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ARTICLE TYPE

High-Performance n-Channel Field Effect Transistors Based on Solution-Processed Dicyanomethylene-Substituted Tetrathienoquinoid

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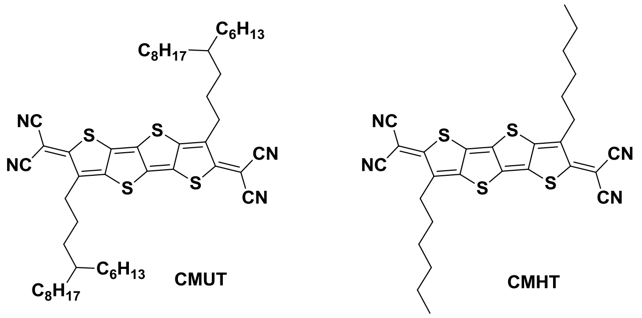
Abstract

Solution-processable tetrathienoquinoidal semiconductor **CMHT** was synthesized and characterized. Single crystal diffraction result showed **CMHT** adopted slipped π-π stacking in the crystal. Multiple intermolecular interactions, such as S···N and S···C (the carbon on the cyano group), were existed among neighbor molecules, which formed a 2-dimensional charge transport network. Solution processed thin film transistors of **CMHT** displayed high electron mobility up to 0.22 $cm^2V^{-1}s^{-1}$ in ambient condition, one of the highest electron mobility for quninoidal semiconductors. The correlation between the molecular packing of **CMHT** and the transistor performance was studied by AFM and XRD.

Introduction

N-channel organic semiconductors have attracted great attentions because of their wide applications in organic logic circuits, ambipolar transistors and p-n junctions.[1-6] Currently, the development of high performance n-channel organic semiconductors is largely lagged behind that of their p-channel counterparts,[7-12] because of the difficulty to design and synthesize strong electron withdrawing units[13-15] and the low stability of the charge carriers of n-channel organic semiconductors (electrons) to water and oxygen trapping.[16] Till now, the lack of solution processable, ambient stable and high performance n-channel organic semiconductors has become one of the bottlenecks of organic thin film transistors (OTFTs),[17] hence it is important and needed to design and synthesize solution processable high performance n-channel organic semiconductors with ambient stability.[18, 19]



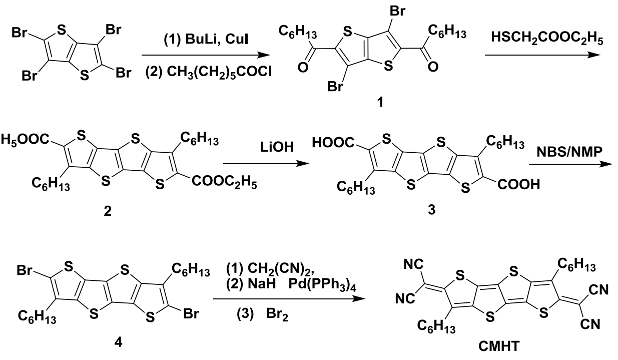
Scheme 1. The chemical structures of **CMUT** and **CMHT**.

Dicyanomethylene-substitutedquinoidal compounds have low LUMO energy levels (< -4.0 eV) and are good candidates for ambient stable n-channel organic semiconductors.[20-23] Recently, we reported a dicyanomethylene-substitutedtetrathienoquinoid semiconductor **CMUT** (chemical structure see scheme 1).[24] This compound displayed one of the highest mobility reported for solution processable and ambient stable n-channel organic semiconductors, suggesting the potential applications of tetrathienoquinoid as high performance n-channel organic semiconductors. To explore the molecular packing - property relationship of tetrathienoquinoid will help us to understand their high performance and further enlighten the design of new high performance materials. However, due to the long and branched alkyl chains, the attempts to obtain the single crystal and the detail packing behaviour of **CMUT** in thin film were failed, which hindered the understanding of the correlation between molecular packing of tetrathienoquinoid and charge transport properties. With the aim to solve the above puzzles and further investigate the applications of tetrathienoquinoid organic semiconductors in organic transistors, herein dicyanomethylene-substitutedtetrathienoquinoid with hexyl substituents (**CMHT**, chemical structure see Scheme 1) was design and synthesized. Solution processed TFT based on **CMHT** displayed high electron mobility up to 0.22 $cm^2V^{-1}s^{-1}$ in ambient conditions. The molecular packing pattern of CMHT in crystals and thin films, and its correlation to device performance were thoroughly studied.

Experimental section

Synthesis and Characterizations

General: All chemicals and solvents were commercial available and used directly. 2,3,5,6-tetrabromothieno[3,2-b]thiophene was synthesized according to the reported procedure.[25] ^1H NMR (300 MHz) and ^{13}C NMR (100 MHz) spectra were obtained in $CDCl_3$ on varian Mercury (300 MHz or 400 MHz) instrument with TMS as internal reference. Mass spectra (EI-MS) were performed on a Shimadzu Qp-5050A Spectrometer using an electron impact ionization procedure (70eV), and MALDI-TOF spectra were carried out on a Voyager-DE STR Mass Spectrometer. Elemental analyses were conducted on an Elementary Vario EL III element analyzer. The out-of-plane X-ray diffraction (XRD) patterns were recorded on a 2-kW Rigaku X-ray diffraction system with Cu Ka radiation (λ = 1.54 Å). The atomic force microscopy (AFM) measurements were carried out on a Nanoscope IIIa atomic force microscopy in tapping mode.



Scheme 2. The synthetic route of **CMHT**.

2,4-di(1,1’-heptanone)-3,6-dibromothieno[3,2-b]thiophene (1)

To a mixture of 2,3,5,6-tetrabromothieno[3,2-b]thiophene(2.28 g, 5 mmol) in 50 mL dry THF, n-butyl lithium (4.2 mL, 2.5 M in hexane) was added dropwise at -78 ^{o}C and the resulting mixture was stirred another 2 hours. CuI (1.89 g, 10 mmol) was added and then the temperature was allowed to increase to -23 ^{o}C. The mixture was stirred for another 2 hours before recooled to -78 ^{o}C and then heptanoyl chloride (1.49 g, 10 mmol) was added quickly. The final mixture was allowed to warm to room temperature and was stirred for 2 hours. This reaction then was quenched with 20 mL water and extracted with ethyl acetate. The combined extracts were dried over anhydrous $MgSO_4$, filtered and distillation of solvent under reduced pressure to give the crude products, which was crystallized from ethanol and filtered to afford compound **1** (1.49 g, 57%). M. p., 160-161 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 6H), 1.29−1.46 (m, 12H), 1.72−1.82 (m, 4H), 3.08 (t, 4H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 14.18, 22.64, 24.10, 28.99, 31.75, 41.65, 106.55, 143.55, 143.43, 193.05; MS (EI) m/z =382 (M^+-2C_5H_{10}); Anal. Calcd for $C_{20}H_{26}O_2S_2$: C, 45.99; H, 5.02%; Found: C, 46.20; H, 4.82%.

2,6,-Dicarboethoxy-3,7-dihexylthieno[3,2-b]thieno[2’,3’:4,5]thieno[2,3-d]thiophe-ne(2)

Compound **1** (1.99 g, 3.82 mmol) was mixed with K_2CO_3 (3.16 g, 138 mmol) and DMF (20 mL). To this mixture, ethyl mercaptoacetate (1.10 g, 9.17 mmol) was added dropwise. The reaction mixture was stirred for 20 hours at 60 ^{o}C, and then poured into water(50 mL). The solid collected by filtration was flash chromatographed on silica. Light petroleum-dichloromethane (ratio 5:1) eluted compound **2** **(**1.36 g, 63 %). M. p., 173 – 174 ^{o}C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.89(t, 6H), 1.31-1.44 (m, 18H), 1.71-1.76 (m, 4H), 3.14 (t, 4H); 4.38 (q, 4H);^{13}C NMR (100 MHz, $CDCl_3$)δ 14.08, 14.33, 22.59, 29.18, 29.31, 29.40, 31.60, 61.10, 127.33, 133.61, 134.52, 143.43, 144.24, 162.49; MS (EI) m/z = 564 (M+); Anal. Calcd for $C_{28}H_{36}O_4S_4$: C, 59.54; H, 6.42%; Found: C, 59.85; H, 6.43%.

3,7-dihexylthieno[3,2-b]thieno[2’,3’:4,5]thieno[2,3-d]thiophene 2,6,-dicarboxylateacid (3)

To the mixture of THF (18 mL), methanol (3 mL), water (2 mL) and LiOH-H_2O (2.10 g, 50 mmol), compound **2** (1.13 g, 2 mmol) and a catalytic amount of tetrabutylammoniumiodide were added. The mixture was refluxed overnight. Solvent was evaporated and the residue was acidified with concentrated HCl to pH=2. The solid was filtered and washed with water three times. The solid was dried to give compound **3** (1.0 g, 98%).M. p., 320-321^{o}C; ^{1}H NMR (300 MHz, DMSO-D6) δ 0.85 (t, 6H), 1.26-1.36 (m, 12H), 1.63−1.70 (m, 4H), 3.11 (t, 4H), 13.38 (b, 2H);MS (MALDI-TOF) m/z = 509.4 (M^++H).

2,6,-Dibromo-3,7-dihexylthieno[3,2-b]thieno[2’,3’:4,5]thieno[2,3-d]thiophene (4)

The compound **3** (0.51 g, 1.0 mmol) and NBS (0.53 g, 3 mmol) were added to the mixture of NMP (15 mL) and water (0.75 mL). This mixture was stirred over night under nitrogen at room temperature. The mixture then was added water (40 mL) and extracted with light petroleum. The combined extracts were dried over anhydrous $MgSO_4$ and filtered. Distillation of solvent under reduced pressure gave the crude product, which was flash chromatographed on silica. Light petroleum eluted compound **4** (0.46 g, 79 %). M. p., 193 - 194^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 6H), 1.30−1.38 (m, 12H), 1.69−1.74 (m, 4H), 2.74 (t, 4H);MS (EI) m/z = 578 (M^+); Anal. Calcd for $C_{22}H_{26}Br_2S_4$: C, 45.68; H, 4.53%; Found: C, 45.91; H, 4.75%.

2,6,-bis(dicyanomethylene)-3,7-dihexylthieno[3,2-b]thieno[2’,3’:4,5]thieno[2,3-d]-thiophene (CMHT)

CMHT was synthesized according to the reported procedure[23, 24] in the yield of 73 %.M. p., 267 - 268^{o}C. The ^{1}H-NMR and ^{13}C-NMR of **CMUT** are not obtained because of its poor solubility. MS (MALDI-TOF) m/z = 547.44 (M^++H); Anal. Calcd for $C_{28}H_{26}N_4S_4$: C, 61.50; H, 4.79; N, 10.25%; Found: C, 61.74; H, 4.62; N, 10.17%.

Device Fabrication and Characterization

The Si/SiO_2 substrates were cleaned and modified with octadecyltrichlorosilane (OTS) according to the previously reported procedures.[26, 27]The devices were fabricated with a top-contact bottom-gate configuration. The gate electrode and gate dielectric layer were n-type heavily doped Si and a thermally grown SiO_2 layer of 300 nm (the specific capacitance was measured to be 10 nF.cm^{-2}), respectively. Thin films of **CMHT** were prepared by drop casting of 1 mg/mL o-dichlorobenzene solution on octadecyltrichlorosilane (OTS) - treated SiO2/Si wafers at 150^{o}C. The Au source and drain electrodes were deposited by vacuum evaporation through a shadow mask, which results in a channel length of 31 μm and a width of 273 μm. A Keithley 4200 semiconductor parameter analyzer were used to measure the electrical properties of the devices at room temperature in ambient condition. The field-effect mobility of electrons (μ_e)and the threshold voltage (V_{TH}) were calculated from saturation region, according to the expression $I_{DS}=(W/2L)\mu_e C_i(V_G-V_{TH})^2$($I_{DS,}$ drain-source current; W, channel width; L, channel length; C_i, capacitance per unit area of the gate

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dielectric layer; V_{TH}, threshold voltage).

Results and discussion

The synthetic route of **CMHT** was illustrated in Scheme 2. Starting from 2,3,5,6-tetrabromothieno[3,2-b]thiophene, compound **1** was obtained through a lithium reaction in a moderate yield (57%). Compound **1** reacted with ethyl mercaptoacetate in the presence of base to give thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-b]thiophene diethyl ester **2** with a yield of 63%. Basic hydrolysis of **2**, followed by acidification with HCl, afforded compound **3** in high yield (98%). Compound **3** was decarboxylized and brominated with NBS/NMP in high temperature to give **4**. The target compound **CMHT** was synthesized by reacting **4** with malononitrile through a Pd-catalyzed Takahashi coupling reaction, followed by oxidation with bromine. Comparing with **CMUT**, the solubility of **CMHT** decreased dramatically in common organic solvents such as dichloromethane, chloroform, chlorobenzene and dichlorobenzene (less than 0.5 mg/mL), which was ascribed to the replacement of the long and branched 3-hexylundecyl substituents with hexyl chains.

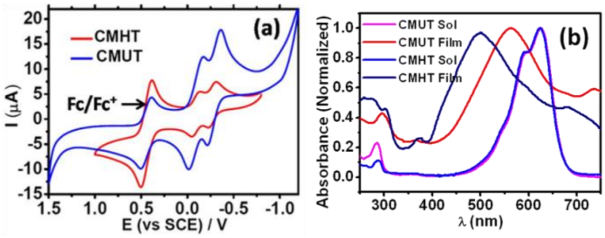

Figure 1. (a) Cyclic voltammograms of **CMHT** and **CMUT** (10^{-3} mol/L) with 0.1 mol/L Bu_4NPF_6 as electrolyte in CH_2Cl_2 solutions under scan rate of 50 mV/s^{-1} (Ferrocene was used as internal standard); (b) UV-vis absorption spectra of **CMHT** and **CMUT** in dichloromethane solution (1×10^{-3} mol/L) and on quartz substrate (as deposited thin-film).

The combined solution cyclic voltammograms (CV) of **CMHT** and **CMUT** (0.001mol/L) in CH_2Cl_2 were shown in Figure 1a. The much weaker wave peaks of **CMHT** than that of **CMUT** was due to its bad solubility. Similar as that of **CMUT**, **CMHT** displayed two reversible reduction peaks. The first half-wave potential ($E^{1/2}_1$) was at - 0.10 V and the corresponding LUMO energy level calculated from CV was -4.3 eV (same as that of **CMUT**), suggesting the difference of alkyl chains did not affect their LUMO energy levels. Figure 1b illustrated the absorption spectra of **CMHT** and **CMUT** in solution and on the films. They showed the same absorption spectra in CH_2Cl_2 solution, and the optical energy gaps (E_g^{opt}) estimated from the onset of the absorption in solution was 1.8 eV. The film of **CMHT**, prepared by dropping a hot o-dichlorobenzene solution (1 mg/mL) to the quartz substrate at 150 ℃, exhibited a strong absorption band at λ_{max} = 498 nm, a blue shift as large as 127 nm to that of solution. This blue shift is the largest one observed in the thienoquinoid compounds and more than two times larger than that of **CMUT** (60 nm), indicating that minimizing steric bulkiness is an effective way to enhance the intermolecular interaction. Similar as **CMUT**, **CMHT** displayed a shoulder absorption at 685 nm, which was a typical Davydow splitting and suggested **CMHT** adopted H-type aggregation in the thin films.

To investigate the charge transport properties of **CMHT**, the foremost task is to prepare its large-scale thin films on the substrates. As the solubility of **CMHT** is very low in organic solvents at room temperature, the film was solution processed at high temperature which can dramatically increase the solubility. The SiO_2/Si wafers were treated with octadecyltrichlorosilane (OTS) to avoid the electron trapping by hydroxyl groups of SiO_2 surface. Drop-casting s solution of **CMHT** in o-dichlorobenzene was on OTS-treated SiO_2/Si substrate at 150 ℃, large-scale thin films were successfully prepared. Varying the concentration in the range of 0.1 to 1 mg/mL did not change the molecular packing in the films as they displayed the same family Bragg reflections.

The transistors with a bottom-gate, top-contact configuration were fabricated and tested in ambient condition. The fabrication and testing details were described in experimental section. The devices showed typical n-channel characteristics and the corresponding output and transfer curves were illustrated at Figure 2. The electron mobility was in the range of 0.08~0.22 $cm^2V^{-1}s^{-1}$ and the current on/off ratio was about 1×10^4.

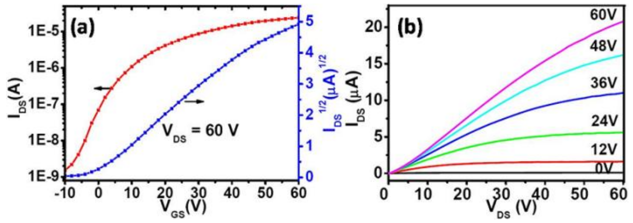

Figure 2. The thin film transistor characteristics of **CMHT**. (a) transfer and (b) output curves.

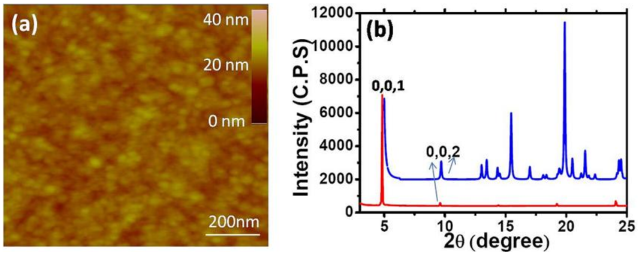

Figure 3. (a) AFM images (1×1 μm) of drop-casted thin film of **CMHT**; (b) The XRD pattern of drop-casted thin films (the red line), which fit well with the simulated powder pattern from bulk single crystal of **CMHT** (the blue line).

The thin-film microstructures and morphologies, which strongly affected the transistors' performance, were investigated by atomic force microscopy (AFM) and X-ray diffraction (XRD)

(Figure 3). XRD result showed, similar as that of **CMUT**, the **CMHT** thin films exhibited high crystalline, indicated by the multiple single family Bragg reflections up to the fifth progression. The lattice d-spacing of **CMHT** thin films estimated from the diffraction peaks was 18.46 Å. AFM image revealed clearly grain boundaries were existed in **CMHT** films, and the size of the grain was several nanometers. The smaller grain size as well as more and larger grain boundaries between source and drain electrodes exert negative effect on the transistor performance of **CMHT**. Even though, the mobility of 0.22 cm^2/Vs is still one of the highest performance for TFT devices based on thiophenequinoidal compounds.

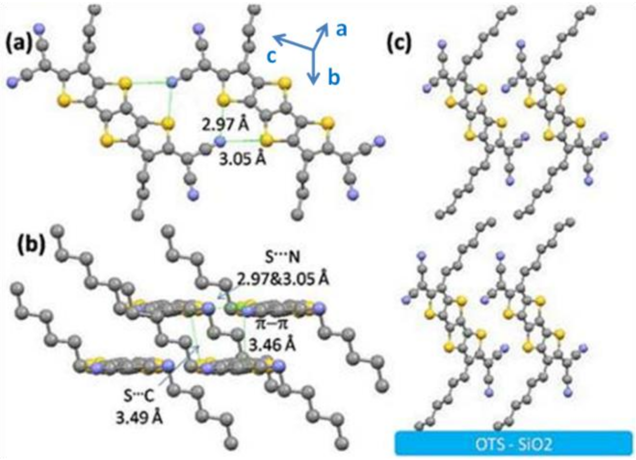

Figure 4. (a) Intermolecular non-bonded contacts (S···N) between the conjugated cores (The sulfur, nitrogen and carbon atoms are marked with color of yellow, blue and grey, respectively); (b) The π–π stacking of conjugated backbone and the intermolecular non-bonded contacts (S···N and C···S) among the conjugated cores; (c) The proposed packing pattern of **CMHT** on OTS-SiO_2 substrate in the thin films.

With the aim to deeply understand the high performance of tetrathienoquinoid compounds, the molecular packing pattern of **CMHT** was studied by single crystal. Single crystals of **CMHT** were grown by recrystallization in a hot o-dichlorobenzene solution. The crystal structure belonged to triclinic space group with a = 5.2700(8) Å, b = 7.2800(11) Å, c = 18.461(3) Å, α = 92.723(2)°, β = 96.980(3) ° and γ = 110.788(3) °. The conjugation core of **CMHT** exhibited planar structure and the hexyl substituents were turned out of the plane, affording a chair-like configuration in the crystals. **CMHT** adopted face-to-face slipped π-π stacking with stacking distance of 3.46 Å (a typical π-π stacking distance). Interestingly, multiple strong intermolecular interactions such as S···N and S···C (the carbon on the cyano group) were found between the neighbouring molecules (Figure 4). These interactions as well as π-π interactions formed a 2-dimensional network in the crystals which facilitated charge transport.[28] The thin film diffraction peaks of **CMHT** fit very well with the simulated powder pattern of the single crystals (Figure 3b), suggesting **CMHT** adopted the same molecular packing in the bulk single crystals and the thin films. The lattice d-spacing of **CMHT** thin films (18.46 Å) was equal to the length of c-axis (18.46 Å) in the single crystals. Thus, we inferred that the **CMHT** crystallites on the films had their c axis perpendicular to the substrate surface. This edge-on packing structure with the face-to-face π-π stacking and multiple intermolecular interactions benefited the electron transport and should be responsible for the high performance of tetrathienoquinoid semiconductors.

Conclusions

In conclusion, dicyanomethylene-substituted tetrathienoquinoid semiconductor **CMHT** was successfully synthesized. High electron mobility up to 0.22 $cm^2V^{-1}s^{-1}$ in ambient condition was observed based on solution processed thin films of **CMHT**. Single crystal diffraction results showed **CMHT** adopted slipped π-π stacking in the crystals, and strong intermolecular interactions such as S···N and S···C (the carbon on the cyano group) interaction were found among neighbouring molecules. These interactions formed 2-dimensional electron transporting network in the crystals. Thin film XRD results demonstrated **CMHT** adopted the same molecular packing in single crystals and thin films, suggesting the slipped π-π stacking as well as the multiple intermolecular interactions among neighbouring molecules are responsible for the high performance of tetrathienoquinoid organic semiconductors.

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Notes and references

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† The crystallographic information files (CIFs) for **CMHT** is available free of charge via the Internet at http://pubs.acs.org.

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