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Thermally Stable Organic Thin Film Transistors Based on 2-(anthracen-2-yl)tetracene

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ABSTACT: Organic semiconductors with high mobility and high thermal stability are of great importance for practical application of organic electronics. To explore new semiconductors by taking advantage of the intrinsic properties of tetracene molecule, herein, we report the design and synthesis of a novel p-type tetracene derivatives, 2-(anthracen-2-yl)tetracene (TetAnt). Top contact organic thin-film transistors (OTFTs) based on TetAnt show a hole mobility of up to 0.79 cm² V⁻¹ s⁻¹. In addition, a high mobility of $\sim 0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is maintained even after thermal stressed to a high temperature of 290 °C, indicating the excellent thermal stability of TetAnt.

Graphical abstract



1. Introduction

Organic thin film transistors (OTFTs) have drawn much attention due to their low cost, low-temperature fabrication, compatibility with flexible substrates, and the ability to fabricate large area devices. The performance of OTFTs has been continuously improved in recent years as a result of dedicated efforts [1-5]. Numerous researches have been devoted to develop high mobility organic semiconductors. Among them, organic semiconductors based on benzothieno [3,2-b] benzothiophene (BTBT) [6-8] and polyacene compounds [9] such as anthracene [10-14], tetracene [15-18] and pentacene [19-21] have been extensively investigated for p type organic semiconductor materials.

Extension of π -conjugation and introduction of alkyl chains are two important methods to tune the properties of organic semiconductors and boost the performance of resulting devices. Among the most widely studied acene based compounds, anthracene offers a wide band gap, high fluorescence quantum yield and high mobility. Moreover, anthracene is a typical p-type organic semiconductor with a low carbon to hydrogen ratio, a highly conjugated plane structure, good thermal stability. Aromatic hydrocarbons such as thiophene, phenyl, naphthalene, and bithiophene are typically introduced to connect with anthracene to expand the π -conjugated system and induce potential versatility. The introduction of an aromatic substituent at the 2-position [22, 23] or 2,6-position [24, 25] can effectively improve the degree of conjugation and planarity, thereby enhancing the device performance based on corresponding compounds. For acene based compounds, it is found that as the number of benzene ring repeating units increases, the highest occupied molecular orbital (HOMO) level energy increases, which is beneficial for efficient hole injection [26]. That is partly the

reason why the pentacene and its derivatives show better semiconducting properties, but their stability is inferior to tetracene and anthracene based counterparts [27]. Extensive efforts are also devoted to develop high mobility semiconductors based on tetracene core. For instance, Meng *et al* reported that the hole transport in OTFT devices can be improved by introduction of phenyl into tetracene, which results from the increased electronic coupling between two neighboring molecules. Two p-type tetracene derivatives, namely 2-(4-dodecyl-phenyl)-tetracene (C12-Ph-TET) and 2-phenyl-tetracene (Ph-TET) with hole mobilities of up to 1.80 cm² V⁻¹ s⁻¹ and 1.08 cm² V⁻¹ s⁻¹ were demonstrated, respectively, compared to only 0.12 cm² V⁻¹ s⁻¹ for tetracene [28].

Along with mobility, the device thermal stability is another concern for OTFTs, which is of vital importance for their practical application. The thermal stability of OTFTs is highly dependent on the thermal stability of the used organic semiconductors. There are a few reports on the thermal stability of OTFTs containing thermally stable organic semiconductors realized via oligomerization of appropriate aromatic units [25, 29-31]. For example, Yokota *et al* reported a highly thermally stable flexible OTFT based on a thermally stable organic semiconductor, DPh-DNTT, which maintains 80% its original mobility upon heating to 250 °C [30].

Based on the above studies, we expect that bonding anthracene and tetracene together may result in a high mobility and thermally stable p-type semiconductor material. Considering all these aspects, herein, we design and synthesize a new compound, namely 2-(anthracene-2-yl)tetracene (TetAnt). Its thermal, photochemical, electrochemical, and charge transport characteristics as well as consequent impact on the thermal stability of resulting OTFTs are systematically investigated. Modest

mobility approaching $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and high device thermal stability are demonstrated for the OTFTs based on TetAnt.

2. Results and discussion

2a. Synthesis

The synthetic route of TetAnt is depicted in Scheme 1. Phenylboronic acid and naphthalen-2-ylboronic acid were bought from Energy Chemistry. 2-bromoanthracene and 2-(anthracene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were synthesized according to literature [32], and the 2-bromo-tetracene was synthesized according to a delivered patent [33]. At last, TetAnt compound was obtained by Pd-mediated Suzuki coupling and pure compound was gained by vacuum sublimation. The chemical structure of TetAnt was confirmed by elemental analysis and mass spectrometry.



Scheme 1. Synthetic routes of compound TetAnt

2b. Thermal properties

The thermal properties of TetAnt were firstly examined by thermogravimetric analysis (TGA). The results are shown in Fig. 1. TGA was measured under N_2 atmosphere with a scanning rate of 10 °C/min. The decomposition temperature (temperature corresponding to a 5% weight loss) is determined to be 428 °C. Differential scanning calorimetry (DSC) analysis under N_2 showed a reversible

process of melting and recrystallization, but unfortunately no endothermic or exothermic peaks were found for TetAnt during scan between 25 °C and 380 °C even after several trials (not shown here). The TGA and DSC results indicate the excellent thermal stability of TetAnt, indicating that the introduction of tetraphenyl group improves the thermal stability.



Fig. 1. Thermogravimetric analysis of TetAnt.

2c. Photochemical and electrochemical properties

The photochemical and electrochemical properties of TetAnt were investigated by UV-Vis absorption spectroscopy and cyclic voltammetry (CV). The absorption spectra of TetAnt in 1, 2-dichlorobenzene solution and in thin film are shown in Fig. 2a. As seen from the figure, the absorption spectra of TetAnt in solution and in thin film have similar triple finger shape with the onset of 556 nm in solution and 566 nm in thin film, respectively. The redshift of 10 nm and an enhanced ratio of the first vibration peak intensity compared with the second one indicate clearly J-aggregation in the thin film. The absorption onset of 566 nm for TetAnt in thin film gives an estimated optical bandgap of 2.19 eV.

CV measurement of TetAnt thin film was performed to calculate its ionization potentials. Since the irreversible reduction behavior (Fig. 2b), only HOMO level could be estimated. According the onset of first oxidation potential of TetAnt, HOMO level is calculated to be -5.51 eV. Combined the values of optical band gap and the HOMO level, the LUMO level is calculated to be -3.32 eV for TetAnt. The introduction of tetraphenyl groups has undoubtedly narrowed the bandgap and raised the HOMO level.



Fig. 2. (a) Normalized UV-vis absorption spectra of TetAnt in solution and thin film; (b) CV curves of TetAnt. The oxidation potential is obtained at the onset of the cyclic voltammogram.

2d. Single crystal structure and calculated mobility

High quality single crystals of TetAnt were grown by physical vapor transport method for single crystal structure analysis. The single crystal structure of TetAnt was determined by X-ray diffraction. X-ray crystallographic results (CCDC 1982781) reveal that TetAnt crystals belong to P1 space group with crystal parameters of a= 5.9760(2) Å, b= 7.4945(2) Å, c= 21.8325(7) Å and α = $83.770(3)^{\circ}$, β = $89.241(3)^{\circ}$, γ = $89.720(3)^{\circ}$. The molecular length of TetAnt is 20.495 Å (Fig. 3a). The torsion angle between the central anthracene and tetracene rings is below 1°. The TetAnt molecules adopt a typical arrangement of herringbone packing (Fig. 3b). Moreover, several C-H- π interactions with distance ranging from 2.963 Å to 3.152 Å are

observed between each TetAnt molecule and its nearest six neighbor molecules (Fig. 3c). High charge carrier mobility is expected from such a dense packing structure. So, we calculated the mobility of TetAnt using Gaussian 09 D01 version software, with B3LYP(D3) functional and 6-311G(d, p)² basis set, based on the single crystal structure. When one TetAnt molecule is chosen as the center, the charge transfer integrals for the surrounding six molecules are between 34.21 meV and 68.26 meV (Fig. 3b). In addition, the reorganization energy of TetAnt is 92.7 meV. The calculated hole mobility of TetAnt is $1.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, much higher than that of 2-anthryl-2-anthracence (2Ant, 0.52 cm² V⁻¹ s⁻¹) as listed in Table S1 [34].



Fig. 3. (a) Molecular length of TetAnt, (b) herringbone packing and (c) short contacts in TetAnt.2e. Charge transport properties

We fabricated bottom-gate top-contact OTFT devices based on TetAnt by thermal evaporation under N_2 to evaluate their charge transport properties. Different substrate temperatures (T_{sub}) were chosen to optimize the device performance. The fabrication and characterization details are descripted in the Experiment part. The device parameters, including mobility (μ), threshold voltage (V_{TH}), and the on/off current ratio (I_{on}/I_{off}) are summarized in Table 1. Representative transfer and output curves are shown in Fig. 4.

T_{sub} (°C)	$\mu_{h,max}(cm^2V^{\!-\!1}s^{\!-\!1})$	$\mu_{h,ave}(cm^2V^{\!-\!1}s^{\!-\!1})$	$\mathbf{I_{on}}/\mathbf{I_{off}}$	$V_{\text{TH}}(V)$
30	0.04	$(3.18 \pm 0.76) imes 10^{-2}$	$(1.95 \pm 0.81) imes 10^5$	-18.4 ± 1.2
60	0.07	$(5.69 \pm 0.97) imes 10^{-2}$	$(6.20 \pm 2.28) imes 10^5$	-18.8 \pm 1.6
90	0.11	$(8.27 \pm 1.54) imes 10^{-2}$	$(4.60 \pm 3.14) imes 10^5$	$\textbf{-15.5}\pm\textbf{3.8}$
120	0.79	$(5.92 \pm 1.02) imes 10^{-1}$	$(3.02 \pm 1.35) imes 10^{6}$	-21.6 \pm 1.5
150	0.19	$(1.69 \pm 0.15) imes 10^{-1}$	$(3.65 \pm 0.97) imes 10^5$	-12.2 ± 2.2

Table 1. Performance of OTFTs based on TetAnt deposited at different substrate temperatures.

Typical p-type transport properties are observed for all devices. As seen from Table 1, increasing the substrate temperature helps a lot to improve the device performance, with the mobility increases by twenty times from T_{sub} of 30 °C to T_{sub} of 120 °C (the highest value ~0.8 cm² V⁻¹ s⁻¹). A modest mobility value higher than 0.15 cm² V⁻¹ s⁻¹ even maintains at T_{sub} of 150 °C. The saturation current increases with the mobility as evidenced by the transfer and output curves shown in Fig. 4. Negative differential resistance are observed in the saturation part of some output curves, which probably results from hole traps induced by penetration of moisture to the conducting channel during measurement. The on/off is high than 10⁵ for all devices thanks to the suppression of the off current. However, the threshold voltages are not satisfactory, which probably due to the mismatch of the HOMO level of TetAnt (-5.51 eV) with the work function of gold (5.1 eV).



Fig. 4. (a-e) Representative transfer curves of TetAnt OTFTs deposited at 30 °C, 60 °C, 90 °C, 120 °C, 150 °C, respectively; (f-j) corresponding output curves.

2f. Morphological characterization

To understand the relationship between the device performance and the morphology, atomic force microscope (AFM) and X-ray diffraction (XRD) were performed to analyze TetAnt thin films with a thickness of ~40 nm deposited on the octyltrichlorosilane (OTS)-treated n⁺-Si/SiO₂ substrate at different substrate temperatures. The AFM images as shown in Fig. 5 reveal that the grain size increases with the substrate temperature. Thin films deposited at T_{sub} of 120 °C (Fig. 5d) show obviously larger grains ($\sim 1 \mu m$) than those deposited at lower substrate temperature. Noncontinuity and large surface roughness (RMS = 35.5nm) are observed for T_{sub} of 150 °C which severely degrade the device performance. The AFM results indicate that increasing the substrate temperature is beneficial for the surface morphology and grain size of TetAnt thin films, which is consistent with the device performance. However, the grain sizes is not large enough compared to BTBT derivatives. And large surface roughnesses are observed in all TetAnt thin films, which should be the main reasons for the relative low mobility of TetAnt based OTFTs. Since the initial growth mode of the first several layers are important for the charge transport of OTFTs, we also measured the AFM images of TetAnt layer with a thickness of ~3 nm deposited at T_{sub} of 30 °C and 120 °C. The AFM images and the cross-section profiles imply a layer by layer growth mode, but the high density of nuclei limits the size of grains [35].



Fig. 5. (a~e) AFM height images of thin films ($5\mu m \times 5\mu m$) of TetAnt deposited on OTS-treated Si/SiO₂ substrates at different substrate temperature.

Thin films of TetAnt with a thickness of ~40 nm were further investigated by XRD to reveal their crystallinity and molecular orientations. As shown in Fig. 6, high order reflection peaks assignable to (001) are observed for all TetAnt thin films. The d spacing value is ~2.22 nm, which is consistent with the molecular length of TetAnt and c value of the single crystal parameters. This indicates an edge-on structure on the substrate, which is beneficial for carrier transport. Furthermore, the position of reflection peaks does not change much when the substrate temperature increases, implying that increasing the substrate temperature does not severely change the molecular packing. The intensity of diffraction peaks in XRD patterns of different substrate temperatures increases with the substrate temperature below 120 °C, indicating an improvement in crystallinity. Both AFM and XRD results justify that increasing the substrate temperature is beneficial for OTFT devices based on TetAnt thin films.



Fig. 6. XRD patterns of TetAnt thin films deposited at different substrate temperatures.

2g. Thermal stability of OTFT devices.

We have performed thermal stress test using devices of TetAnt ($T_{sub} = 120$ °C) to evaluate the device thermal stability. The device was put on the heater all the time during the measurement in air with a temperature increasing rate of 20 °C/min. Transfer curves were taken *in situ* 2min after the corresponding temperature was reached. For organic semiconductors, prolonged heating, especially heating above the glass transition temperature or the melting point, usually leads to morphology changes and device performance degradation. According to TGA and DSC, TetAnt compound has good thermal stability. Good thermal stability is also expected for its OTFT devices. As shown in Fig. 7a, device based on TetAnt maintains half of its initial value even at a high temperature of 290 °C, though it shows a decrease tendency as a function of the temperature. Transfer curves shift to positive direction as shown in Fig. 7b. Devices show no performance when the temperature is higher than 290 °C due to the serious channel damage caused by continuous annealing (Fig. S2).



Fig. 7. (a) Mobility of OTFT devices based on TetAnt in situ measured at different temperatures; (b) Transfer curves of TetAnt based OTFTs in situ measured at different temperatures.

3. Conclusion

To conclude, we have designed and synthesized a novel p-channel tetracene derivative, TetAnt. Increasing the substrate temperature is beneficial for OTFTs based on TetAnt and a high hole mobility up to $0.79 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is demonstrated at T_{sub} of 120 °C. Moreover, OTFTs based on TetAnt show high thermal stability up to 290 °C. Our results here indicate TetAnt is a promising candidate for practical applications in future organic electronics.

4. Experimental section

4a. Synthesis and characterization

2-Bromoanthraquinone [32] In a 250 ml round-bottomed flask, anhydrous acetonitrile (75 mL), copper (II) bromide (15.00 g, 67.1 mmol), isoamyl nitrite (9 mL, 67.1 mmol) were added at 0 °C and stirred for 20 minutes. Then the mixture was warmed to RT and stirred for one hour. And then cooled to 0 °C, 2-aminoanthraquinone (7.5 g, 33.5 mmol) dissolved in THF (100 mL) was added quickly to the resulting solution and the mixture was stirred at 0 °C for 2 h. After the reaction was completed, the solvents were removed by rotary evaporation and dark

brown solid was obtained and then was purified using column chromatography to obtain 2-bromoanthraquinone as a yellow solid (yield: 30%, 3.00 g).

2-Bromoanthracene A part NaBH₄ (4.69 g, 123.9 mmol) was added to a solution of 2-bromoanthraquinone (5.95 g, 20.72 mmol) in a mixed solvent of isopropanol and THF (1: 1, 150 mL) at 0 °C and the mixture was stirred for 3 hours. Then the mixture was warmed to RT and another NaBH₄ (2.34 g, 62.3 mmol) was added. The mixture was stirred at RT overnight, and then DI water (7 mL) was added. The resulting mixture was stirred for another 12 hours. After the solvents were removed under reduced pressure, HCl (3M) was slowly added the obtained residue until foaming ceased. The resulting solution was stirred under reflux for 6 hours. The resulting suspension was filtered, and the residue was purified using column chromatography to obtain the title compound (yield: 21%, 1.5 g).

2-(Anthracene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane A 500 mL round bottom flask was charged with (12.10 g, 36 mmol) 2-dibromoanthracene, (10.98 g, 43.2 mmol) bis(pinacolato)diboron, (7.21 g, 73.2 mol) potassium acetate and 2% mol [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II); complex with dichloromethane. Then 250 mL dimethyl sulfoxide was added to the mixture and the suspension was purged with nitrogen for 15 minutes. The resulting mixture was stirred at 95 °C for 12 hours. The mixture was extracted with dichoromethane and the organic layer was dried with anhydrous MgSO₄ after poured into 500 mL ice water. The residue obtained by evaporated the solvent was purified by column chromatography to give bright yellow solid. (yield: 50%, 9.76 g).

4-Bromo-1,2-bis(dibromomethyl)benzene Under UV light, bromine (2.73 mL, 53 mol) was slowly added to 4-bromo-*o*-xylene (2.50 g, 9.0 mol) which was dissolved in

30 mL CCl₄ in a two-necked round bottom flask. Then the reaction mixture was stirred at RT for one hour. After the reaction was completed, the reaction mixture was washed with water and concentrated under reduced pressure. The precipitate was filtered off and washed with hexane and get a white solid after dried in a vacuum drying box (2.68 g, 56%)

8-Bromotetracene-5,12-dione [33] In a 500 ml round bottom flask, 4-bromo-1,2-bis-dibromomethylbenzene (10.00 g, 20 mol), 1,4-naphthoquinone (3.15g, 20 mol), and NaI (34.40 g, 230 mmol) in 150 ml DMAc were added. The mixture was refluxed overnight. After cooling down, the reaction mixture was poured into 250 ml water. The precipitate was filtered off and washed with MeOH twice and then purified by vacuum sublimation to give the pure product as a yellow solid (1.80 g, 26%)

2-Bromotetracene Al wire (6.57 g, 240 mmol), HgCl₂ (0.13 g, 480 mmol), cyclohexanol (150 ml) and CBr₄ (0.64 g, 1.90 mmol) were added into a 300 ml flask. The mixture was purged with nitrogen for 15 minutes. The reaction was initiated by heating and when the reaction is too intense, one can cool it to slow down the reaction, Then and then completed refluxing 4 added after for hours. 8-bromo-naphthacene-5,12-dione (9.54 g, 24 mmol) into the mixture and was refluxed for 2 days. After cooling down the mixture was poured into MeOH/H₂O/conc. HCl solution (1/1/1, 400 ml). The precipitate was filtered off and washed with MeOH/H₂O/conc. HCl and methanol. The crude product was purified by vacuum sublimation to give pure product as an orange solid. (6.78 g, 78%)

2-(Anthracene-2-yl)tetracene Refer to the synthesis steps of 2,2'-bianthracene, Yield: 40%. Because of the low solubility in solvent, the NMR was not measured. HRMS.

(MALDI) m/z: calcd for $C_{32}H_{20}$ [M⁺H]⁺ 404.51, found 404.6796. Anal. Calcd for $C_{32}H_{20}$; C, 95.05; H, 4.95;. Found C, 93.04; H, 5.41.

4b. General procedures and experimental details

Fabrication and characterization of OTFT devices. Organic thin film transistors were fabricated based on n^+ -Si/SiO₂ (300nm) substrate with a top-contact structure. The substrates were firstly ultrasonically washed with acetone, deionized water and isopropanol for 15min, sequentially. After dried with N₂ flow, the substrates were exposed to UV/Ozone treatment for 15min and then treated with OTS in N_2 golvebox. For OTS treatment, the substrates were immersed in the OTS solution (25mg/mL in toluene) for one and a half hours at 60 °C, and then washed with pure toluene. Organic semiconductor layer (~40 nm) was deposited on the OTS treated n⁺-Si /SiO₂ substrates by thermal evaporation in high vacuum at various substrate temperatures, and then the gold source and drain (~40 nm) were thermally deposited on the organic semiconductor layer under a pressure of about 6×10^{-5} Pa through shadow masks. The channel width to length ratio is 10. The electrical characterization of the OTFTs was performed by Keysight B1500A parameter analyzer on a probe station in ambient air. The hole mobility was extracted from the equation (V_{DS} = -40V), I_{DS} = (W/2L) μ C_i $\left(V_{GS}-V_{TH}\right)^2$, where I_{DS} is the source-drain current, W is the channel width and L is the channel length, C_i is the capacitance per unit area of the SiO₂ gate dielectric (1.12×10^{-4}) F/m^2), V_{GS} is the gate voltage and V_{TH} is threshold voltage.

Cyclic voltammetry TetAnt thin films were deposited onto platinum electrode by thermal evaporation. To detect the HOMO and LUMO levels, $0.1 \text{ mol } L^{-1}$

tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) anhydrous acetonitrile (CH_3CN) solution was prepared. The CV data were acquired using Ag/Ag^+ as the reference electrode (+0.08 V vs. Ag/Ag^+ nonaqueous reference electrode) at a scan rate of 100 mV s⁻¹ under nitrogen atmosphere. The Ag/Ag^+ electrode was prepared by soaking Ag wire into a 0.01 mol L⁻¹ AgNO₃ solution in dry CH_3CN and 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu_4NPF_6).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at XXX.

Notes

The authors declare no competing financial interest.

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Highlights:

- A high hole mobility of $1.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is calculated and hole mobility up to 0.79 cm² V⁻¹ s⁻¹ is demonstrated experimentally for TetAnt.
- Thin film morphology and performance of organic transistors based on TetAnt are very sensitive to the substrate temperature.
- Half of the original mobility is maintained even after thermal stressed up to 290 .

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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