

Supporting Information

FET performance and substitution effect on 2,6-dithienylanthracene devices prepared by photoirradiation of their diketone precursors

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1. Photoreaction of **1a** and **1b** in solution.

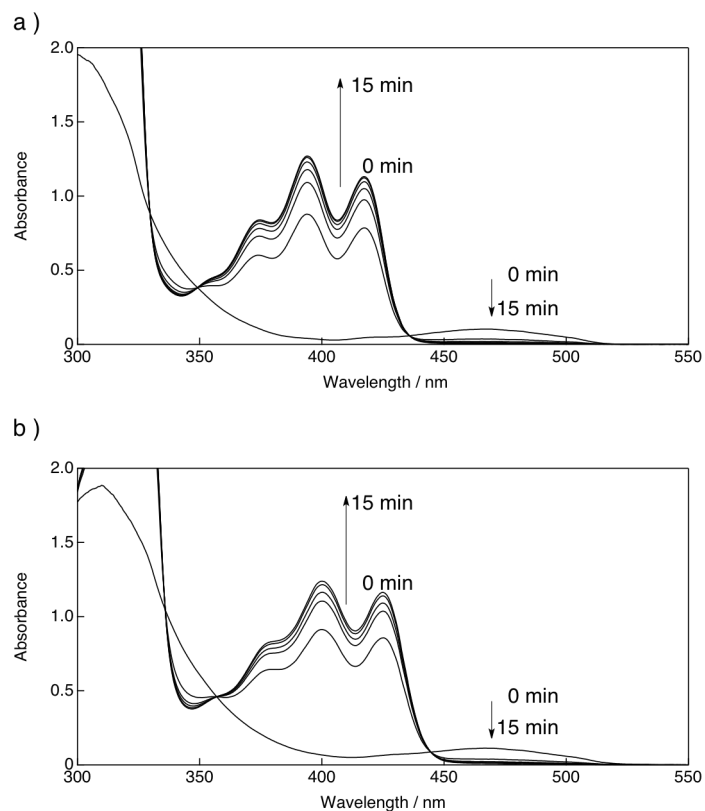


Fig. S1 a) Change in absorption spectra during photolysis ($\lambda_{\text{ex}} = 468$ nm) of **1a** in toluene (8.7×10^{-5} M).; b) Change in absorption spectra during photolysis ($\lambda_{\text{ex}} = 468$ nm) of **1b** in toluene (8.2×10^{-5} M).

2. OFET-Devices Fabrication and Measurements

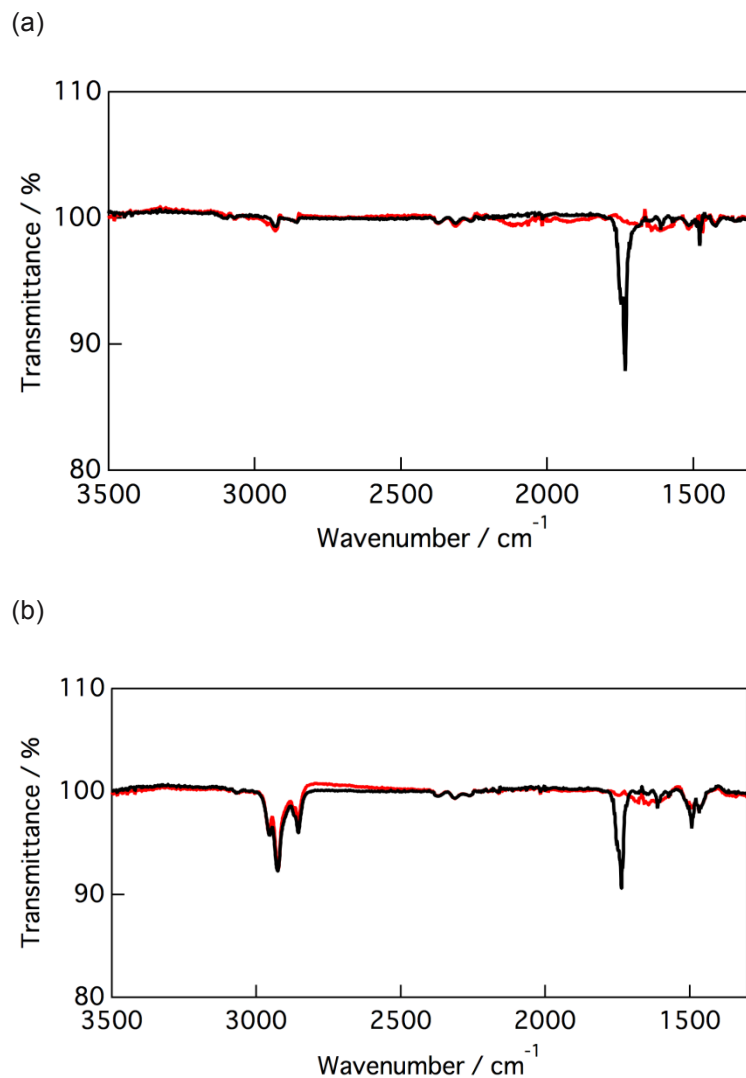


Fig. S2 IR spectra of spun-cast films of (a) **1a** (black line) and **DTAnt** (red line) and (b) **1b** (black line) and **DHTAnt** (red line) on glass plate.

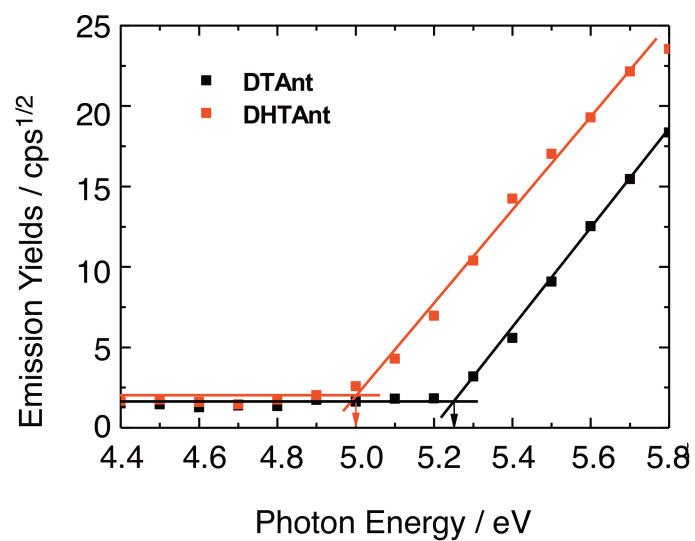


Fig. S3 Photo energy-photo emission plots of **DTAnt** and **DHTAnt**. The ionization potential was estimated from photoelectrons when the monochromatic light was irradiated to the film. The onset of the photoelectron counts to increasing photon energy corresponds to ionization potential.

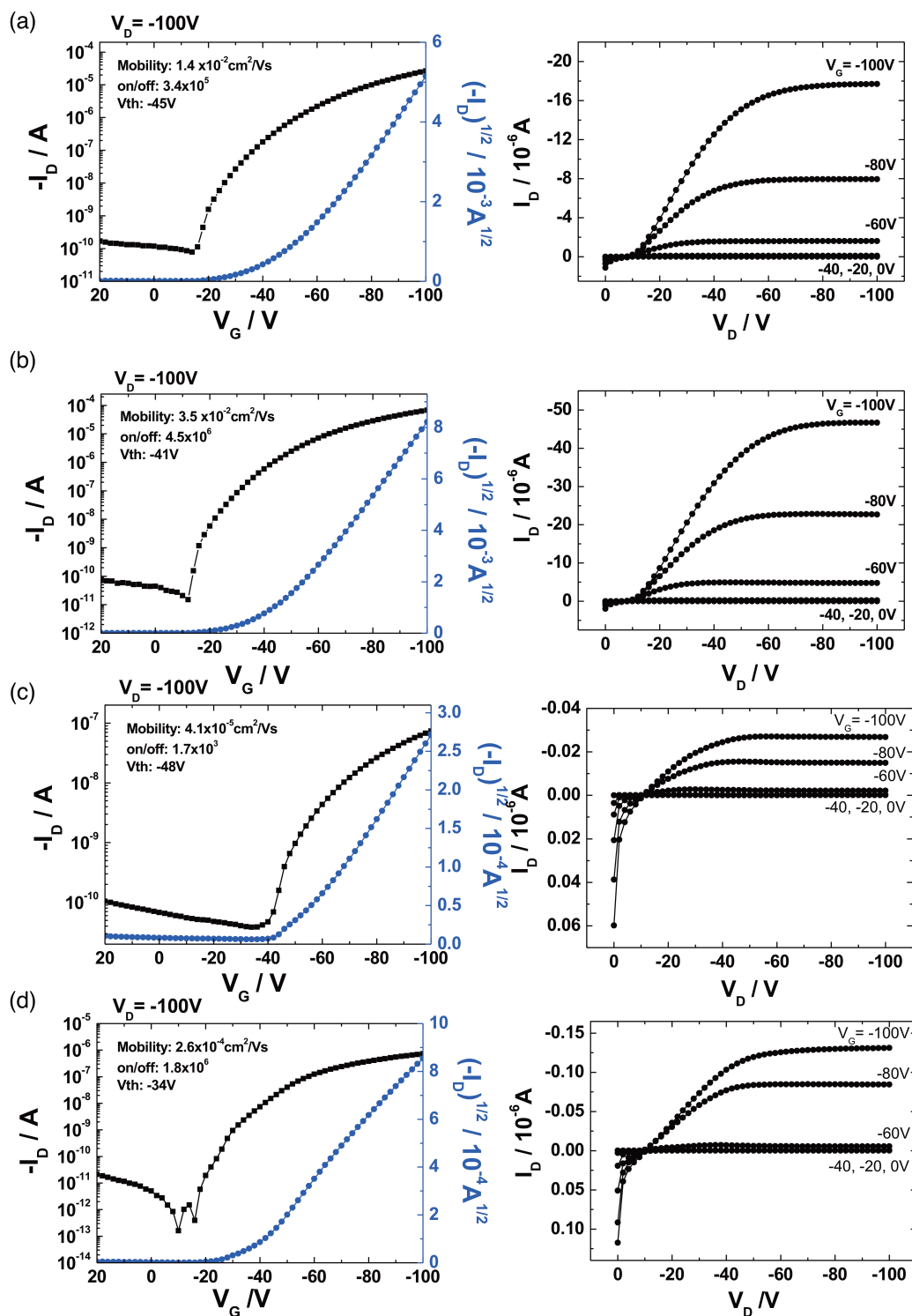


Fig. S4 I-V curves of **DTAnt** prepared with annealing temperature at (a) rt and (b) 60 °C; **DHTAnt** prepared with annealing temperature at (c) rt and (d) 60 °C.

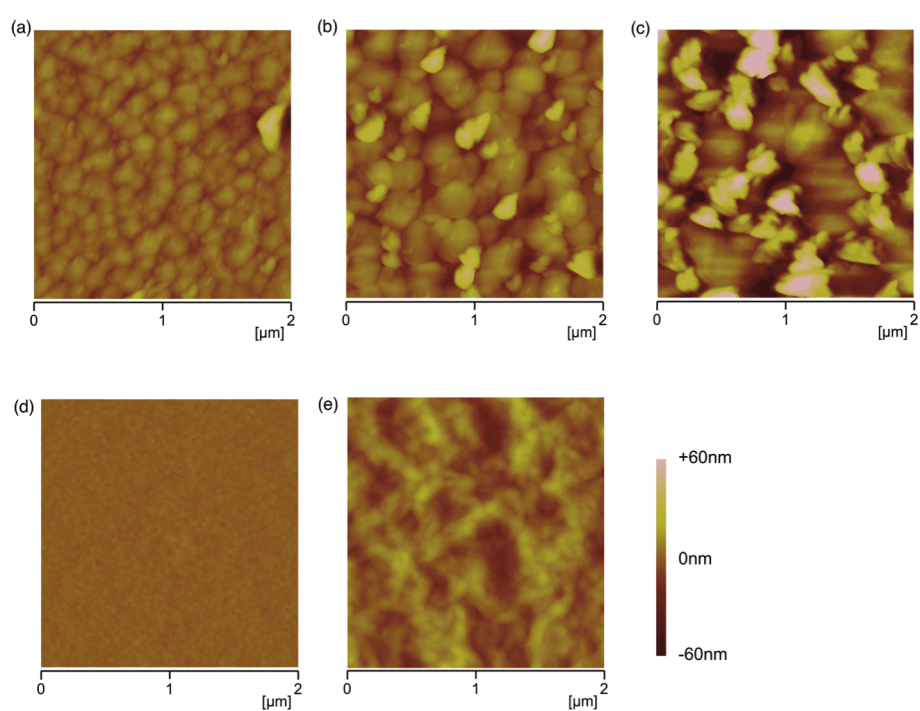


Fig. S5 AFM image of **DTAnt** (Upper stand) and **DHTAnt** (Lower stand) films prepared from **1a** and **1b** by solution process followed by photoirradiation. (a) Annealing temperature was rt and RMS = 5.94 nm; (b) 60 °C, 11.0 nm (c) 80 °C, 25.5 nm; (d) rt, 1.16 nm; (e) 60 °C, 7.94 nm.

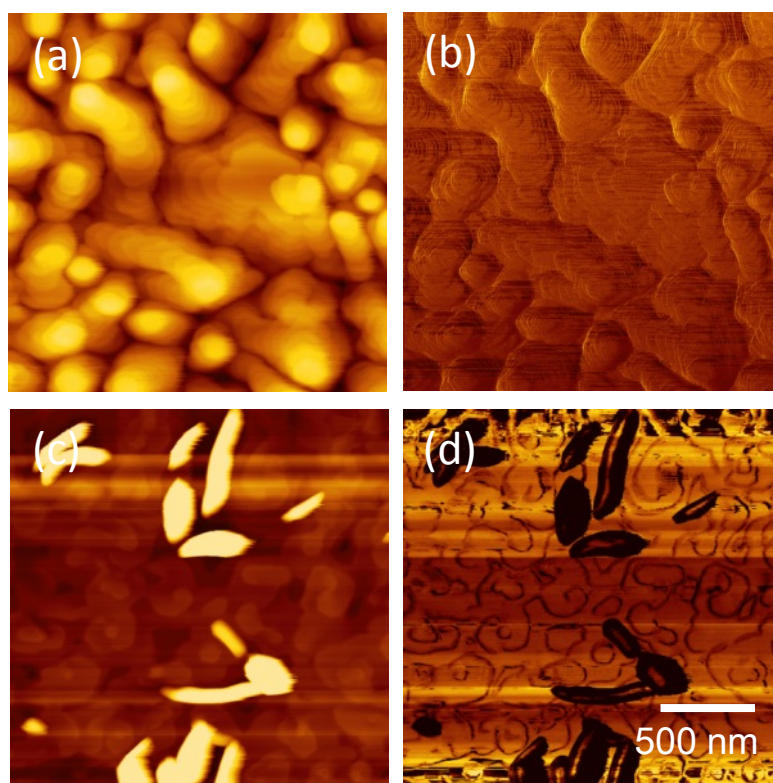
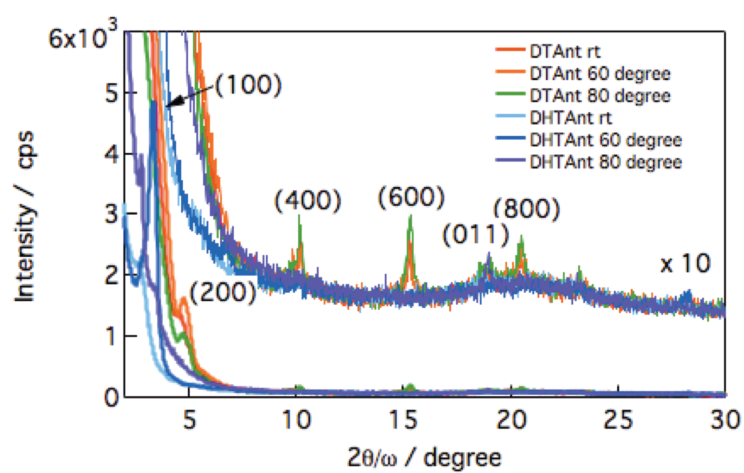


Fig. S6 AFM topographic (a) and phase (b) images of **DTAnt** film evaporated onto a quartz substrate in non-contact mode using a SiN cantilever (OMCL-AC200TS) with the spring constant of 200 N/m at 137.2 kHz. Images of (c) and (d) are topographic and phase images observed for evaporated **DHTAnt** onto a quartz substrate, respectively. Dark-bright dynamic ranges of images (a) and (c) correspond to the height of 36 and 53 nm, respectively.

(a)



(b)

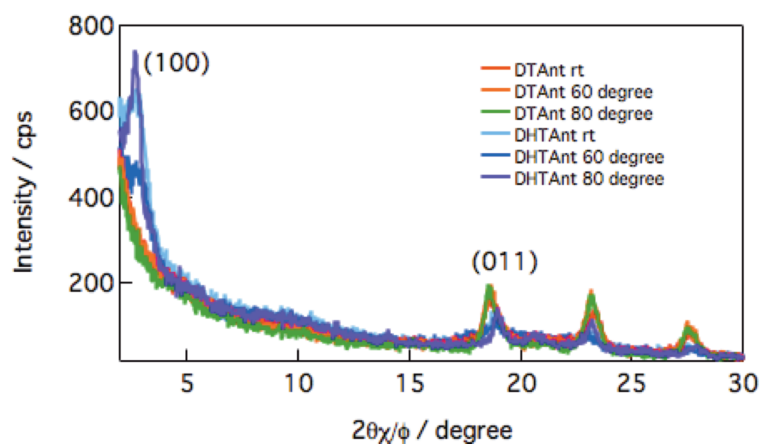


Fig. S7 (a) Out of plane and (b) in plane XRD patterns of **DTAnt** and **DHTAnt**.

4. Flash-photolysis time-resolved microwave conductivity (FP-TRMC)

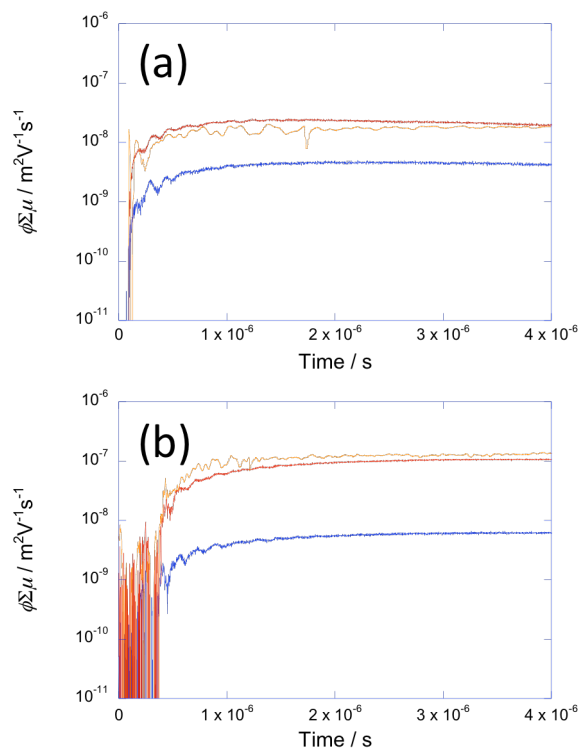


Fig. S8. Observed conductivity transients monitored for the thin film of (a) spun-cast **DTAnt** (red line), vacuum deposited **DTAnt** (orange line), and **1a** (blue line), (b) spun-cast **DHTAnt**, vacuum deposited **DHTAnt** (orange line), and **1b** (blue line), respectively. The compounds were coated on quartz substrates and the transients were recorded at RT under an excitation at 355 nm, $1.7 \sim 2.2 \times 10^{16}$ photons/cm².

1. Experimental

OTFT-device fabrication and characterization of films An *n*-type heavily doped Si wafer with a SiO₂ layer was used as the gate electrode and dielectric layer. The chloroform (including 1% trichlorobenzene) solution of **1a** (20 mg/mL) was spin-coated on the silicon substrate. The chloroform solution of **1b** (20 mg/mL) was spin-coated on the silicon substrate. The surface was treated with GR650 glass resin supplied from Technoglass. The **1a** and **1b** films were irradiated with high brightness LED area lamp (Edmund Optics) with a wavelength of 470 nm and an intensity of 300 mW/cm² for 60 min. The gold source and drain electrodes were prepared by vacuum deposition through a metal shadow mask. The channel length (*L*) and width (*W*) were 50 μm and 5.5 mm, respectively. Measurements of OTFT devices were carried out using a semiconductor parameter analyzer (Agilent, 4155C) in a nitrogen glove box where the concentrations of H₂O and O₂ are less than 1 ppm. The mobilities were determined in the saturation regime by using the equation of $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, 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_T is the threshold voltage. The channel length of *L* was adjusted based on the each microscope image of the electrodes. The film structures were observed by a digital microscope (Olympus, LEXT OLS4000) and a scanning atomic force microscope (Bruker, Dimension Icon). IR spectra of the organic thin films were measured by FT-IR spectrometer with attenuated total reflectance configuration (Shimadzu, IR Prestige-21). Ionization potential was determined by atmospheric photoelectron spectroscopy (Riken Keiki, AC-3). The vacuum deposited films were observed by a Nano Navigator Nano Cute from SII-Nanotechnology Inc. in tapping mode using a SiN cantilever (OMCL-AC200TS) with the spring constant of 200 N/m at 137.2 kHz from Olympus Co. Ltd.

Photochemical reactions The photocleavage reactions were carried out in a quartz UV cell which was irradiated by monochromatic excitation light through a monochromator (Ritsu MC-10N) by a 500 W xenon lamp (Ushio XB-50102AA-A) and monitored by OCEAN OPTICS high resolution spectrometer system HR-4000 with light source DH-2000-BAL.

Flash-photolysis time-resolved microwave conductivity (FP-TRMC) The nanosecond laser pulses from a Nd: YAG laser (third harmonic generation, THG (355 nm) from Spectra Physics, INDY-HG, FWHM 5–8 ns) have been used as excitation sources with the excitation photon density of 9.1×10^{15} photons cm⁻² (5.1 mJ/cm²). For time-resolved microwave conductivity (TRMC) measurement, the microwave frequency and power were set at ~9.1 GHz and 1–10 mW respectively, so that the motion of charge carriers can not be disturbed by the low electric field of the microwave. The TRMC signal picked up by a diode (rise time < 1 ns)

is monitored by a Tektronix TDS3033 digital oscilloscope. All the above experiments were carried out at room temperature. The transient photoconductivity ($\Delta\sigma$) of the samples is related to the reflected microwave power ($\Delta P_r/P_r$) and sum of the mobilities of charge carriers via:

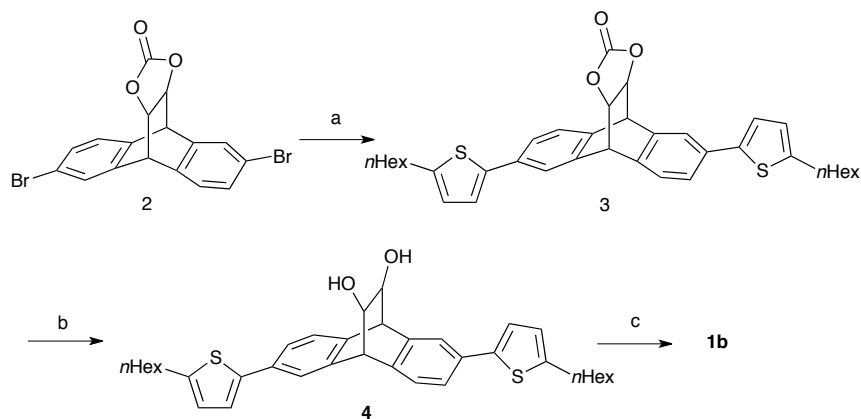
$$\langle \Delta\sigma \rangle = \frac{1}{A} \frac{\Delta P_r}{P_r} \quad (1)$$

$$\Delta\sigma = e\phi N(\mu_+ + \mu_-) \quad (2)$$

where A , e , ϕ , N and μ_{\pm} are a sensitivity factor, elementary charge of electron, photocarrier generation yield (quantum efficiency), the number of absorbed photons per unit volume and mobilities of positive or negative charge carriers, respectively.

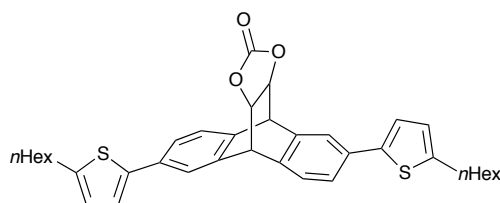
The powder samples were placed onto a quartz substrate using an adhesive tape. The adhesive tape was confirmed not to show detectable TRMC signal. The experiments were performed at room temperature under ambient condition.

5. Synthesis and Characterization of compounds



Scheme S1 Synthesis and conditions: (a) $\text{Pd}(\text{PPh}_3)_4$, 2-(tributylstannyl)-5-hexylthiophene, toluene, reflux, overnight, 78%; (b) aqueous NaOH, THF, reflux, 1 h, 94%; (c) TFAA, *dry*-DMSO, *dry*- CH_2Cl_2 , N, N-(*iso*-Pro) $_2$ EtN, -60°C , 1.5 h, 41%.

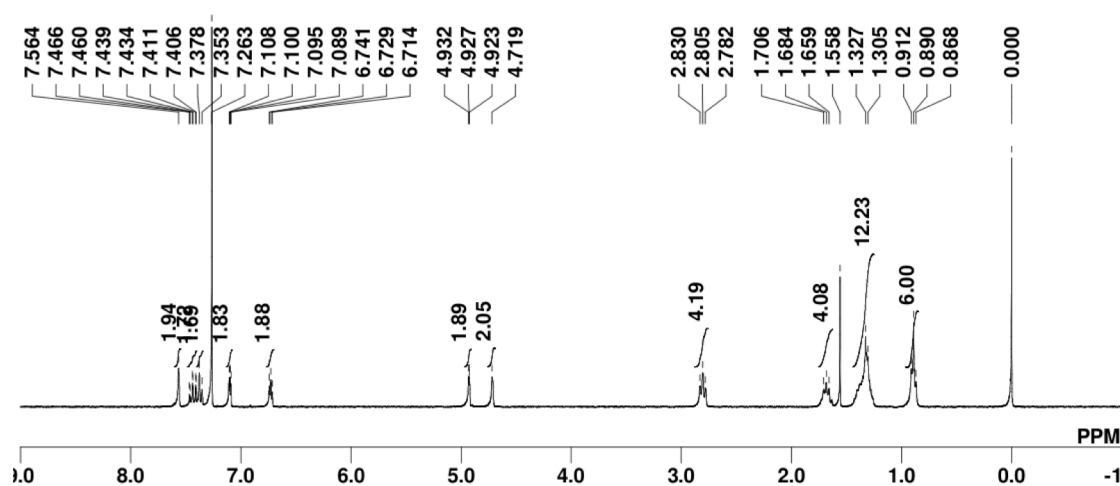
General ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer using tetramethylsilane as an internal standard. ESI mass spectra were measured on JEOL JMS-MS T100LC spectrometer. Melting points were measured on Yanako MP-J3. Elemental analyses were performed on Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.



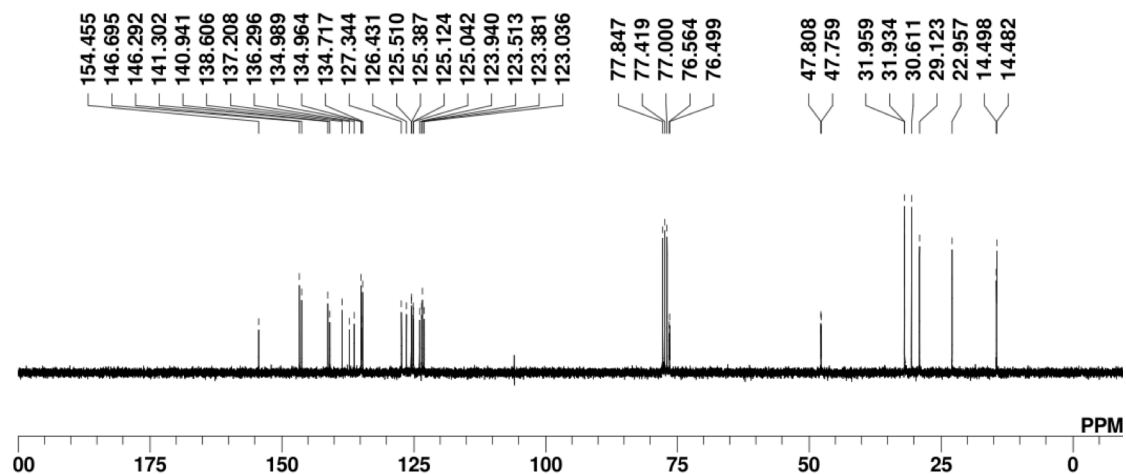
Synthesis of **3**

In schlenk flask, **6** (1.50 g, 3.55 mmol), 2-(Tributylstannyl)-5-hexylthiophene (4.68 g, 10.2 mmol) were suspended with *dry*-toluene (20 mL). The suspension was degased by freeze-pump-thaw cycling and replaced with an argon atmosphere. After Pd(PPh₃)₄ (416 mg, 0.360 mmol) was added to the suspension, the mixture was warmed to 100 °C and stirred for overnight. The reaction mixture was cooled to rt and filtrated with celite. The organic solvent was removed under reduced pressure. The crude product was purified on 10 wt% Na₂CO₃ in silica gel column chromatography (CH₂Cl₂: hexane = 1: 2) to yield a pale yellow oily solid (1.70 g, 2.85 mmol, 80%).

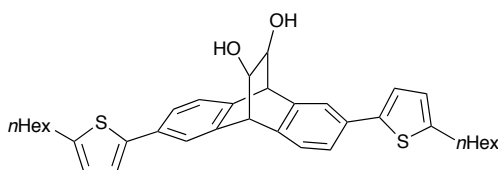
¹H NMR (300 MHz; CDCl₃): δ = 7.56 (s, 2H), 7.44 (m, 2H), 7.37 (m, 2H), 7.10 (m, 2H), 6.74-6.71 (m, 2H), 4.93 (m, 2H), 4.72 (m, 2H), 2.83-2.78 (m, 4H), 1.73-1.63 (m, 4H), 1.40-1.27 (m, 12H), 0.91-0.87 (m, 6H); ¹³C NMR (75 MHz; CDCl₃): δ = 154.46, 146.70, 146.29, 141.30, 140.94, 138.61, 137.21, 136.30, 134.99, 134.96, 134.71, 127.34, 126.43, 125.51, 125.39, 125.12, 125.04, 123.94, 123.94, 123.51, 123.38, 123.04, 73.56, 73.50, 47.81, 47.76, 31.96, 31.93, 30.61, 29.12, 22.96, 14.49, 14.48; MS (ESI) m/z: 619 [M+Na⁺]; Anal. Calcd. for C₃₇H₄₀O₃S₂ • 1/8H₂O: C, 74.18; H, 6.77.; Found: C, 74.17; H, 6.64.



¹H NMR spectrum of **3** in CDCl₃

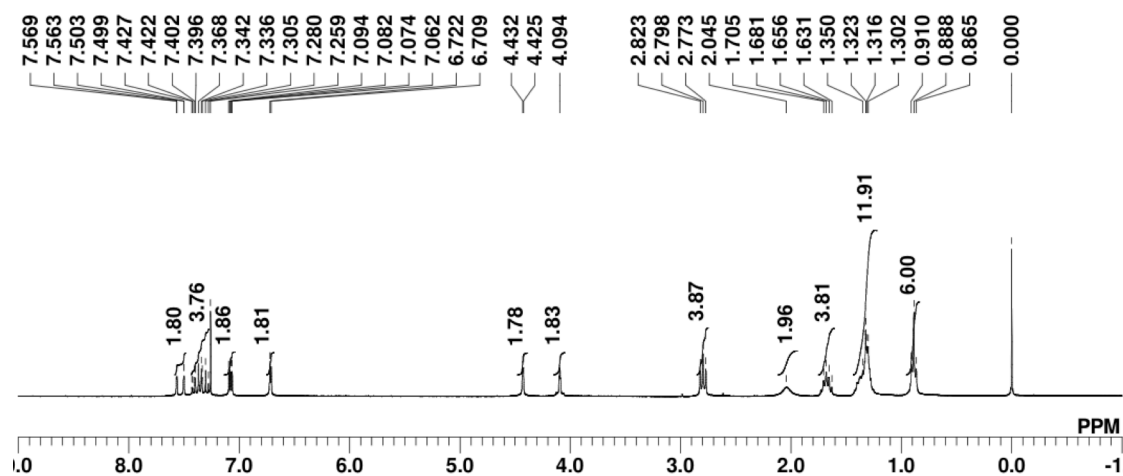


^{13}C NMR spectrum of **3** in CDCl_3

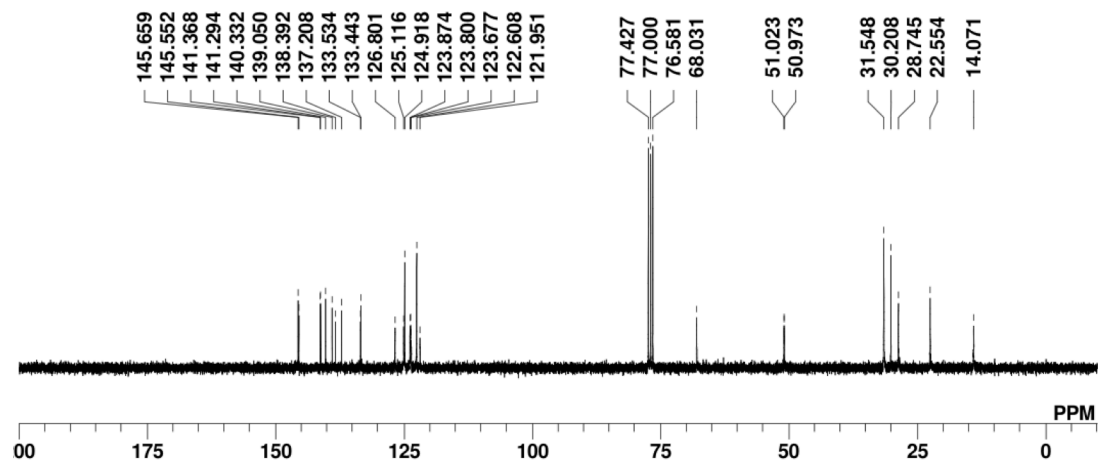


Synthesis of **4**

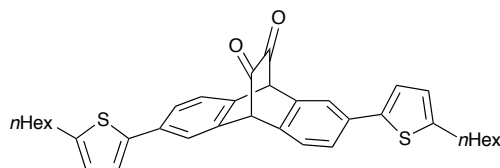
7 (1.07 g, 1.79 mmol) was dissolved with THF (46 mL). Aqueous 4 M-NaOH (30 mL) was added to the solution. The reaction mixture was refluxed for 1.5 h and cooled to rt. The reaction mixture was extracted with CHCl_3 and washed with water and brine. The organic layer was dried over Na_2SO_4 . The organic solvent was removed under reduced pressure. The crude product was purified on silica gel column chromatography (CHCl_3) to give **8** as a pale yellow solid (0.963 g, 1.69 mmol, 94%). ^1H NMR (300 MHz; CDCl_3): δ = 7.53 (dd, J = 19.6, 1.6 Hz, 2H), 7.43-7.28 (m, 4H), 7.08 (dd, J = 5.9, 3.6 Hz, 2H), 6.72 (d, J = 3.6 Hz, 2H), 4.43 (d, J = 2.2 Hz, 2H), 4.10 (m, 2H), 2.80 (t, J = 7.6 Hz, 4H), 2.04 (s, 1H, -OH), 1.68 (quint, J = 7.2 Hz, 4H), 1.40-1.28 (m, 12H), 0.89 (t, 3H, J = 6.8); ^{13}C NMR (75 MHz; CDCl_3): δ = 145.65, 145.55, 141.36, 141.29, 140.33, 139.04, 138.40, 137.20, 133.53, 133.44, 126.80, 125.11, 124.91, 123.87, 123.67, 123.65, 123.61, 121.95, 121.92, 68.03, 51.03, 50.98, 31.55, 30.22, 28.75, 22.56, 14.08; MS (ESI) m/z : 593 [$\text{M}+\text{Na}^+$]; m.p. 83 °C; Anal. Calcd. for $\text{C}_{36}\text{H}_{42}\text{O}_2\text{S}_2$: C, 75.74; H, 7.42. Found: C, 75.59; H, 7.33.



¹H NMR spectrum of 4 in CDCl₃



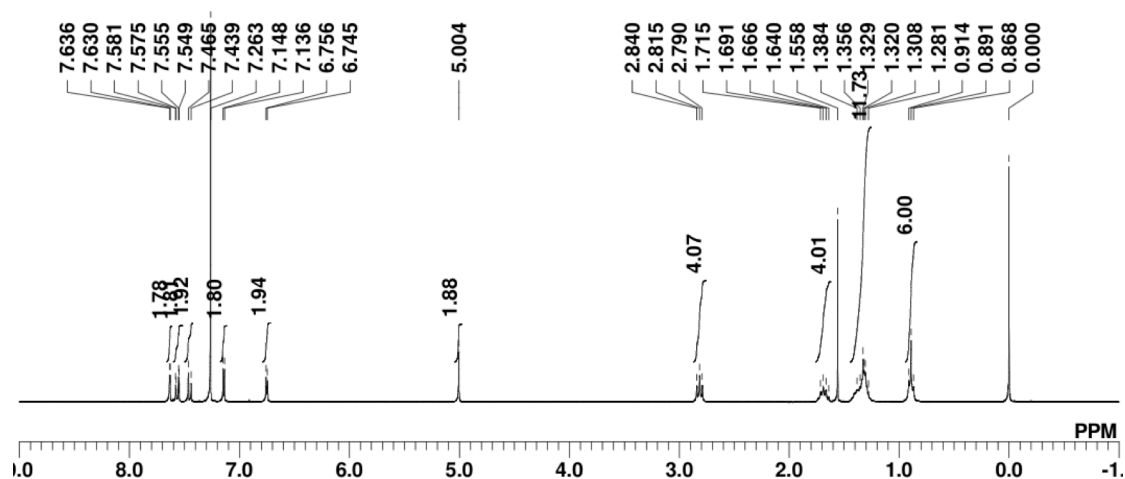
¹³C NMR spectrum of 4 in CDCl₃



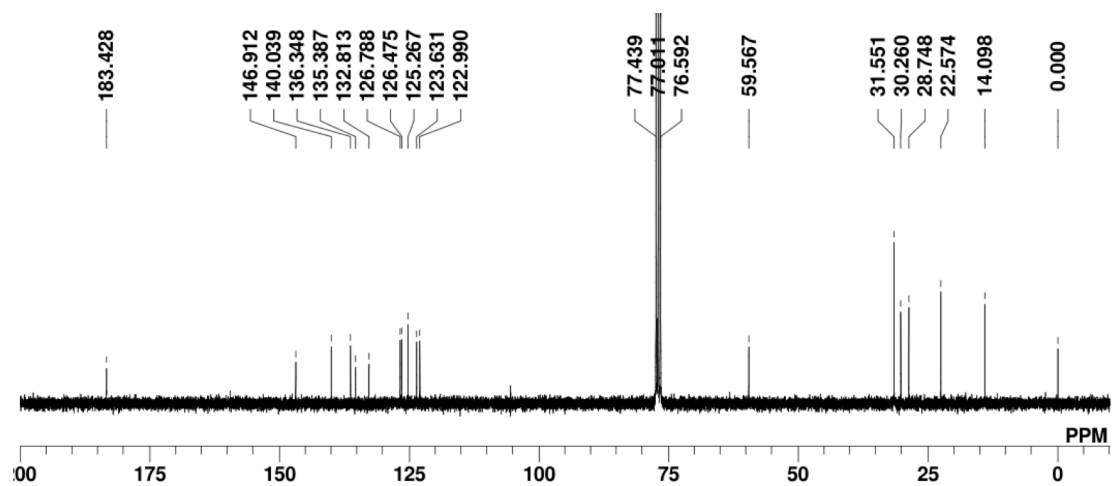
Synthesis of **1b**

Trifluoroacetic anhydride (2.3 ml, 17 mmol) was added dropwise to a mixture of *dry*-DMSO (2.3 ml, 32 mmol) and *dry*-CH₂Cl₂ (8.0 ml) at –60 °C under an argon atmosphere. After stirring for 10 min, diol **8** (543 mg, 9.52 mmol) dissolved in *dry*-CH₂Cl₂ (3.0 ml) was added dropwise over 5 min. After stirring for 90 min, *N,N*-(*iso*-pro)₂EtN (5.8 ml, 33 mmol) was added dropwise and the stirring was continued for additional 60 min at –60 °C. The temperature of the reaction mixture was warmed to rt and then the mixture was extracted with CH₂Cl₂. The organic layer was washed with 1 M-HCl, water and brine. The organic layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The residue was purified on silica gel column chromatography (CHCl₃ : hexane = 3 : 1) and recrystallized from CHCl₃/hexane to give compound **1b** as yellow solid (220 mg, 3.88 mmol, 41%).

¹H NMR (300 MHz; CDCl₃): δ = 7.63 (d, *J* = 1.7 Hz, 2H), 7.56 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 3.6 Hz, 2H), 6.75 (d, *J* = 3.6 Hz, 2H), 5.00 (s, 2H), 2.81 (t, *J* = 7.6, 4H), 1.69 (quint, *J* = 7.8 Hz, 4H), 1.41–1.28 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (75 MHz; CDCl₃): δ = 183.41, 146.90, 140.03, 136.33, 135.37, 132.80, 126.78, 126.46, 125.26, 123.62, 122.98, 59.56, 31.55, 30.26, 28.75, 22.57, 14.10; MS (ESI) *m/z*: 589 [M+Na⁺]; m.p. 150 °C; HR-ESI *m/z* = 589.22248, calcd for C₃₆H₃₈NaO₂S₂ = 589.22109 [M+Na⁺].



¹H NMR spectrum of **2b** in CDCl₃



^{13}C NMR spectrum of **2b** in CDCl_3