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An Ultra Closely π-Stacked Organic Semiconductor for High Performance Field-Effect Transistors**

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Since the first organic field-effect transistor (OFET)[1] was reported in 1986, there has been remarkable progress in the development of OFETs. However, there remain some key challenges in this field,namely the mobility (most OFETs with a mobility lower than 1 $cm^2 V^{-1} s^{-1}$), on/off ratio and environmental stability.[2,3] Moreover, quantum mechanical calculations[4,5] and structural analysis[6] have predicted that high mobility can be obtained when conjugated molecules have strong interactions with neighboring molecules to maximize the overlap of π molecular orbits. Hence, theoretically speaking, a π stacked structure is expected to provide more efficient orbital overlap and thereby facilitates carrier transport. However, so far, the organic semiconductors which exhibit high mobility and high on/off ratio usually possess herringbone structure, e.g., rubrene and pentacene,[7,8] which results in reduced intermolecular electronic couplings. The fundamental aspects of carrier transport in OFETs, especially the role of solid-state packing, are still under scrutiny.[9] It is imperative to establish the structure-properties relationship both experimentally and theoretically for the carrier mobility of organic semiconductors.

Phthalocyanines have attracted attentions in OFETs for some years because of their remarkably chemical and thermal stabilities, as well as non-toxicity and good field-effect properties.[10,11] TiOPc is known as one of the most efficient organic photoconductors[12] in the near-IR region and is currently used in more than 90 % laser printers. In contrast to other phthalocyanines, e.g., copper phthalocyanine,[10,11] TiOPc is a nonplanar and polar molecule[13] with the titanyl group located perpendicular to the macro cycle, with the outer phenyl rings making an angle of 7° with respect to the C-N inner ring, so that the molecule has a shallow square-pyramid structure (Fig. 1a). Three crystal structures of TiOPc have been reported so far,[13] a monoclinic phase I (hereafter β-TiOPc), a triclinic phase II (hereafter α-TiOPc), and a triclinic phase Y. In the triclinic α-structure, TiOPc molecules form concave and convex pairs with significant molecular overlaps and very short intermolecular distances, N6-N6 (3.145 Å) in the convex pair and C9-C28 (3.211 Å) in the concave pair (Fig. 1b). These π–π molecular contacts are surprisingly close and no such equivalent close contacts can be recognized in phases I and *Y*[13] of TiOPc as well as in other organic semiconductors.[6,9,14,15] These indicate α-TiOPc can be a very promising organic semiconductor, because both molecular modeling[4,5] and experimental evidences[6,9,15] suggest that high mobility is expected for organic semiconductors with such dense packing structure due to the close π–π molecular contacts.

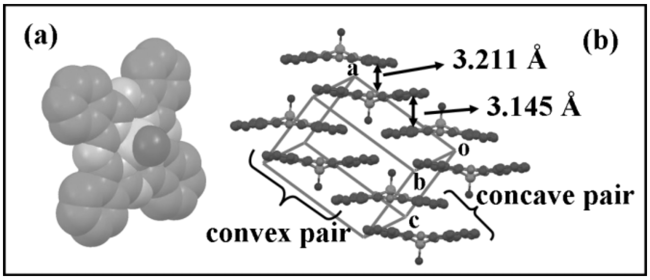

Figure 1. a) Space-filling molecular model of titanyl phthalocyanine (TiOPc). b) molecular stacking of α-TiOPc crystal showing the π-stacking structure with concave pair and convex pair with significant molecular overlaps and very short intermolecular distances.

The pioneer work of TiOPc OFETs were first performed by Tada et al.[16] They carried out the investigation of TiOPc by using vacuum deposited films on pure Si/SiO_2 substrates. Regretfully, their results displayed a low hole mobility ($\sim 10^{-5}$ $cm^2 V^{-1} s^{-1}$) in their OFETs. We reproduced their experiments and confirmed the not ideal performance of TiOPc on pure Si/SiO_2 substrates (hole mobility of $\sim 10^{-4}$–10^{-5} $cm^2 V^{-1} s^{-1}$ measured in air, see Supporting Information 1). Ultraviolet-visible-near-infrared (UV-NIR) absorption spectra of TiOPc films on the pure quartz (SiO_2) substrate were shown in Figure 2a. In the case of substrate

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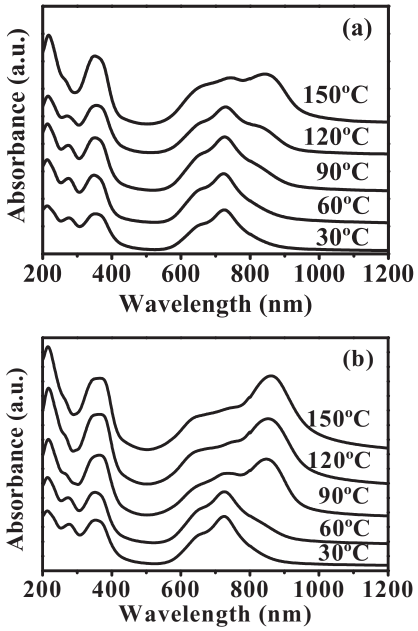

Figure 2. Ultraviolet-visible-near-infrared (UV-NIR) absorption spectra of TiOPc films under various substrate temperatures on a) pure quartz (SiO_2) substrates and b) OTS-modified quartz substrates.

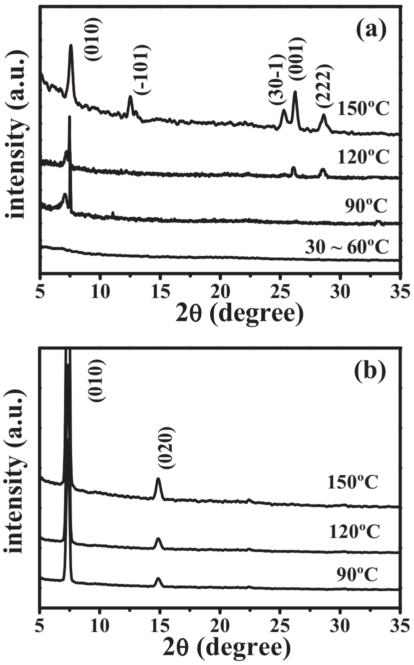

Figure 3. X-ray diffraction patterns of TiOPc film under various substrate temperatures on a) pure Si/SiO_2 substrates and b) OTS-modified substrates.

deposition temperature below 60 °C the characteristic absorption bands indicated these films were in amorphous-phase state.[17] At the deposition temperature higher than 90 °C, the appearance of the peak at around 720 nm indicated that these films still contained amorphous phase. The weak shoulder peak at around 800–850 nm at the temperature of 90–120 °C and the broad absorption band between 600 to 900 nm at 150 °C could be assigned to the mixture of α and/or β phase of TiOPc. The results suggested that the vacuum deposited films of TiOPc on pure quartz (SiO_2) surface were in amorphous or in mixed-phases states, which probably resulted in the poor OFETs characteristics of our and Tada et al.'s devices on the pure Si/SiO_2 substrates,[16] since only α-TiOPc can give the ultra close molecular π–π contacts.

X-ray diffraction patterns (XRD) of TiOPc films deposited on pure Si/SiO_2 substrates at different temperature were shown in Figure 3a. No visible XRD signal was observed when the substrate temperature was below 60 °C, indicating the amorphous nature of the films. At 90 °C, a weak peak at 6.8° ($d = 12.9$ Å) and an intense peak at 7.5° ($d = 11.8$ Å) emerged, in which the former was attributed to the XRD signal of a specific amorphous phase of TiOPc and the latter corresponded to α-TiOPc.[18–20] At 120 °C, the peaks at 26.2° and 28.6°, which were due to β-phase and α-phase, respectively, were observed as well as the peaks at 6.8° and 7.5°. More complicated XRD peaks appeared at 150 °C, in which the diffraction peaks at 7.5°, 12.5°, 25.3°, and 28.6° were assigned to α-phase and the diffraction peak at 26.2° was belonged to β-phase.[18–20] It was further confirmed from the XRD results that the vacuum deposited films of TiOPc on pure Si/SiO_2 surface were in amorphous or in mixed-phases states, which were consistent with the UV-NIR results.

Yonehara and Brinkmann et al.[18–20] found surface modifications of substrates with organic thin layers exerted remarkable effects on the molecular alignment of vacuum deposited TiOPc films. A highly ordered α-TiOPc film with an "edge-on" molecular orientation was selectively grown on the surfaces of the gold substrate modified with a self-assembled monolayer of octadecanethiol.[18] As we know, a popular surface modification of Si/SiO_2 substrates for the fabrication of silicon based OFETs is to self-assemble a monolayer of octadecyltrichlorosilane (OTS) on the gate insulator of SiO_2 so that the contact between organic semiconductor and SiO_2 gate insulator could be improved and followed the improved field-effect performance of OFETs. Actually, OTS possesses the same chemical structure with octadecanethiol except the difference of their end anchoring groups, implying OTS maybe has the same effect as octadecanethiol for obtaining ordered α-TiOPc films.

Figure 2b described the UV-NIR spectra of TiOPc films on the OTS-modified quartz substrates under various temperatures. It was obvious that the Q-band absorption (600–900 nm) of TiOPc film changed with the increasing substrate temperature considerably. At deposition temperature below 60 °C, the main absorption at 720 nm was assigned to the amorphous phase. When TiOPc was deposited at 90 °C, the absorption characteristics were mainly α-phase[17] regardless a weak peak at 730 nm (probably due to a few amorphous phase). Upon the deposition temperature higher than 120 °C, pure α-phase of TiOPc was obtained as shown in Figure 2b, in which their characteristic Q-band absorption displayed no contamination peak.

The XRD patterns of TiOPc films deposited on OTS-modified Si/SiO$_2$ substrates at 90, 120, 150 °C were displayed in Figure 3b. An intense peak at 7.5° ($d = 11.8$ Å) due to the diffraction from (010) plane of α-phase[18–20] was observed, especially for 150 °C, indicating highly ordered α-phase films with the (010) lattice plane parallel to the substrate, i.e., TiOPc molecules preferentially stood on substrates with an "edge-on" style orientation (Fig. 4b), in which the molecular plane made an angle of 62° with respect to the substrates.[18,19] Moreover, the appearance of the second-order diffraction peak at 15.0° ($d = 5.9$ Å) further enhanced the high order of the vacuum deposited films. Hence, it was promising that high performance OFETs could be available based on the highly ordered vacuum deposited films with the "edge-on" molecular orientation because charge transport was along the π-stacking direction in this case.[21]

Top-contact devices (Fig. 4a) were fabricated at substrates temperature of 150 °C by using the OTS-modified Si/SiO$_2$ substrates and were measured in air at room temperature. A typical output and transfer characteristics of the OFETs were shown in Figure 4c and d, respectively. Apparently, the α-TiOPc devices exhibited excellent p-type field-effect modulation characteristics in air. The field-effect mobility (μ) in the saturated region and threshold voltage (V_T) were calculated using the following equation:

$$I_{DS} = \frac{W}{2L} C_i \mu (V_{GS} - V_T)^2 \qquad (1)$$

where W and L is the channel width and length, respectively, C_i is the dielectric capacitance, μ is the field-effect mobility, V_T is the threshold voltage. The field-effect mobility (μ), on/off current ratio (I_{on}/I_{off}) and threshold voltage (V_T), were estimated at around 3.31 cm^2 V^{-1} s^{-1}, 1.2×10^7 and –17.8 V, respectively. Totally 161 selected devices were examined during the past 15 months. The distribution of devices mobility was shown in Figure 4e. Over 90 % devices exhibited hole mobility over 1 cm^2 V^{-1} s^{-1} with the highest hole mobility near 10 cm^2 V^{-1} s^{-1}. To our knowledge, this was one of the highest hole mobility for thin film OFETs up to date. The high perfor-

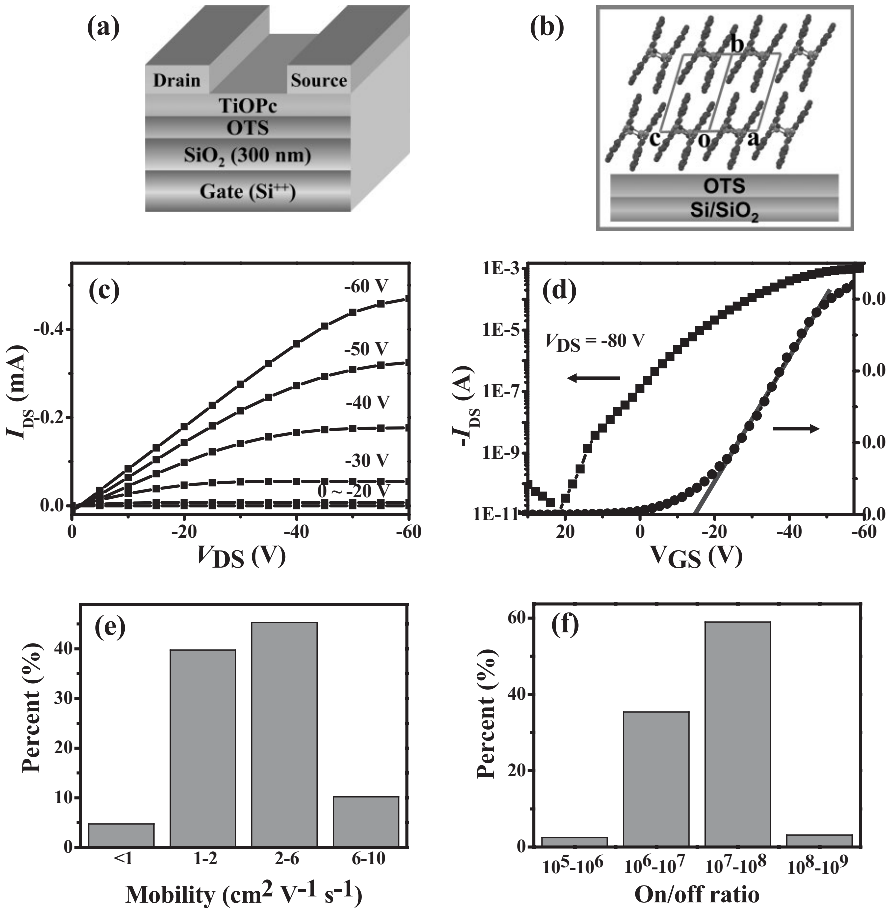

Figure 4. a) Schematic devices structure used in this study. b) the "edge-on" style molecular orientation of α-phase TiOPc with (010) lattice plane parallel to the substrates. c) output characteristics and d) transfer characteristics of TiOPc OFETs fabricated on OTS-modified substrates at the substrate temperature of 150 °C. e) mobility distribution of 161 devices. f) on/off ratio distribution of 161 devices.

mance was due to the ultra close π-stack of α-TiOPc and favorable "edge-on" molecular orientation with respect to substrates. The corresponding on/off ratio of Figure 4e devices was shown in Figure 4f. Over 97 % devices exhibited on/off ratio over 10^6. The corresponding threshold voltage (not shown) was in the range of –13.3 V to –22.5 V. Moreover, all devices exhibited good stability and reproducibility in air, which was probably due to the remarkable chemical and thermal stabilities of TiOPc. The stability of series devices with different mobility was examined over 180 days. A typical curve of performance versus storage time was shown in Figure 5, the mobility and on/off current ratio had ~20 % decrease in the first few days, then, reached a stable case with little degradation. The threshold voltage (not shown) exhibited a small positive or negative shift, but was still in the range of –13.5 V to –25.0 V. These results definitely demonstrated the high performance of the OFETs of α-TiOPc and its potential applications in near future.

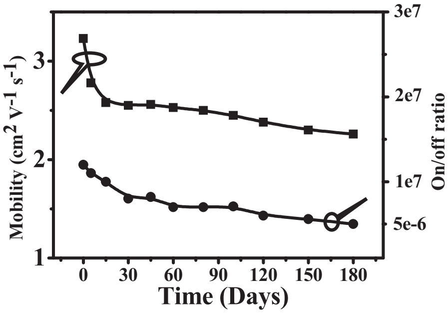

Figure 5. The stability of TiOPc devices in air and at room temperature.

In addition, in order to obtain a quantitative insight into the mobility of TiOPc in α-phase, quantum mechanics was used to estimate its holes mobility.[3,5,14,22,23] An incoherent hopping model was used to describe the holes mobility of α-TiOPc at room temperatures[14] in which charge can transfer only between adjacent molecules. As we know, in π-conjugated systems, a strong coupling exists between the geometric and electronic structures which control transport properties.[24,25] According to semi-classical electron transfer theory and extensions thereof,[26,27] there are two major parameters that determine self-exchange electron-transfer rates and ultimately charge mobility: (i) the electronic coupling (transfer integral) between adjacent molecules, which needs to be maximized and (ii) the reorganization energy λ, which needs to be small for efficient transport.[23,28,29] The intermolecular electronic couplings are obtained by directly evaluating the dimer Fock matrix with unperturbed monomer's molecular orbits at the DFT/pw91pw91/6-31g* (Lanl2dz) level, and the reorganization energies are obtained through performing the quantum chemical calculations at hybrid density functional theory (DFT) level with the B3LYP functional and a 6-31g*(Lanl2dz) basis set.[30–32] (for details, see Supporting Information 2) We find that (i) the strongest nearest-neighbor electronic coupling is as high as 0.143 eV, which is higher than that of pentacene (the calculated largest value is 0.093 eV by our direct method with site-energy correction,[33] in references the largest coupling was found to be 0.137 eV from frontier orbital splitting without site-energy correction,[5]) (ii) the hole reorganization energy is predicted to be 0.079 eV, which is lower than that of pentacene molecule (0.095–0.099 eV in references,[5,22,23,28] and our calculation give a value 0.082 eV). Similarly, the electronic coupling and the reorganization energy λ of α-TiOPc are found to be much more optimum than that of copper phthalocyanine, CuPc—another typical organic semiconductor, the largest coupling is at ~0.048 eV and the hole reorganization energy is predicted to be 0.17 eV. Thus, the theoretical calculations confirm that TiOPc is an excellent potential candidate for OFETs due to the significant molecular overlaps and very short intermolecular distances when the film structural properties are optimized.

Experimental

Titanyl phthalocyanine (TiOPc) was purchased from Aldrich Chemical Co. (USA) and further purified three times by gradient sublimation before using. Fabrication of the devices followed the conventional procedure. The heavily doped, n-type Si wafer containing a 300 nm-thick SiO_2 layer was used as substrate. Treatment of Si/SiO_2 wafer (or quartz) with OTS was carried out by vapor deposition method. The clean wafers were dried under vacuum at 100 °C for 0.5 h in order to eliminate the influence of the moisture. After cooling to room temperature, a little drop of OTS was placed near the wafers. Subsequently, this system was heated to 120 °C and maintained for 2 h under vacuum. TiOPc was deposited on the substrates by thermal evaporation under a pressure of $4\sim6\times10^{-4}$ Pa with the deposition rate at 0.1–0.3 Å s^{-1}. The deposition rate and film thickness were monitored by ULVAC CRTM-6000. The resulting film (65 nm) was cooled to the room temperature in the vacuum. Subsequently, 50 nm thick gold source and drain electrodes were deposited via an interdigital shadow mask. The channel length and width were 0.11 mm and 5.30 mm, respectively. To minimize the influence of heat (radiation), a small (0.4 mm in diameter) and short (25 mm in length) tungsten wire was used as thermal evaporation boat. The FET characteristics were measured with a Keithley 4200 SCS, a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air. X-ray diffraction (XRD) was measured on D/max2500 with Cu Kα source ($\lambda = 1.541$ Å). Ultra-visible-near-infrared (UV-NIR) absorption spectra were obtained on Jasco V-570.

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