). The mobility ($\mu_{FET}$) up to 0.12 cm$^2$ V$^{-1}$ s$^{-1}$ with a current on/off ratio of 1–3 × $10^5$ was reproducibly obtained. This $\mu_{FET}$ is close to that of amorphous silicon devices, even if still lower than that of acenes. The enhanced $\mu_{FET}$ is attributed to improved film order, indicated by thin-film X-ray diffraction.

Most importantly, devices of **PhT2** exhibit great stability, no matter if an OTS monolayer is employed or not. OFETs with **PhT2** as the active layer were stored in ambient condition (exposure to both air and room light), and the electrical performance was measured periodically. In a period of four months, the devices both with and without OTS treatment exhibited almost unchanged device performance, as shown in Fig. 3. For devices with and without OTS treatment, $\mu_{FET}$ of 0.12 ± 0.02 cm$^2$ V$^{-1}$ s$^{-1}$ (see Fig. 3) and 0.045 ± 0.003 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, was observed. Meanwhile, the devices showed small variation of current on/off ratio and $V_T$. After four months, $I_{on}/I_{off}$ and $V_T$ were (4 ± 1) × $10^5$ and −(27 ± 3) V (see Fig. 3) for the device with OTS treatment, and (7 ± 3) × $10^4$ and $V_T$ = −(12 ± 3) V for the device without OTS treatment. The lower HOMO level (−5.40 eV) of **PhT2** than oligothiophenes and high film quality may be responsible for the good device stability.

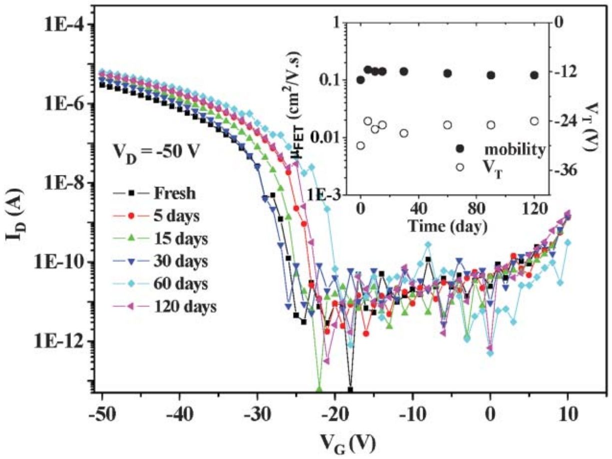

**Fig. 3** The transfer curves of the **PhT2** device with OTS substrate treatment upon storage in ambient condition (inset: mobility and threshold voltage time-dependence).

To test the device photostability, a **PhT2** device was irradiated with UV light with wavelength of 365 nm in an inert atmosphere. The device performance was almost unchanged up to 6 h with $\mu_{FET}$ = 0.046 ± 0.004 cm$^2$ V$^{-1}$ s$^{-1}$, $I_{on}/I_{off}$ = (7 ± 3) × $10^4$ and $V_T$ = −(12 ± 3) V, as shown in Fig. 4. This is consistent with the great photostability of **PhT2** as aforementioned.

In summary, we have successfully demonstrated a novel class of semiconducting materials based on phenanthrene for OFET

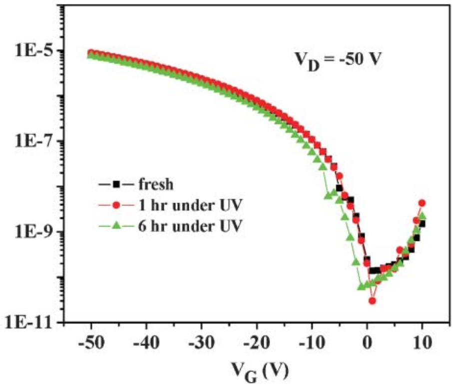

**Fig. 4** The transfer curves of **PhT2** device before and after UV irradiation.

application. To our best knowledge, this is the first report for high-performance semiconductors with phenanthrene as the construction unit. These materials exhibit high OFET mobility up to $0.12\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$ and current on/off ratio up to $3 \times 10^5$. Importantly, the devices are very stable and exhibit no significant performance variety during long-time storage under ambient conditions and under UV irradiation.

This work was supported by 973 Project (2002CB613404) of the Chinese Ministry of Science and Technology, NSFC (Nos. 20423003, 20521415 and 20474063), Hundreds Talents Program of Chinese Academy of Sciences, and Distinguished Young Scholar Foundation of Jilin Province (No. 20040101).

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