

Electronic Supplementary Information (ESI)

High-Mobility Anthracene-based X-shaped Conjugated Molecules for Thin Film Transistors

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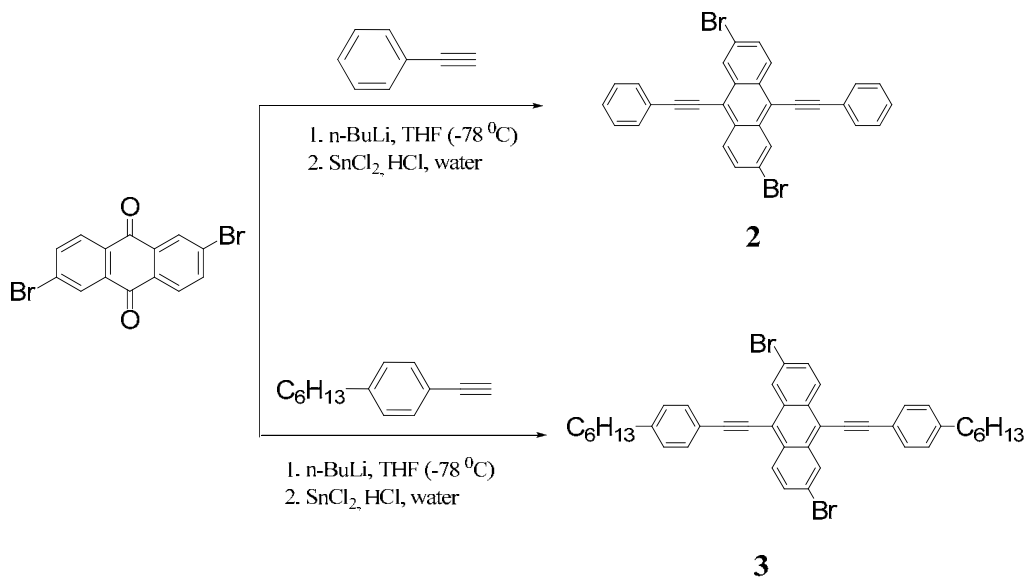
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S1. Synthesis

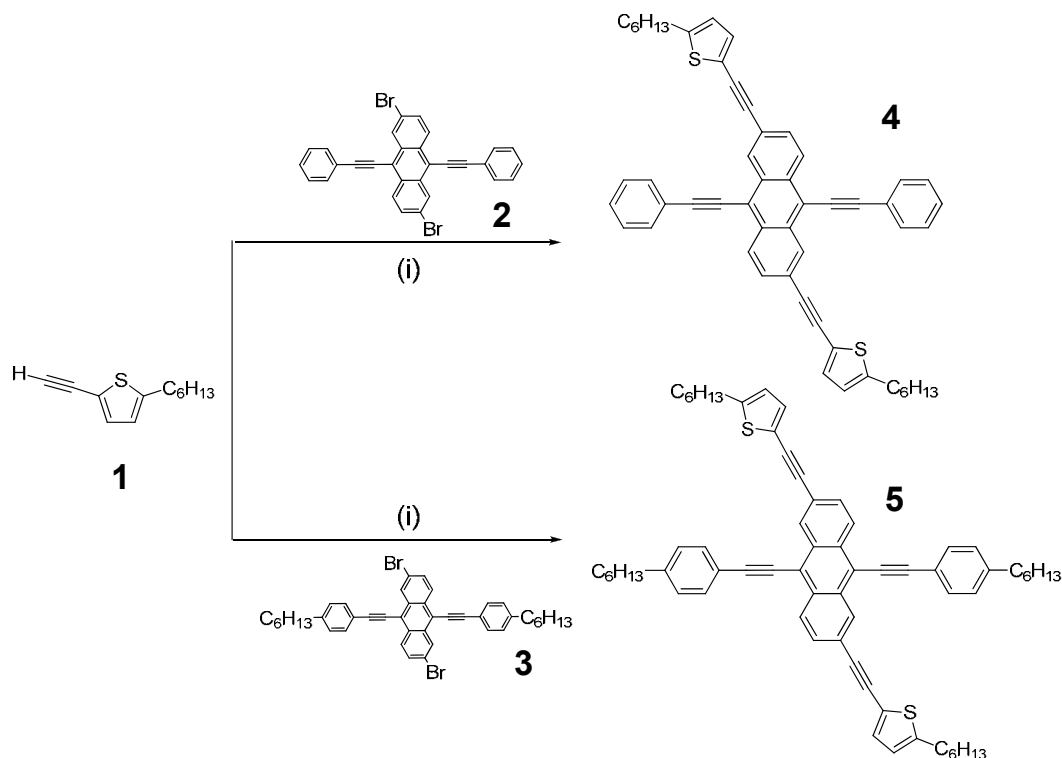


Synthesis of 2,6-Dibromo-9,10-bis(phenylethynyl)anthracene (2): In a 250 mL, oven dried, mag.-stirred round bottom flask (RBF), ethynylbenzene (0.394 g, 3.86 mmol) was dissolved in freshly distilled tetrahydrofuran (30 mL). The solution was then cooled to –78 °C. *n*-BuLi (1.57 mL, 3.92 mmol, 2.5 M sol'n. in hexane) was then added dropwise over 15 minutes. The mixture was stirred for 30 min, then 2,6-dibromoanthracene-9,10-dione (0.574 g, 1.57 mmol)¹ was added at -78 °C. The mixture was allowed to stir at room temperature for 3 hours, and then quenched with water, SnCl₂, and HCl. After completing the reaction, the solution was poured into methanol to collect the precipitates. Yield 0.82 g, 68 %.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta(\text{ppm})$ 8.77 (s, 2H), 8.48 (d, $J = 9.0$ Hz, 2H), 7.75 (d, $J = 7.4$ Hz, 4H), 7.66 (d, $J = 4.5$ Hz, 2H), 7.42-7.48 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta(\text{ppm})$ 133.04, 131.96, 131.02, 130.97, 129.46, 129.25, 129.20, 128.81, 123.11, 122.16, 118.22, 103.44, 85.57. HR-MS (EI) m/z (M^+): Calcd for $\text{C}_{30}\text{H}_{16}\text{Br}_2$, 533.96; found, 533.96. Anal. Calcd. for $\text{C}_{30}\text{H}_{16}\text{Br}_2$: C, 67.19 ; H, 3.01, found : C, 67.22 ; H, 3.01.

Synthesis of 2,6-Dibromo-9,10-bis((4-hexylphenyl)ethynyl)anthracene (3): The preparation method is identical with that of **2**. Instead of ethynylbenzene, 1-ethynyl-4-hexylbenzene was employed. After completing the reaction, the solution was poured into methanol to collect the precipitates. Yield 0.74 g, 67 %.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta(\text{ppm})$ 8.77 (s, 2H), 8.49 (d, $J = 9.4$ Hz, 2H), 7.64-7.68 (m, 6H), 7.28 (d, $J = 7.8$ Hz, 4H), 2.68 (t, 4H), 1.62-1.70 (m, 4H), 1.30-1.39 (m, 12H), 0.90 (t, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta(\text{ppm})$ 144.55, 132.85, 131.88, 130.77, 130.72, 129.42, 129.16, 128.88, 121.96, 120.32, 118.14, 103.72, 85.10, 36.21, 31.86, 31.31, 29.10, 22.73, 14.14. HR-MS (EI) m/z (M^+): Calcd for $\text{C}_{42}\text{H}_{40}\text{Br}_2$, 702.15; found, 702.14. Anal. Calcd. for $\text{C}_{42}\text{H}_{40}\text{Br}_2$: C, 71.60 ; H, 5.72, found : C, 71.62 ; H, 5.64.



Synthesis of 5,5'-(9,10-bis(phenylethynyl)anthracene-2,6-diyl)bis(ethyne-2,1-

diyl)bis(2-hexylthiophene), 4 : An oven dried, mag.-stirred, 100 mL RBF was charged with a solution of **2** (0.30 g, 0.056 mmol), bis(triphenylphosphine)palladium(II) dichloride (0.020 g, 0.003 mmol), and copper iodide (0.005 g, 0.003 mmol) in a mixture of freshly distilled tetrahydrofuran (10 mL), triethylamine (15 ml) and diisopropylamine (5 ml). 2-Ethyl-5-hexylthiophene (**1**) (0.45 g, 0.224 mmol) was then added and the mixture heated at 80 °C for 16 hours. After completing the reaction, the solution was poured into methanol to collect the precipitates. The crude solid was purified by recrystallization from acetone to give **4** as reddish crystals. Yield 0.30 g, 71 %.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) : $\delta(\text{ppm})$ 8.72 (s, 2H), 8.56 (d, $J = 9.0$ Hz, 2H), 7.81 (d, $J = 7.8$ Hz, 4H), 7.64 (d, $J = 9.0$ Hz, 2H), 7.49-7.44 (m, 6H), 7.22 (d, $J = 3.5$ Hz, 2H), 6.73 (d, $J = 3.5$ Hz, 2H), 2.85 (t, 4H), 1.72-1.66 (m, 4H), 1.40-1.25 (m, 12H), 0.92-0.88 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta(\text{ppm})$ 148.96, 132.53, 131.84, 131.75, 131.45, 130.22, 129.10, 128.85, 128.57, 127.39, 124.38, 123.10, 121.72, 120.30, 118.18, 102.97, 93.13, 85.81, 85.52, 31.54, 30.28, 28.73, 22.58, 14.10. HR-MS (EI) m/z (M^+): Calcd for $\text{C}_{54}\text{H}_{46}\text{S}_2$, 758.30; found, 758.31. Anal. Calcd. for $\text{C}_{54}\text{H}_{46}\text{S}_2$: C, 85.44 ; H, 6.11 ; S, 8.45 found : C, 85.23; H, 6.02; S, 8.58.

Synthesis of 5,5'-(9,10-bis((4-hexylphenyl)ethynyl)anthracene-2,6-yl-diyl)bis(ethyne-2,1-diyl)bis(2-hexylthiophene), 5: The preparation method is identical with that of **6**. Instead of 2,6-dibromo-9,10-bis(phenylethynyl)anthracene, **2**, 2,6-dibromo-9,10-bis((4-hexylphenyl)ethynyl)anthracene, **3** was employed. After completing the reaction, the solution was poured into methanol to collect the precipitates. The crude solid was purified by recrystallization from acetone to give **5** as reddish crystals. Yield 0.65 g, 87 %.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta(\text{ppm})$ 8.73 (s, 2H), 8.57 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.2$ Hz, 4H), 7.63 (d, $J = 9.0$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 4H), 7.21 (d, $J = 3.5$ Hz, 2H),

6.72 (d, $J = 3.5$ Hz, 2H), 2.85 (t, 4H), 2.70 (t, 4H), 1.72-1.63 (m, 8H), 1.39-1.25 (m, 24H), 0.92 (t, 12H). ^{13}C NMR (100 MHz, CDCl_3): $\delta(\text{ppm})$ 148.90, 144.16, 132.48, 131.74, 131.45, 130.31, 128.99, 128.69, 127.46, 124.35, 121.60, 120.35, 120.23, 118.26, 103.26, 93.19, 85.39, 85.28, 36.04, 31.73, 31.54, 31.31, 30.29, 28.97, 28.73, 22.63, 22.58, 14.14, 14.10. HR-MS (EI) m/z (M^+): Calcd for $\text{C}_{66}\text{H}_{70}\text{S}_2$, 926.49; found, 926.49. Anal. Calcd. for $\text{C}_{66}\text{H}_{70}\text{S}_2$: C, 85.48 ; H, 7.61 ; S, 6.92 found : C, 85.50 ; H, 7.74 ; S, 6.87.

S2. Instrumentation

^1H NMR spectra were recorded on a Varian Mercury NMR 400Hz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. High resolution mass analysis was performed on a JMS-700 MStation mass spectrometer (JEOL, resolution 60,000, m/z range at full sensitivity 2,400).

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 (temperature rate $10^\circ\text{C}/\text{min}$ under N_2). The redox properties of X-shaped

molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were coated on a platinum plate using chloroform as a solvent. The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in a freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s.

The grazing-incidence X-ray diffraction (GI-XRD) measurements were performed at the 8C1 and 3C2 beam line (wavelength ~ 1.54 Å) at the Pohang Accelerator Laboratory (PAL). The measurements were obtained in a scanning interval of 2θ between 3° and 35° . The film samples were fabricated by drop-casting on silicon wafer, followed by drying at 50°C under vacuum (solvent: chloroform, conc. of the solution: 10 mg/mL)

Atomic force microscopy (Digital Instruments Multimode equipped with a nanoscope IIIa controller) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. The film samples were fabricated by spin-coating (1500 rpm) on silicon wafer followed by drying at 50°C under vacuum (solvent: chloroform, conc. of the solution: 10 mg/mL)

In order to study absorption behavior, the films of two molecules were fabricated on quartz substrates as follows. The solution (3 wt%) of each molecule in chloroform

was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 50°C for 24 hours under vacuum. Absorption spectra of samples in a film and solution state (chloroform, conc. 1×10^{-5} mole/L) were obtained using a UV-VIS spectrometer (HP 8453, photodiode array type) in the wavelength range of 190-1100 nm.

S3. OTFT Fabrication

For the characterization of TFT performance, bottom gate top contact device geometry was employed. On the heavily n-doped Si/SiO₂ substrate the spin-coated films (thickness ~40-50 nm) of **1** and **2** were prepared with chloroform as a solvent. Surface modification was carried out with octyltrichlorosilane (OTS) to make hydrophobic dielectric surface. Source and drain electrodes were then thermally evaporated (100nm) through shadow mask with channel width and length of 1500 μm and 150 μm (or 100 μm), respectively. All the field effect mobilities were extracted in the saturation regime using the relationship $\mu_{sat} = (2I_{DS}L)/(WC(V_g - V_{th})^2)$, where I_{DS} means saturation drain current, C is capacitance of SiO₂ dielectric, V_g is gate bias, and V_{th} is threshold voltage. The device performance was evaluated in air using Keithley 237 high voltage sourcemeter at ambient conditions.

S4. ^1H and ^{13}C NMR spectra of 1

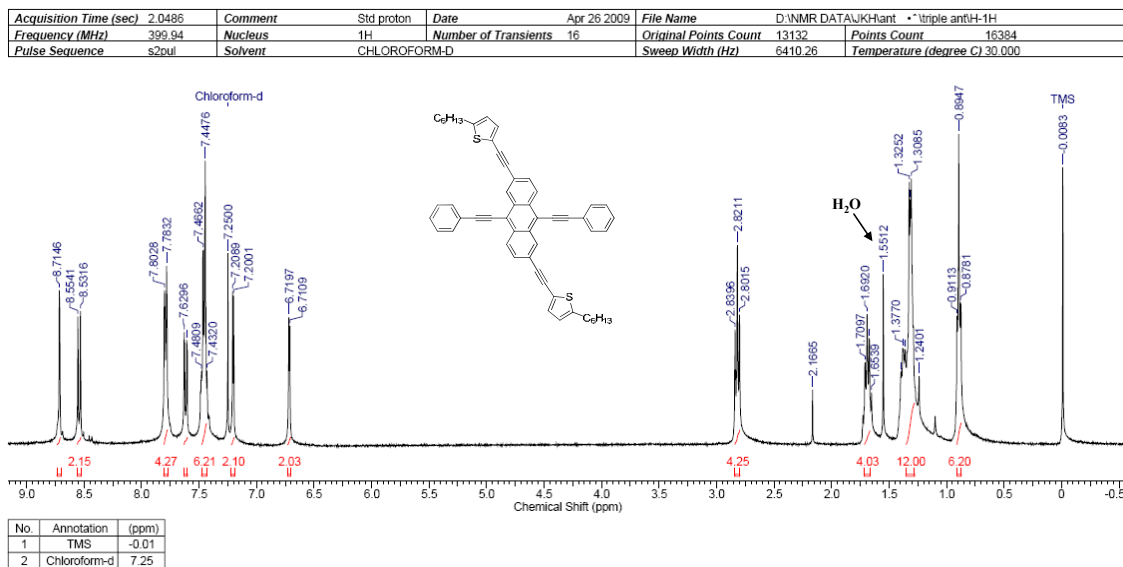


Figure 1S. ^1H NMR spectrum of 1.

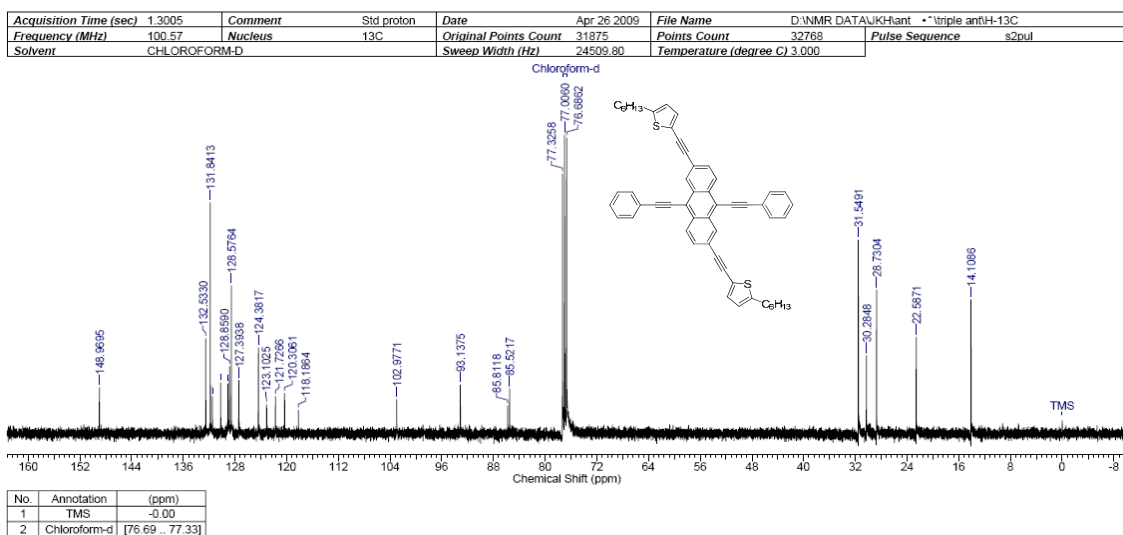


Figure 2S. ^{13}C NMR spectrum of 1.

S5. ^1H and ^{13}C NMR spectra of 2

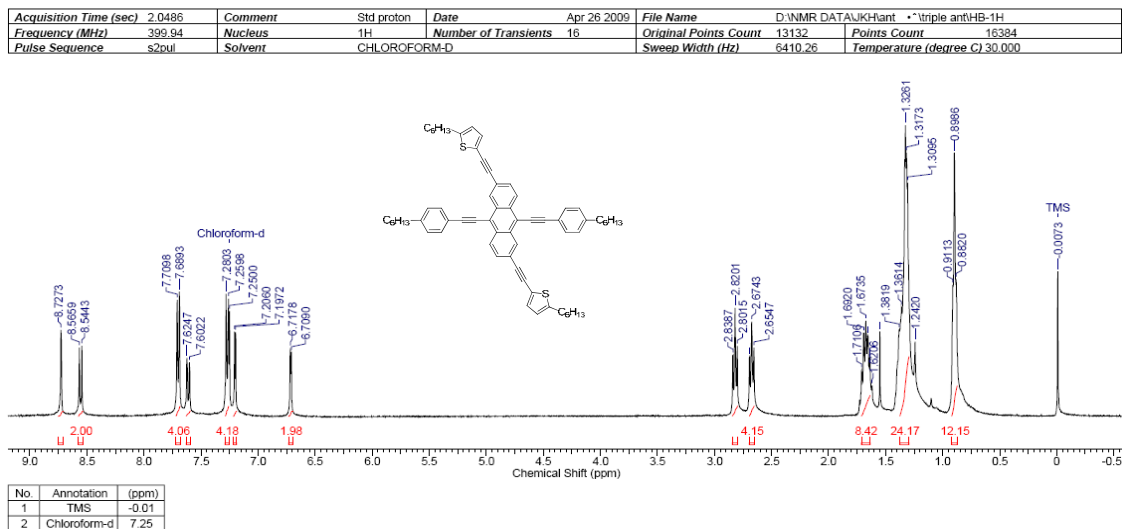


Figure 3S. ^1H NMR spectrum of 2.

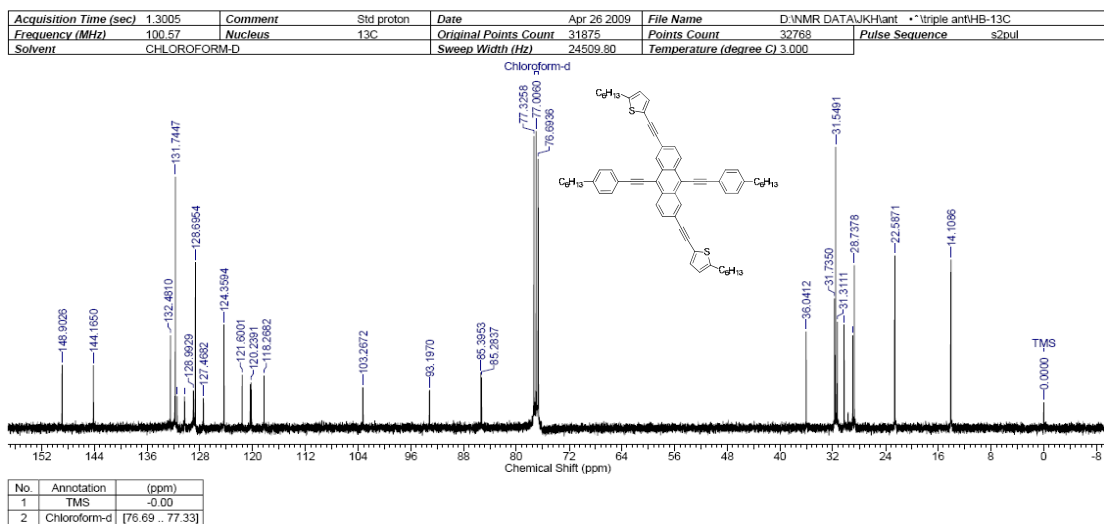
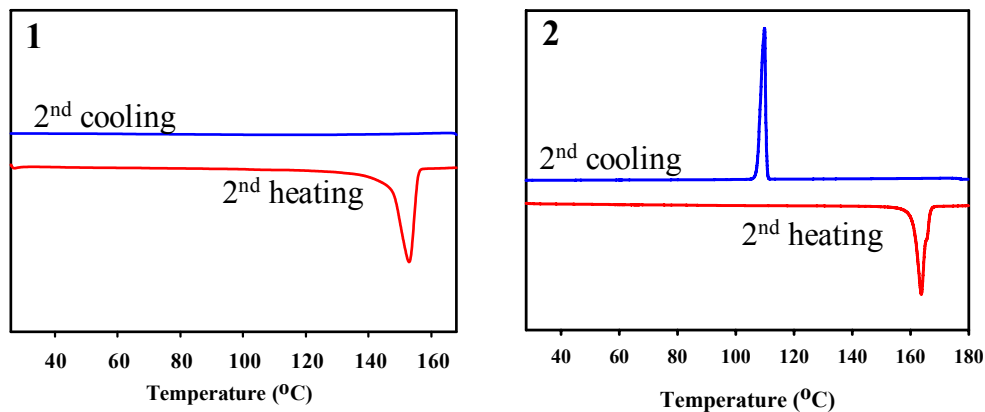


Figure 4S. ^{13}C NMR spectrum of 2.

S6. Thermal analysis data: DSC



	1	2
T_d	409°C	426°C
T_m	153°C	164°C
T_c	—	110°C

Figure 5S. DSC traces of 1 and 2 during heating and cooling cycles.

DSC measurements (Mettler, DSC821^e temperature rate 5°C under N₂) were carried out in a heating (cooling) cycle. Molecule 1 showed a monotropic behavior having melting behavior during heating cycle only, which is coincided with the results of XRD; Molecule 2 showed an amphotropic behavior having a melting temperature during heating cycle and a crystallization temperature during cooling cycle. (see Figure 1S)

S7. CV analysis data

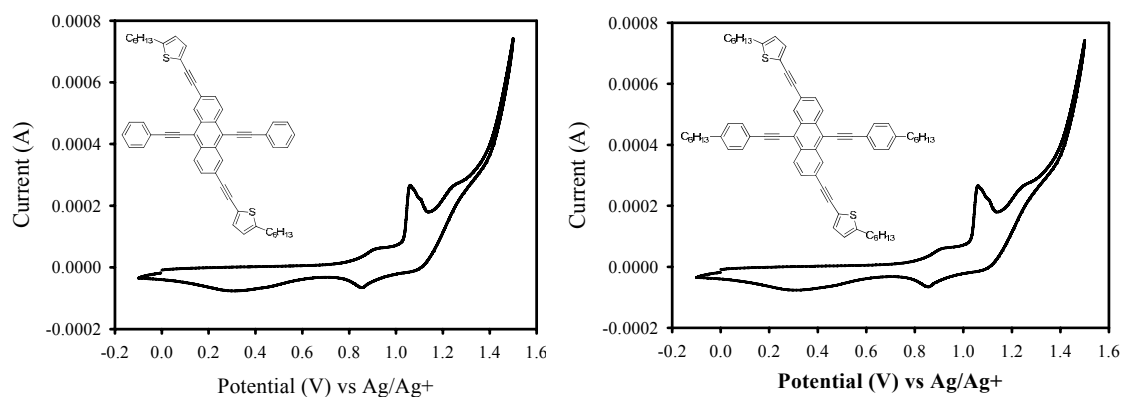


Figure 6S. Cyclic voltammograms of 1 and 2 in solid states.

S8. AFM Topography.

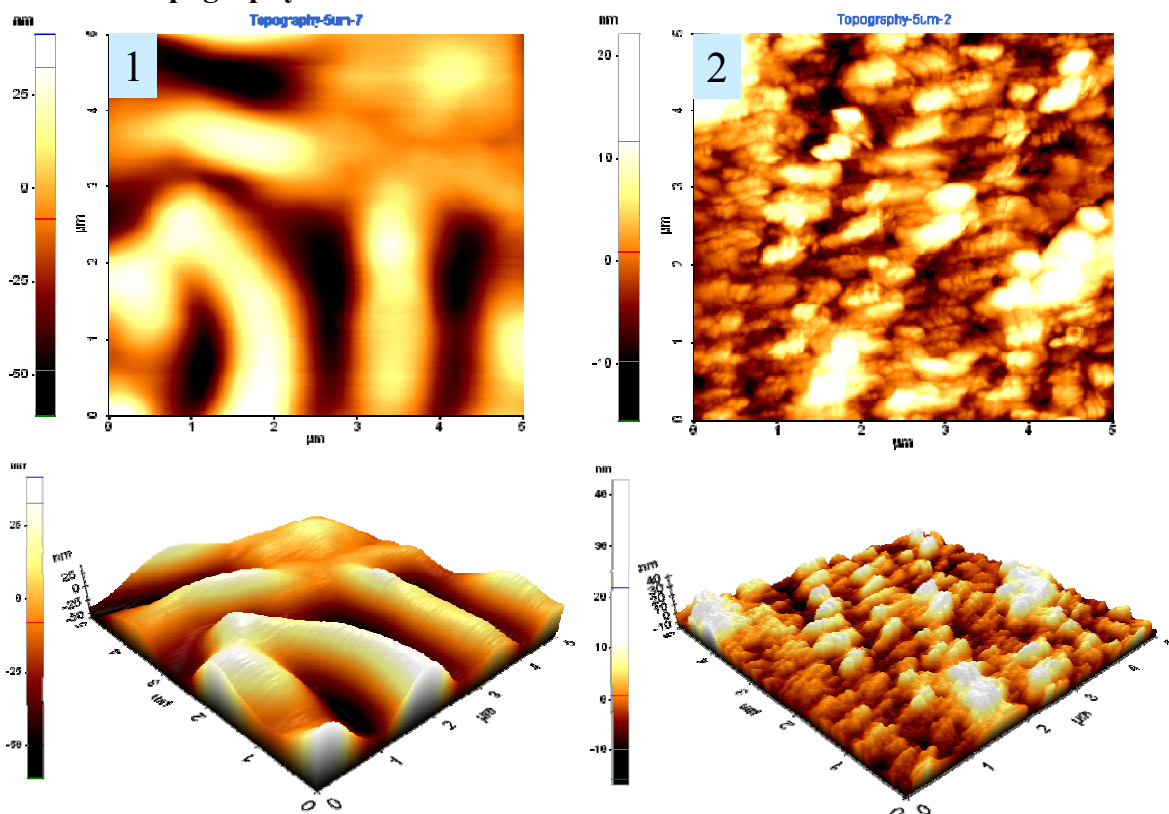


Figure 7S. AFM topography(2D and 3D) images of 1 and 2. *Sample: as-spun film.

(5 μm x 5 μm).

S9. XRD and GI-XRD results

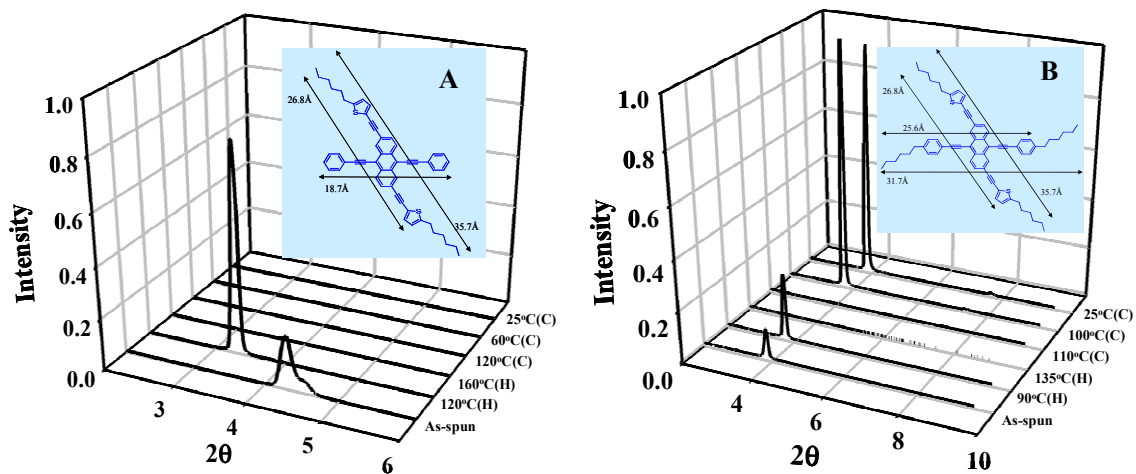


Figure 8S. XRD patterns of spin-coated thin films of **1** (A) and **2** (B) at different temperature during heating and cooling cycle. *(solid line) as-spun film, (dotted line) after annealing at 120°C for 20 min. Molecule **1** showed a monotropic behavior having melting behavior during heating cycle only, which is coincided with the DSC results; Molecule **2** showed an amphotropic behavior having a melting behavior during heating cycle and a crystallization temperature during cooling cycle.

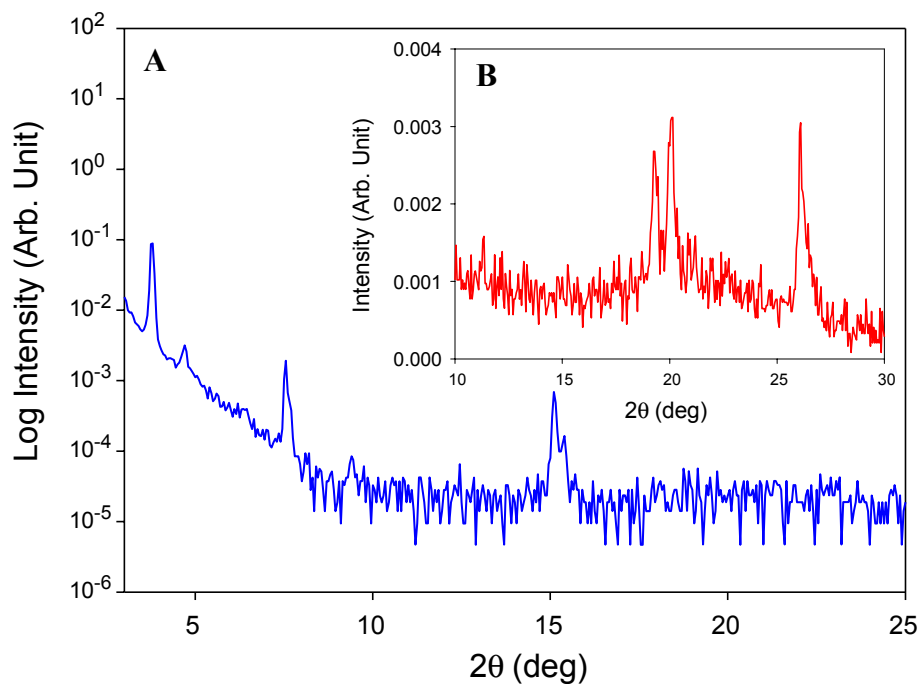


Figure 9S. GI-XRD patterns of **1**. (A) Out-of-plane and (B) In-plane diffraction scattering. The comparison of two diffractograms gives the absolute information of edge-on orientation of the molecules.

References

- 1 P. Hodge, G. A. Power and M. A. Rabjohns, *Chem. Commun.*, 1997, 73.