

Supporting Information

Dicyanomethylene-substituted Fused Tetrathienoquinoid for High-Performance, Ambient-Stable, Solution-Processable n-Channel Organic Thin-Film Transistors

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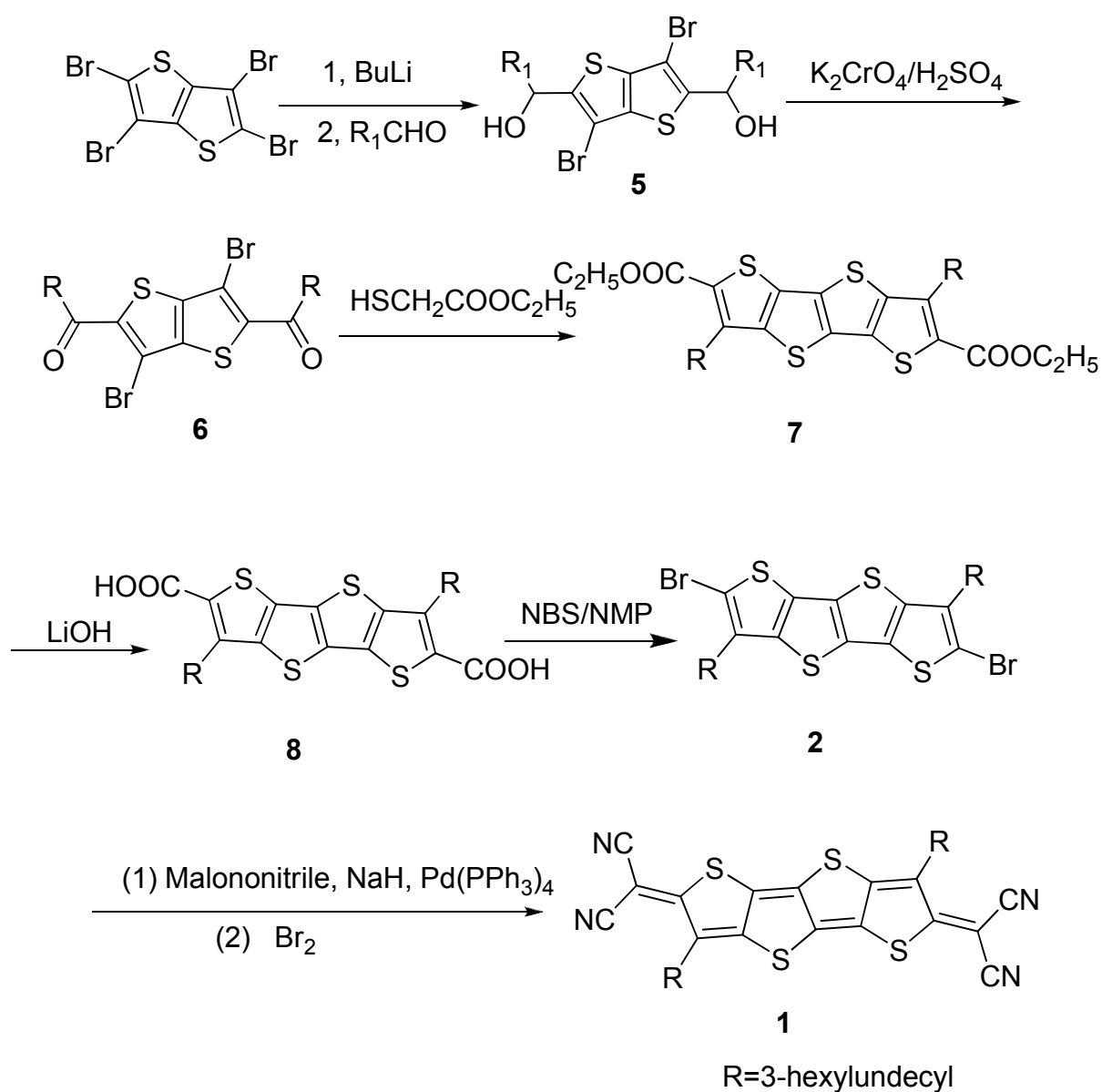
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1. Syntheses and Characterizations

General: The synthetic procedure of compound **1** is listed in the Scheme S1. All chemicals and solvents were purchased from Across, Aldrich, Alfa Aesar, Puyang Huicheng Chemicals Co. Ltd and Sinopharm Chemical Reagent Co. Ltd. 2,3,5,6-tetrabromothiopheno[3,2-b]thiophene and 4-hexyldodecanal were synthesized according to the reported procedure.^{S1 S2} NMR spectra were obtained in CDCl₃ on varian Mercury (300 MHz or 400 MHz) instrument with TMS as internal reference. Mass spectra (EI-MS) were carried out 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. Element analyses were performed on an Elementar Vario EL III element analyzer.



Scheme S1. The synthetic route of compound **1**

2, 4-di [1, 1'-(3-hexyl) undecanol]-3, 6-dibromothieno [3, 2-b] thiophene (5)

To a mixture of 2,3,5,6-tetrabromothieno[3,2-b]thiophene(2.28 g, 5mmol) in 50 mL dry THF, n-butyllithium (4.2 mL, 11mmol, 2.5M in hexane) was added dropwise at -78°C. After the addition was finished, the resulting mixture was stirred another 2 hours and then 4-hexyldodecanal (2.95g, 11mmol) was added quickly. The final mixture was allowed to warm to room temperature and was stirred for another 2 hours. The reaction mixture was quenched with 20mL water and extracted with ethyl acetate. The combined extracts were dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the crude product was purified through flash chromatographed on silica (petroleum-ethyl acetate (ratio 20:1) as eluant), affording compounds A (1.22g) and B (1.31g) (68%). A: ¹H-NMR (300 MHz, CDCl₃): 0.88 (t, J = 6.0Hz, 12H), 1.25(br, 54H), 1.45(br, 2H), 1.81-1.88(m, 4H), 5.07 (t, J = 6.6Hz, 2H); MS (MALDI-TOF): m/z=817.5 (M⁺-OH). B: ¹H-NMR (300 MHz, CDCl₃): 0.88 (t, J = 6.0Hz, 12H), 1.25(br, 54H), 1.81-1.89(m, 4H), 2.50 (br, 2H), 5.06 (t, J = 6.6Hz, 2H). MS (MALDI-TOF): m/z = 817.1 (M⁺-OH). Compound A and B are enantiomers and used directly for the next step.

2, 4-di [1, 1'-(3-hexyl) undecanone]-3, 6-dibromothieno [3, 2-b] thiophene (6)

Compound **5** (2.5g, 3.0 mmol) mixed with acetone (15 mL). To this mixture, chromic acid solution (13mL) was added dropwise at room temperature. The mixture was stirred for 5 hours. Then acetone was evaporated and the rest of the mixture was extracted with ethyl acetate (2×20 mL). The combined extracts were washed with brine (2×15 mL) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the crude product was purified through flash chromatographed on silica, affording 1.53g **6** (61%). M.p., 54-55 °C; ¹H-NMR (300 MHz, CDCl₃): 0.88 (t, J = 6.3Hz, 12H), 1.28 (br, 50H), 1.69-1.76 (m, 4H), 3.07 (t, J = 7.5Hz, 4H); MS (MALDI-TOF): m/z = 831.5 (M⁺+H).

2, 6, -Dicarboethoxy-3,7-di[(3-hexyl)undecyl]thieno[3,2-b]thieno[2',3':4,5]thieno [2,3-d]thiophene (7)

Compound **6** (1.38g, 1.66mmol) was mixed with K₂CO₃ (0.92g, 6.64mmol) and DMF(15mL). To this mixture, ethyl mercaptoacetate (0.44g, 3.65mmol) was added dropwise. The reaction mixture was stirred for 48 hours at 60 °C under nitrogen and then poured into water(30mL). The solid was collected by filtration. The product **7** was purified through recrystallization from ethanol and afforded 0.82g (yield, 56%). M.p., 102-103°C; ¹H-NMR (300 MHz, CDCl₃): 0.89 (t, J = 6.0Hz, 12H), 1.28(br, 50H), 1.41 (t, J = 7.2Hz, 6H), 1.65-1.71 (m, 4H), 3.15 (t, J = 8.1Hz, 4H), 4.39 (q, J = 8.1Hz, 4H); MS (MALDI-TOF): m/z = 873.7 (M⁺+H).

**3,7-di[(3-hexyl)undecyl]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene 2, 6,
-dicarboxylate acid (8)**

To the mixture of THF (15mL), methanol (2.5mL), water (1.5mL) and LiOH-H₂O (1.2g, 31.6mmol), compound **7** (0.82g, 0.94mmol) and a catalytic amount of tetrabutylammonium iodide were added. The mixture was refluxed overnight. Solvent was evaporated and the residue was acidified with concentrated HCl to pH=2. The solid formed was filtered and washed with water three times. The solid was dried to give **10** (0.75g, 99%). M.p., 301-302 °C. Due to the poor solubility, no NMR spectrum was obtained. MS (MALDI-TOF): m/z = 817.1 (M⁺+H); HRMS (MALDI): m/z calcd for [C₄₆H₇₃O₄S₄⁺] 817.4353, found 817.4386.

2,6-Dibromo-3,7-di[(3-hexyl)undecyl]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (2)

To the mixture of NMP (5mL) and water (0.25mL), compound **8** (0.165g, 0.2mmol) and NBS (0.11g, 0.61mmol) were added. This mixture was stirred over night under nitrogen at room temperature. The mixture then was added water (10mL) and extracted with ethyl acetate. The combined extracts were dried over anhydrous MgSO₄ and filtered. Distillation of solvent under reduced pressure gave the crude product, which was flash chromatographed on silica (Light petroleum as eluant), affording compound **3** (0.13g, 72%). M.p., 58-59 °C; ¹H-NMR (300 MHz, CDCl₃): 0.88 (t, J = 6.0Hz, 12H), 1.27 (br, 50H), 1.61-1.68 (m, 4H), 2.70 (t, J = 8.1Hz, 4H); MS (MALDI-TOF): m/z = 888.4 (M⁺+H); HRMS (MALDI): m/z calcd for [C₄₄H₇₀S₄Br⁺] 805.3559, found 805.3538.

2,6,-bis(dicyanomethylene)-3,7-di[(3-hexyl)undecyl]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d] thiophene (1)

Malononitrile (79mg, 1.2mmol) was added to an ice-salt cooled suspension of sodium hydride (58mg, 2.4mmol) in 1, 2-dimethoxyethane (15mL) under nitrogen stream. The mixture was stirred at room temperature for another 20 min. Then **2** (0.27g, 0.3mmol) and tetrakis(triphenylphosphine)palladium (69mg, 0.06mmol) were added, the solution was heated to reflux for 4 hours. The resulting solution was treated with saturated bromine water (20mL) and the precipitation was filtered. After being washed with water and dried under vacuum, the crude product was purified by flash chromatograph on silica (Light petroleum-dichloromethane (ratio 3:1) as eluant), affording 0.196g compound **1** (yield,77%). M.p., 216-217 °C; ¹H-NMR (300 MHz, CDCl₃): 0.89 (t, J = 6.0Hz, 12H), 1.27 (br, 50H), 1.46 (br, 2H), 1.61-1.66 (m, 4H), 2.91 (t, J = 8.7Hz, 4H); MS (MALDI-TOF): m/z = 855.6(M⁺);

Anal. Calcd for $C_{28}H_{36}O_4S_4$: C, 70.21; H, 8.25; N, 6.55%; Found: C, 69.97; H, 8.26; N, 6.35%.

2. Thermal gravity analysis (TGA)

TGA was measured on a TAQ500 instruments under a dry N_2 flow at a heating rate of $10^\circ C/min$.

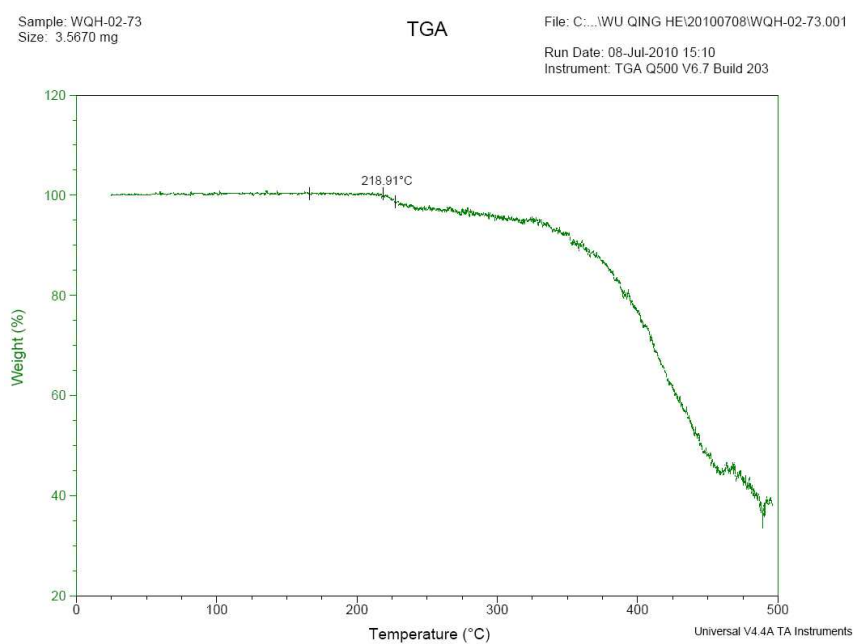


Figure S1. TGA result of compound **1**.

3. Stimulated molecular length of compound 1

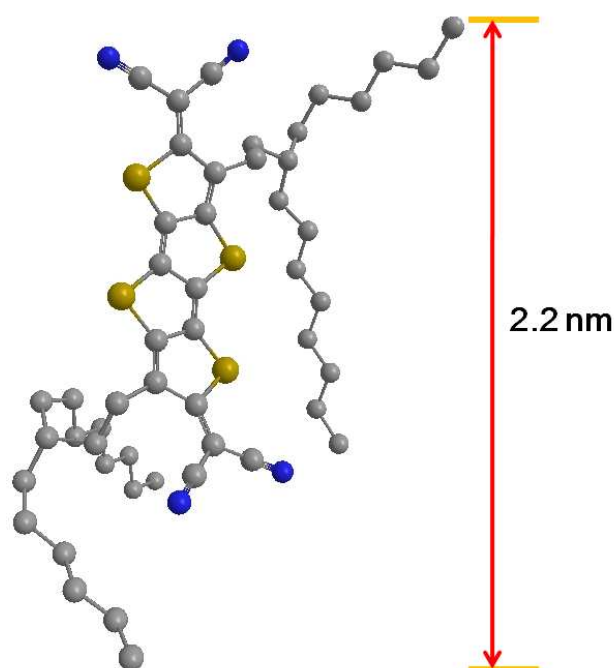


Figure S2. The stimulated molecular length of **1**.

4. Device Fabrication and Characterization

The devices are top-contact bottom-gate structure. The gate is n-type heavily doped Si. A thermally grown SiO_2 layer of 300 nm (the specific capacitance was measured to be 10 nF cm^{-2}) was used as the gate dielectric layer. Thin films of **1** were prepared by drop casting of 5 mg/mL chlorobenzene solution on octadecyltrichlorosilane (OTS)-treated SiO_2/Si wafers. Au source and drain electrodes were deposited by vacuum evaporation on the top of the organic film through a shadow mask. The resulting device had a channel length of $31 \mu\text{m}$ and a width of $273 \mu\text{m}$. Electrical measurements were carried out at room temperature in air using a Keithley 4200 semiconductor parameter analyzer. The field-effect mobility of electrons (μ_e) and the threshold voltage (V_{TH}) were calculated by fitting a straight line to the plot of the square root of I_{DS} vs V_{G} (saturation region), according to the expression $I_{\text{DS}} = (W/2L)\mu_e C_i (V_{\text{G}} - V_{\text{TH}})^2$. Where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, and V_{TH} is the threshold voltage.

A pronounced non-linear onset in the output-curves at low drain voltage was observed. We believe that the pronounced non-linear onset in the output-curves is due to the contact resistances (RC). The RC consists of two main parts. One is the resistance of metal/organic

interface (R_{int}). In our report, the work function of Au electrode did not match the energy level of the semiconductor ($E_{\text{LUMO}} = 4.3 \text{ eV}$), this brought R_{int} . The other is the resistance of organic semiconductors itself. In our work, the transistors were top-contact bottom-gate structure, so the resistance of semiconductor between metal electrode and conducting channel (R_{bulk}) also contributed to the RC.

5. Mobility Distribution of the Devices

54 devices have been fabricated and tested. The mobility distribution is shown below. The average mobility of the total 54 devices is $0.43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

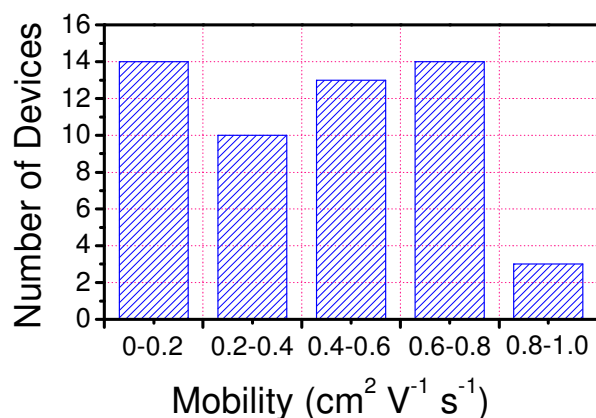


Figure S3. Mobility distribution of the devices.

6. Air-Stability of the Devices

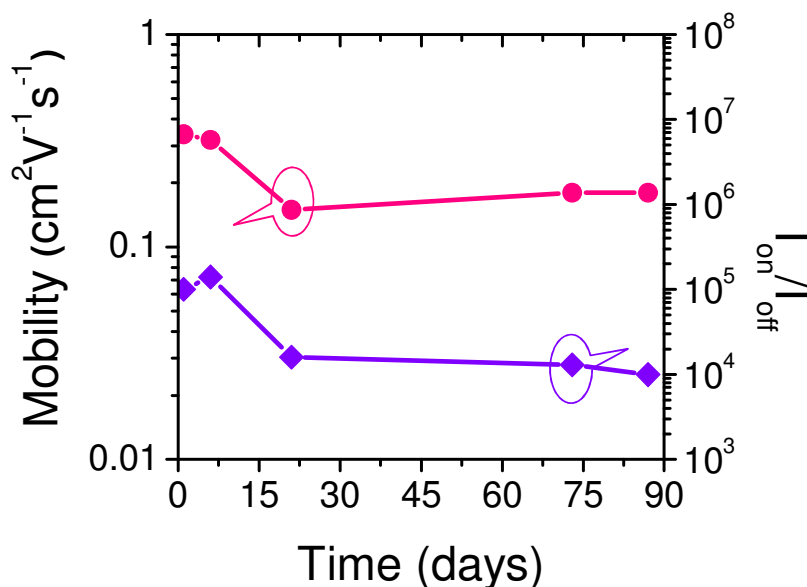


Figure S4. Long term air-stability measurements of a typical device of **1** over a period of 87 days. The devices were stored in a semitransparent plastic box (to keep out dusty) without any further actions to exclude the exposure of light or humidity.

7. Stability of the Devices Under Continuous-Working Conditions

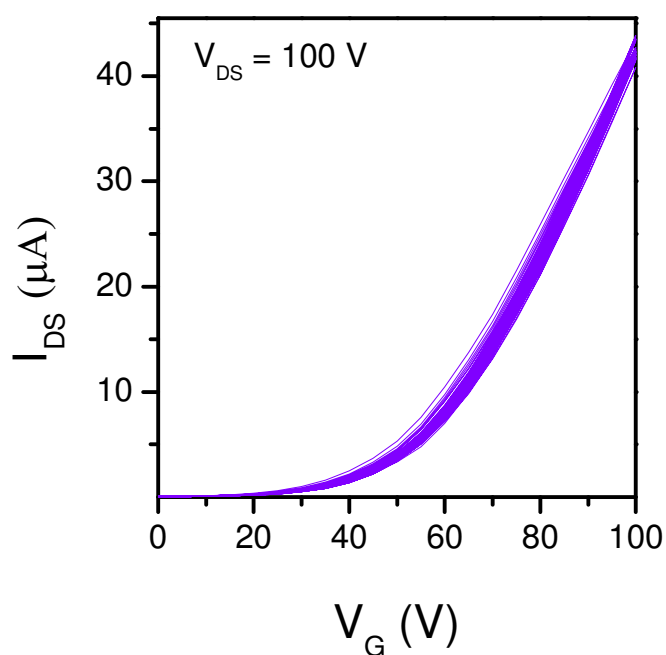


Figure S5. Stability of the devices under continuous-working conditions (measured in air). The drain was biased at 100 V, the gate voltage was swept from 0 V to 100 V and back to 100 V (one scan) with a step of 5 V. The number of scans is 100.

8. References

- S1. Lance S. Fuller.; Brian Iddon.; Kevin A. Smith. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 22 3465-3470
- S2. Tilak P. Wijesekeras.; Shanthad David.; John B. Paine III.; Brianr. Jamesa.; Davidd Dolphin. *Can. J. Chem.* **1988**, 66, 2063-2071