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A new pseudo rubrene analogue with excellent film forming ability

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A novel pseudo rubrene analogue, 6,11-di(thiophen-2-yl)-tetracene-5,12-dione (DTTDO) was synthesized, in which two thienyl groups and two carbonyl groups replacing four phenyl groups in the rubrene molecule were connected to the backbone of tetracene. This compound was characterized by single crystal X-ray structure analysis, thermogravimetric analysis, absorption spectra and electrochemical measurements. Unlike rubrene, DTTDO exhibited excellent film forming ability by normal vacuum deposition, indicating its promising applications in organic thin film transistors.

DTTDO, thin films, organic field-effect transistors

1 Introduction

Organic field-effect transistors (OFETs) have attracted great interest during the last thirty years because of their unique advantages such as light-weight, low-cost, and good flexibility [1]. As a core component of OFETs, the organic semiconductor plays a key role in device performance [2]. Of all recently reported organic semiconductors, fused-ring acene derivatives, such as rubrene, have been extensively studied both experimentally and theoretically [3–6] and hold the highest field-effect mobility as the benchmark for organic semiconductors (up to 15–40 cm^2 V^{-1} s^{-1} measured from rubrene single-crystal transistors [7, 8]). In contrast, thin film transistors based on rubrene exhibit very low field-effect performance due to bad film-forming ability [5], which significantly hinders the practical applications of rubrene in large-area electronic devices. Recently, many new unconventional process techniques have been developed to improve the quality of rubrene thin films, such as using the special deposition-process [9–11], developing heteroepitaxial growth methods with the buffer layer [12–15], growing homoepitaxy rubrene thin films on the surface of rubrene single crystals [16] or incorporating a glass-inducing diluent for controlling rubrene thin-film crystallinity [17]. Although significant progresses have been made in this field, most of the techniques always need complicated processes or long processing time [10, 16], or even arousing new dispute that what is responsible for the charge transport properties, the buffer layer or the rubrene [13, 15]? Besides these developed processing techniques, the development of new organic semiconductors by virtue of the unique molecular structure of rubrene with high mobility as well as good film-forming ability has received increasing interest [18, 19], which is very important for the progress of organic thin film transistors (OTFTs).

With this aim in mind, herein, a new rubrene analogue, 6,11-di(thiophen-2-yl)tetracene-5,12-dione (DTTDO), in which two thienyl groups and two carbonyl groups replacing four phenyl groups in the rubrene molecule were connected to the backbone of tetracene (Scheme 1), was designed and synthesized. This compound exhibited good thermal properties, and more importantly good film-forming

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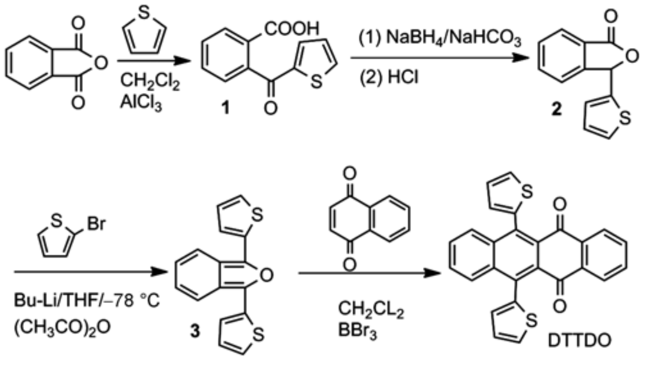

Scheme 1 Synthesis of DTTDO.

ability under vacuum deposition conditions, indicating its promising applications in OTFTs.

2 Experimental

2.1 General methods

All chemicals and solvents were obtained from commercial suppliers and used as received unless otherwise noted. ^{1}H NMR spectra were taken in $CDCl_3$ with TMS (δ 0.00 ppm) as internal standard at room temperature and were recorded on Bruker 400 NMR spectrometer. UV-vis spectra were obtained on a JASCO V-570 UV-vis spectrometer. Cyclic voltammetirc (CV) measurements were conducted using a CHI660C electrochemistry station with tetrabutlyammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte (0.001 M in dry CH_2Cl_2). The working, counter and reference electrodes were Glassy carbon, Pt wire and Ag/AgCl, respectively. Thermogravimetric analysis (TGA) was recorded on a PERKIN ELMER TGA7 apparatus with the scanning rate of 10 °C/min. X-Ray diffraction measurements were obtained in reflection mode at 40 kV and 200 mA with Cu Kα radiation using a 2-kW Rigaku D/max-2500 X-ray diffractometer. AFM images of films were obtained by using a Digital Instruments Nanoscope IIIa Multimode atomic force microscope in air.

2.2 Materials synthesis

*2-(2-thienyl)benzoic acid (**1**) [20, 21]*

A suspension of pthalic anhydride (20 g, 0.135 mol) in dry CH_2Cl_2 (200 mL) was stirred in the flask under nitrogen for 0.5 h, and then anhydrous $AlCl_3$ (37.8 g, 0.284 mol) was added slowly. The mixture was stirred for 0.5 h at room temperature and was treated drop wise with a solution of thiophene (12.5 g, 0.149 mol) in CH_2Cl_2 (100 mL) in 40 min. The mixture was stirred for 3 h at 30 °C. Standard workup yielded the 2-(2-thienyl)benzoic acid (compound **1**) as a white brown solid (24.7 g, 79%).

*3-(thiophen-2-yl)isobenzofuran-1(3H)-one (**2**) [22, 23]*

A hot solution (40 °C) of 2-(2-thenoylbenzoic acid) (11.0 g, 47.7 mmol) in aqueous sodium bicarbonate (5.9 g in 300 mL of H_2O) was treated with $NaBH_4$ (18.0 g, 474 mmol) in portions slowly. After standing overnight, it was heated to refluence for 1 h on the steam bath, cooled to room temperature, and then cautiously acidified with 12 wt% aqueous hydro chloric acid to pH ~2. The mixture was stirred for 2 h at room temperature, and the white solid was filtered to give compound **2** (8.2 g, 80%).

*1,3-di(thiophen-2-yl)isobenzo–furan (**3**) [24, 25]*

At –78 °C, 2-bromothiophene (3.42 g, 21 mmol) resolved in THF was stirred under nitrogen, butyllithium (2.5 M in *n*-hexane, 9.1 mL, 22.6 mmol) was added, when there was synthesized thiophen-2-yllithium solution after 1 h, it was treated with a solution of 3-(thiophen-2-yl)-isobenzofuran-1(3*H*)-one (**2**) (4.4 g, 20.4 mmol) in dry THF, keeping the temperature at –78 °C for 0.5 h until acetic anhydride was added, the temperature was raised to reflux the solution for 10 min, ending the reaction. The solution was extracted by CH_2Cl_2, combined the organic phase and dried by Na_2SO_4, then concentrated in vacuum. The residue was purified by column chromatography to give compound **3** as red solid (2.7 g, 47%).

6,11-di(thiophen-2-yl)tetracene-5,12-dione (DTTDO) [26, 27]

Compound **3** (2.82 g, 10 mmol) and 1,4-naphthaquinone (1.58 g, 10 mmol) were resolved in dry CH_2Cl_2 (50 mL) under nitrogen, then the solution was stirred overnight at room temperature, another 100 mL dry CH_2Cl_2 was added, cooling the solution to –78 °C and BBr_3 (2.88 g, 11.5 mmol) was added, after 0.5 h, solution was heated to reflux for 4 h, then cooling it to room temperature. The solution was dumped into water (250 mL) in beaker, extracted with CH_2Cl_2 combined organic phase and washed with saturation brine, concentrated in vacuum. The residue was purified by column chromatography to give compound DTTDO as yellow solid (1.77 g, 42%). mp 301 °C, ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) δ 8.11 (d, 2H), 7.83 (d, 2H), 7.70 (d, 2H), 7.61 (d, 4H), 7.30(d, 2H), 7.03 (m, 2H); MS (EI) *m/z*: 422 (M^+).

3 Results and discussion

3.1 Thermal, optical and electrochemical properties

The thermal, optical and electrochemical properties of compound DTTDO were measured by thermal gravimetric analysis (TGA), UV-vis spectrum, and cyclic voltammetry (CV). The TGA curve of DTTDO (Figure 1) measured with a heating rate of 10 °C/min under nitrogen demonstrated that this compound had a good thermal stability with the decomposition temperature of 310 °C which was near to

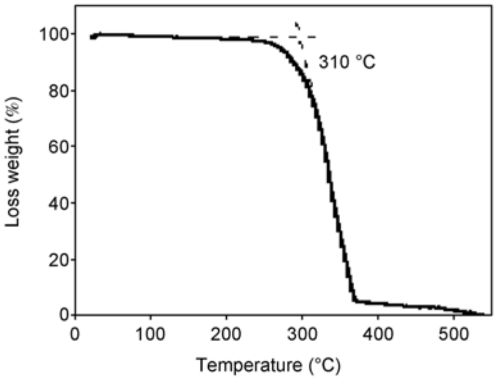

Figure 1 TGA curve of DTTDO with a heating rate of 10 °C/min under nitrogen.

that of rubrene (315–332 °C) [28, 29].

Figure 2 shows the absorption spectra of DTTDO in CH_2Cl_2 solution (10^{-5} M) and in thin film form (50 nm) vacuum deposited on quartz glass substrate. Compared the absorption spectra of DTTDO in thin film with that in solution, it is clearly noted that the maximum absorption in the longer wavelength was red shifted ~17 nm, from 395 to 412 nm, which was induced by the strong intermolecular interactions of DTTDO in the thin films. Additionally, the HOMO-LUMO energy gaps of DTTDO in solution estimated from the initial absorption was 2.90 eV, which was a little higher than the energy gaps (2.6 eV) of rubrene [6].

The cyclic voltammetry of compound DTTDO was performed in dry DMF solution with a concentration of 10^{-3} M (as shown in Figure 3), it is noted that the reduction curve of DTTDO is reversible. While the HOMO level of rubrene was –4.69 eV [6], the LUMO level of DTTDO estimated from cyclic voltammogram was –3.77 eV, combining the LUMO level and the energy band gap the HOMO could be calculated is –6.67 eV, which is much lower than that of rubrene though they have similar energy gaps, just as we can see from Figure 4.

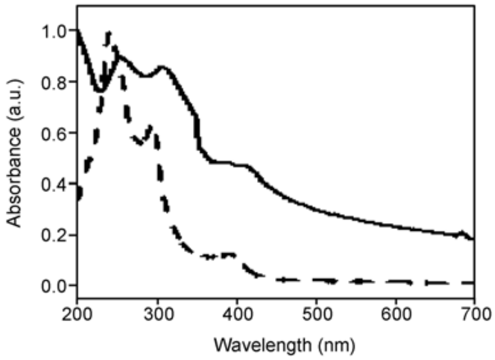

Figure 2 UV-vis spectra of DTTDO. The dashed line represents the solution spectrum with 10^{-5} M in CH_2Cl_2, and the solid line represents the thin film spectrum vacuum deposited on quartz glass.

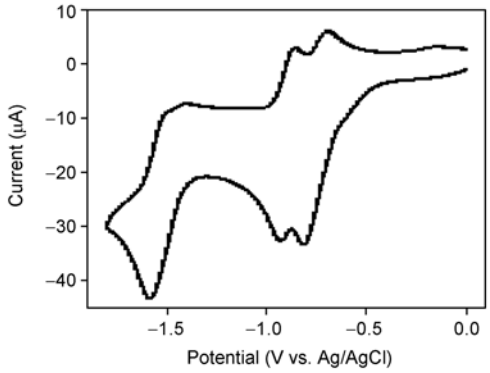

Figure 3 Cyclic voltammogram of DTTDO in DMF solution using Ag/AgCl as the reference electrode.

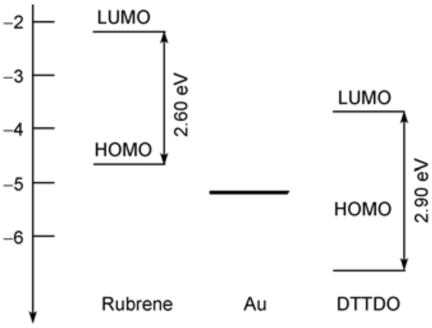

Figure 4 Energy level diagram among rubrene, Au and DTTDO.

3.2 Crystallographic analysis

Single-crystal X-ray crystallography was performed to examine the molecular packing and the intermolecular interactions of DTTDO molecules. The large single-crystals of compound DTTDO used for the single-crystal measurement were obtained from CH_2Cl_2 solution through slow evaporation at room temperature. Single-crystal X-ray diffraction patterns (XRD) of DTTDO crystals demonstrated that this compound crystallized in space group P-1 of triclinic system with unit-cell dimensions of a = 7.7731(16), b = 11.926(2), c = 12.758(3), α = 78.057(7), β = 87.724(9), γ = 76.074(8). As shown in Figure 5(c), in the DTTDO single crystal one unit cell consists of two CH_2Cl_2 solvent molecules and two DTTDO molecules, which further connect together with their neighbour molecules through the S··O interactions with distance of 3.23 Å. Different from the phenyl groups in rubrene, thiophene group has an asymmetric structure because of the presence of sulphur atom which results in two types of DTTDO molecular structure, *trans*- and *cis*-structure. Additionally, the thiophene planes are twisted strongly out of the backbone plane with an angle of approximate 88.8° and the carbonyl oxygen atoms are also out of the plane of tetracene backbone 9° (with ∠OCC angle of 171°, Figure 5(a)). The backbone exhibited a planar structure with very slightly twisted structure between the

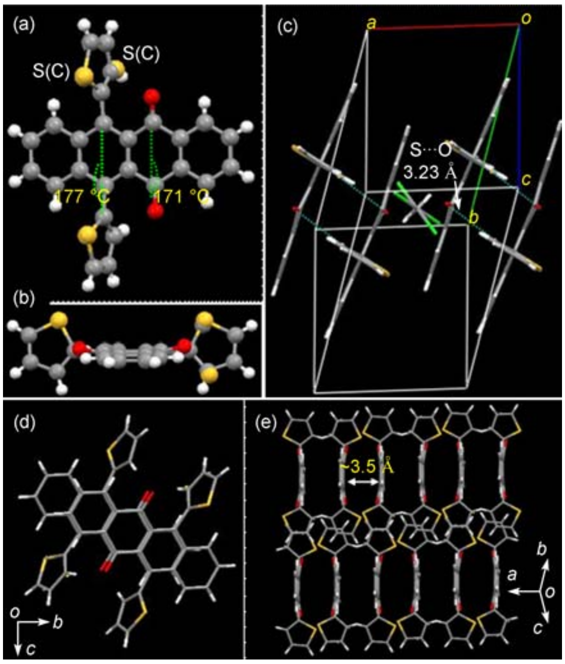

Figure 5 Molecular structure of DTTDO seeing along the (a) tetracene backbone plane and (b) long axis of tetracene backbone, (c) unit-cell of DTTDO single crystal and molecular packing motifs of DTTDO with view of (d) *bc* plane and (e) (011) plane.

end phenyl rings (Figure 5(c)). Interestingly, it is noted that DTTDO molecules in crystals exhibited typical lamellar packing motifs with one-dimensional π-π stacking (with distance of ~3.5 Å) along the a axis (as shown in Figure 5(d) and 5(e)) probably due to the reduced steric effect of thiophene and carbonyl substitutions compared to that of phenyls in rubrene [6].

3.3 Thin films of DTTDO

To examine the film-forming properties of DTTDO molecules, the morphologies of vacuum-deposited thin films both on the bare Si/SiO_2 substrates and on the octadecyltrichlorosilane (OTS) treated Si/SiO_2 substrates under different substrate temperatures were investigated by optical microscopy and atomic force microscopy (AFM). The microscopy images of DTTDO films (Figure 6) showed that at lower substrate temperature of 20 °C and 50 °C, good thin films of DTTDO semiconductor could be obtained on both Si/SiO_2 and OTS-modified substrates although there were still existing some large crystallize grains on bare Si/SiO_2 substrate at 20 °C. Figure 6(c) and 6(f) show the AFM images of DTTDO films on substrate at 20 °C. These results demonstrated that good thin films of DTTDO could be obtained on bare Si/SiO_2 substrates under vacuum deposition conditions (Figure 6(c)), which is different from rubrene thin films in which isolands form and isolated from each other by large areas of exposed SiO_2 [30]. So DTTDO is easier to get good thin films, maybe these are because of the polar of the compound, DTTDO is polar organic compound which was expected to form low-energy interfaces with SiO_2 substrate, while DTTDO and OTS, rubrene and SiO_2 were converse in polar, so the good thin films of DTTDO suggest its promising applications in OTFTs.

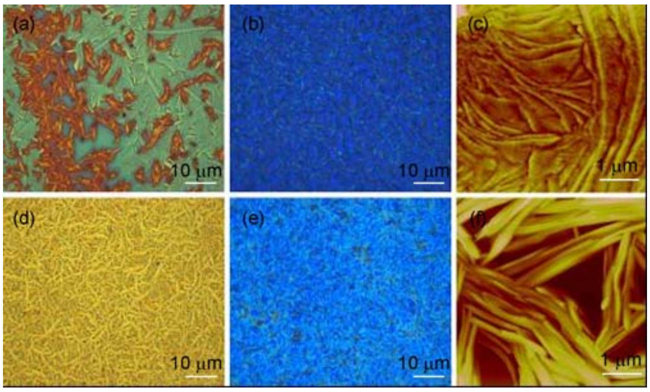

Figure 6 Optical microscopy images of DTTDO thin films vacuum-deposited on substrates at different temperatures: at (a) 20 °C, (b) 50 °C on bare Si/SiO_2 substrates and at (d) 20 °C, (e) 50 °C on OTS-treated Si/SiO_2 substrates. And AFM images of 100-nm-thick thin films at 20 °C, (c) on bare Si/SiO_2 substrate, and (f) on OTS treated Si/SiO_2 substrate.

4 Conclusions

A new semiconductor with thienyl groups and carbonyl groups on the backbone of tetracene was synthesized. Corresponding characterizations demonstrated that DTTDO compound exhibited good thermal and thin-film forming properties. Single crystal X-diffraction analysis indicated that DTTDO molecules in crystals exhibited typical lamellar packing motifs with one-dimensional π-π stacking (with distance of ~3.5 Å) along a axis. Good thin-film forming properties as well as the typical π-π stacking motifs of DTTDO molecules indicate its promising applications in organic thin-film transistors.

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