Soluble Precursor of Hexacene and its Application on Thin Film Transistor

Supplementary Information

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General Information

The ¹H and ¹³C NMR were recorded on a Bruker AV500 spectrometer. The ¹H and ¹³C NMR chemical shifts were reported as δ values (ppm) relative to external Me₄Si. The coupling constants (*J*) were given in hertz. Mass spectra were recorded on a VG70-250S mass spectrometer. Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F₂₅₄ Merck. Column chromatography was performed on Merk Kieselgel Si 60 (40-63mm). Absorption spectra were recorded on a Jasco-550 spectrophotometer. TGA were recorded on a Pyris 1 TGA Lab system. All solvents and reagents were of reagent quality, purchased commercially, and used without further purification. Solid state of ball-milling reaction was evaluated by Retsch MM200. Microwave reaction was performed by CEM Discover SP.

FET fabrication and Characterization

Thin-film transistors were fabricated on a heavily n-doped silicon substrate with a silicon dioxide layer (300 nm) in bottom-gate bottom-contact configurations. The substrates were cleaned by freshly prepared piranha solution (H₂SO₄/H₂O₂ 7:3) for 3 hours and then washed with de-ionized water, and dried with nitrogen gas then cleaned by oxygen plasma. Gold films (as source-drain electrode, thickness = 40 nm, channel width = 500 μ m, length= 15 μ m) were deposited onto Si substrates using a thermal evaporator at a background pressure of 5 x 10^{-6} torr with rate 0.1 nm/s. Typically, 500 Å of gold was deposited on a 50 Å Chromium adhesion layer. After thermal evaporator of metal electrode, the water was placed in an environment saturated with hexamethyldisiloxane (HMDS) for 24 hours, followed by rinsing in toluene then placed into freshly prepared benzylthiol solutions in ethanol (1 mM) at 60°C for 2 days. Before use, each sample was rinsed with several mL of absolute ethanol and gently blown dry with nitrogen gas. The solution of hexacene precursor 1 (0.6wt% in CHCl₃) was spin-coated on the wafer (first 600 rpm for 10 seconds, followed by 900 rpm for 20 seconds). It was then heated to 240 °C for 5 minutes for a convertion to hexacene, afterward it was cooled down to room temperature for 3 minutes. The procedure was repeated three times to achieve a homogeneous film of hexacene. This technique is the same as that described in reference 8, while all the procedures were done in a nitrogen glove box. The electrical measurements were carried out in air using a semiconductor parameter analyzer (Keithley 2400).

Structural data and synthetic procedure

(6S,15R)-diethyl 6,15-dihydro-6,15-(epoxymethano)hexacene-17,17-dicarboxylate 1



To a solution of hexacene **2** (16.4 mg, 0.05 mmol), diethylketomalonate **3** (610 mg, 3.5 mmol), and 1,2-dichlorobenzene (O₂ free, 2 mL) was heated at 160 °C for 5 min with microwave assisted (200 W). After the reaction, the solvent was removed. The crude product was purified by a silica gel chromatograph eluted with hexacne:CH₂Cl₂ (2:1 – 1:2 vol%), followed by washed with iced ethylacetate to afford adduct **1** (20.6 mg, 82%) as white powder. Physical data of **1**: ¹H NMR (CDCl₃, 500 MHz) δ 8.38 (s, 1H), 8.35 (s, 1H), 7.99-7.79 (m, 4H), 7.90 (s, 1H), 7.87 (s, 1H), 7.83-7.81 (m, 2H), 7.46-7.44 (m, 4H), 6.31 (s, 1H), 5.39 (s, 1H), 4.1-3.95 (m, 4H), 1.02-0.94 (m, 6H) ; ¹³C NMR (CDCl₃, 125 MHz) 167.89, 167.75, 137.49, 136.88, 134.09, 133.39, 132.95, 132.56, 131.97, 131.86, 131.00, 130.70, 128.13, 128.07, 128.04, 127.83, 126.67, 126.36, 126.23, 126.19, 125.55, 125.46, 124.31, 124.08, 122.22, 122.11, 82.90, 76.77, 62.00, 48.70, 29.70, 13.81, 13.79 ; HR-EIMS m/z (M⁺); calcd; 502.1780, obsd; 502.1780

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Figure S1.¹H NMR of 1 (500 MHz)



Figure S3. ¹H NMR of dimer of hexacene (inset: proposed structure) in CDCl₃ (500 MHz)



Figure S4. Absorption spectrum of **1** in THF $(1.0 \times 10^{-5} \text{ M})$



Figure S5. Time-dependant thermal loading intensity of X-ray diffraction spectrum for annealing of **1** on SiO₂/Si substrate. 0.6 wt% in CHCl₃ solution. Spin-coat condition was 900 rpm for 30 s. The annealing temperature was 240 °C. Spin-coat and annealing were achieved in the nitrogen atmosphere. The XRD measurements were accomplished at air in the dark. The counts of intensities were taken at $2\theta = 5.41^{\circ}$, indicated (001) peaks.

Table S1 Geometrical isomers of acene dimers, calculated at the B3LYP/6-31G(d) level. Therelative energies (E_{rel}) are based on the total energies corrected with the zero-point vibrationalenergies.

	$C_{2\nu}$ Tetracene dimer	C _{2h} Tetracene dimer
E _{rel}	+0.16 kcal/mol	0 kcal/mol
	Symmetrical pentacene dimer	Asymmetrical pentacene dimer
E _{rel}	Symmetrical pentacene dimer 0 kcal/mol	Asymmetrical pentacene dimer +3.86 kcal/mol
E _{rel}	Symmetrical pentacene dimer 0 kcal/mol	Asymmetrical pentacene dimer +3.86 kcal/mol
E _{rel}	Symmetrical pentacene dimer 0 kcal/mol	Asymmetrical pentacene dimer +3.86 kcal/mol



Figure S6 Device configurations with and without a surface modification by coating a layer of benzylthiol on top of the gold electrode.



Figure S7 Stability test. (a) Device configurations with a surface modification by coating a layer of benzylthiol on top of the gold electrode. (b) The same device stayed at an inert atmosphere, without sealing, for 48 h. A decay of ca. 12% on charge mobility is observed.