

Acetylenic Spacers in Phenyl end-Substituted Oligothiophene Core for Highly Air-Stable Organic Field-Effect Transistors.

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S1. Experimental

S1.1 Synthesis

Toluene and diisopropylamine were respectively distilled under calcium hydride and potassium hydroxide under nitrogen prior to use. Copper iodide was dried under vacuum and stored under nitrogen before use. Phenylacetylene, N-iodosuccinimide, triphenylphosphine, bis(triphenylphosphine) dichloropalladium were purchased (Alfa and Aldrich) and used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker AC 400. Chemical shifts (in δ units, ppm) were referenced to TMS using CHCl_3 ($\delta=7.27$ ppm) and CDCl_3 ($\delta=77.70$ ppm) as internal standards respectively for ^1H and ^{13}C spectra. IR spectra were recorded on a Perkin Elmer 1000 spectrophotometer and absorption spectra on a Hewlett Packard 8453 spectrophotometer. Melting points were measured with an Electrothermal 9100 apparatus. Mass spectrometry was carried out on a JEOL JMS-DX 300 apparatus using FAB^+ ionisation mode.

5,5'-Diiodo-2,2'-bithiophene

In a 250 mL two necked round-bottom flask, 6 mmoles (1g) of bithiophene and 12.10 mmoles (2,72 g) of N-iodosuccinimide were introduced under nitrogen in 50 mL of chloroform-acetic acid (1:1) mixture. After 30 minutes stirring at room temperature, the medium was warmed at 60°C for 30 minutes and then kept under stirring at room temperature for 12 hours. It was diluted with 50 mL of chloroform and treated with 50 mL of a (1M) sodium hydroxide solution and with 50 mL of a 10% sodium sulfite solution. The reaction mixture was extracted with dichloromethane (3×50 mL) and the combined organic phases were washed with a saturated sodium chloride solution. After drying over sodium sulphate and filtration, it was concentrated and the obtained crude brown solid was then recrystallized from a chloroform-methanol mixture to give a grey solid in 75% isolated yield (1.88 g). Mp $165\text{-}166^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.14 (d, 2H, H_{Th} , $J=3.79$ Hz), 6.79 (d, 2H, $J=3.79$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 206.9, 142.0, 137.6, 125.5; IR (KBr, cm^{-1}) 3450, 1636, 1495, 1410, 1057, 943, 865, 793, 788, 454. MS (FAB^+) m/z (%): 419 [M+1]. The spectral data agree with those reported in the literature.^{1,2}

5,5''-Diiodo-2,2':5',2''-terthiophene

This compound was prepared according to the same procedure as 5,5'-diiodo-2,2'-bithiophene involving 3.60 mmoles (0.90 g) of terthiophene, 7.20 mmoles (1.63 g) of N-iodosuccinimide, and 20 mL of a chloroform-acetic acid (1:1) mixture. After treatment and purification, a yellow-green solid was obtained in 88 % yield (1.60 g). ^1H NMR (400 MHz, CDCl_3) δ 7.16 (d, 2H, $J=3.80$ Hz), 7.00 (s, 2H), 6.84 ((d, 2H, $J=3.80$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 138.1, 128.2, 125.5, 125.0, 124.6, 124.2; MS (FAB^+) m/z (%): 500 [M].

5,5''-Bis(2-phenylethynyl)-2,2'-bithiophene (diPhAc-2T)

In a 250 mL round-bottom flask, 3.60 mmoles (1.5 g) of 5,5'-diiodo-2,2'-bithiophene, 7.3 mmoles (0.75 g) of phenylacetylene, 51 mg of bis(triphenylphosphine) dichloropalladium (2 mol %), 34 mg of copper iodide (5 mol %), 75 mg (0.28 mmoles, 8 mol %) of triphenylphosphine, and 45 mL of freshly distilled diisopropylamine were introduced under nitrogen in 90 mL of anhydrous toluene. The medium was stirred at 70°C for three days. After cooling, the diisopropylammonium salts were filtered off and washed with toluene. The filtrate was then concentrated under vacuum, the residue was purified by silica gel chromatography using cyclohexane as an eluent and compound **diPhAc-2T** was obtained as a bright yellow solid in 85 % isolated yield (1.13 g). Mp $167\text{-}169^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (m, 4H, H_{Ph}), 7.34 (m, 6H, H_{Ph}), 7.18 (d, 2H, H_{Th} , $J=3.80$ Hz), 7.09 (d, 2H, H_{Th} , $J=3.80$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 138.0 (C_{Ph}), 132.8 (C_{Ph}), 131.4 (C_{Th}), 128.5 (C_{Th}), 128.4 (C_{Th}), 124.0 (C_{Th}), 122.7 (C_{Ph}), 122.6 (C_{Ph}), 94.5 ($\equiv\text{C}$), 82.4 ($\equiv\text{C}$); IR (cm^{-1}) 3409, 3047, 2193, 1590, 1512, 1483, 1435, 1244, 1177, 1045, 1025, 910, 875, 797, 786, 749, 657; MS (FAB^+) $m/z=366$ [M]; MSHR: Calcd for $\text{C}_{24}\text{H}_{14}\text{S}_2$: 366.0537, Found: 366.0544; UV (THF/nm) λ_{max} (log ϵ): 385 (4.81).

5,5''-Bis(2-phenylethynyl)-2,2':5',2''-terthiophene (diPhAc-3T)

Compound **diPhAc-3T** was prepared according to the same procedure as **diPhAc-2T** involving 3 mmoles (1.50 g) of 5,5''-diiodo-2,2':5',2''-terthiophene, 6 mmoles (0.61 g) of phenylacetylene, 42 mg of bis(triphenylphosphine) dichloropalladium (2 mol %), 28 mg of copper iodide (5 mol %), 63 mg (0.24 mmoles, 8 mol %) of triphenylphosphine, 45 mL of freshly distilled diisopropylamine and 90 mL of anhydrous toluene. After treatment and chromatographic purification, **diPhAc-3T** was isolated as an orange solid in 72% isolated yield (0.97 g). Mp $186\text{-}187^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (m, 4H, H_{Ph}), 7.35 (m, 6H, H_{Ph}), 7.18 (d, 2H, H_{Th} , $J=3.80$ Hz), 7.10 (s, 2H, H_{Th}), 7.08 (d, 2H, H_{Th} , $J=3.80$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 138.3 (C_{Ph}), 136.1 (C_{Th}), 128.4 (C_{Ph}), 128.3 (C_{Th}), 122.7 (C_{Ph}), 122.2 (C_{Th}), 94.5 ($\equiv\text{C}$), 90.1 ($\equiv\text{C}$); IR (cm^{-1}) 3549, 3417, 3047, 2922, 2856, 2191, 1620, 1505, 1439, 1258, 1096, 1063, 1027, 912, 855, 799, 749, 687; UV (THF/nm) λ_{max} (log ϵ): 414 (4.94). Anal. Calcd for $\text{C}_{28}\text{H}_{16}\text{S}_3$ (%): C 75.0 ; H 3.6, Found (%): C 74.3 ; H 3.1.

S1.2 Physicochemical measurements in solution

UV-visible absorption and fluorescence emission spectra were obtained on a Varian Cary 1E spectrophotometer and a Varian Cary Eclipse spectrofluorimeter, respectively. Corrected emission spectra were obtained on dilute solutions (CH_2Cl_2 , conc. $< 10^{-5}$ M) upon excitation at the absorption maximum wavelength.

Supplementary Material (ESI) for *PCCP*
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Cyclic voltammetric (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrodes system based on a platinum (Pt) working electrode (diameter 1.6 mm), a Pt counter electrode and an Ag/AgCl (with 3 M NaCl filling solution) reference electrode were used. Tetrabutylammonium hexafluorophosphate (TBHP) (Fluka) was used as received and served as supporting electrolyte (0.1 M). All experiments were carried out in anhydrous 1,2-dichlorobenzene (electronic grade purity) at 20°C. $E_{1/2}$ values were determined from the cyclic voltammogram at a concentration of 1×10^{-3} M with a scan rate of $250 \text{ mV} \cdot \text{s}^{-1}$. Ferrocene was used as internal standard.

S1.3 Theoretical details

The electronic properties of **DSnTs** and **diPhAc-nTs** ($n = 2, 3$) were determined at the Density Functional Theory (DFT) level, with a 6-311G** split-valence basis set (Gaussian03 package)³, combined to an hybrid potential including both Becke and Hartree–Fock exchange and Lee Yang and Parr correlation (B3LYP) in gas phase.⁴ All relaxed geometries calculations have been characterized by frequencies calculations.

S1.4 Film characterizations

Scanning electronic microscopy (SEM) pictures were realized by a JEOL field emission gun scanning electron microscope (FEG-SEM, model JSM 6320F). Atomic force microscopy (AFM) measurements were done on thin films in air with a SII NanoTechnology inc., S-image operating in the tapping mode. The used cantilever was made of silicon, the resonance frequency was 100 kHz. Furthermore, thin films were analyzed by X-ray film diffractometry (XRD) where thin films of **diPhAc-2T** and **diPhAc-3T** were fabricated by vacuum deposition in a pressure of 5×10^{-5} Pa using K-cell type crucible. Si wafers (covered by SiO₂ layer 300 nm thick) were used as substrates. The deposition rate and final film thickness were 0.83-1.2 Å/s and 10, 50 or 100 nm, respectively. The substrate temperature (T_{sub}) was controlled to be 25, 50 or 80°C. The as-deposited thin films were characterized using X-ray diffraction in air using an X-ray diffractometer (Regaku Co., ATX-G) which was specially designed for characterization of thin films. Both in-plane and out-of-plane diffractions could be measured, because the goniometer has not only conventional $\theta/2\theta$ axes but also in-plane $\theta/2\theta_{\chi}$ axes. The used wavelength of X-ray in the experiments was 0.1542 nm.

S1.5 OTFTs fabrication

The Bottom-Gate Top-Contact (BGTC) configuration was used for the OTFT devices based on **diPhAc-2T** and **diPhAc-3T** derivatives. Highly n-doped silicon wafers (gate), covered with thermally grown silicon oxide SiO₂ (3000 Å, insulating layer), were purchased from Vegatec (France) and used as device substrates. These substrates were used without dielectric surface treatments (bare) or treated with hexamethyldisilazane (HMDS). HMDS treatment was carried out by immersing the Si/SiO₂ in a pure HMDS at room temperature overnight. The capacitance per unit area of either untreated or HMDS-modified silicon dioxide dielectric layers was $1.2\text{-}1.3 \times 10^{-8} \text{ F/cm}^2$. The semiconductor layer was vacuum deposited onto the insulating layers, using an Edwards Auto 306 apparatus, under a pressure of $1\text{-}2 \times 10^{-4}$ Pa to a nominal thickness of 50 nm as determined with an in situ quartz crystal monitor. A deposition rate of 1.2 and 0.83 Å/s was used for **diPhAc-2T** and **diPhAc-3T**, respectively. Substrate temperature (T_{sub}) during deposition was controlled to be 25°C or by heating the block on which the substrates are mounted ($T_{\text{sub}} = 50$ and 80°C). The Au source and drain electrodes (channel length $L = 50 \mu\text{m}$, channel width $W = 1 \text{ mm}$) were evaporated on top of the organic thin film through a shadow mask. Current-voltage characteristics were obtained with a Hewlett-Packard 4140B pico-amperemeter-DC voltage source at room temperature in air and/or under moderate vacuum (36-40 Pa). The source-drain current (I_{D}) in the saturation regime is governed by the equation:

$$(I_{\text{D}})_{\text{sat}} = (W/2L) C_i \mu (V_{\text{G}} - V_{\text{t}})^2 \quad (1)$$

where C_i is the capacitance per unit area of the gate insulator layer, V_{G} is the gate voltage, V_{t} is the threshold voltage, and μ is the field-effect mobility. The on/off ratio values given in Table 2 and Table S1 were determined from the current I_{D} at $V_{\text{G}} = -100 \text{ V}$ to the current I_{D} at $V_{\text{G}} = +100 \text{ V}$ under a constant drain-source voltage $V_{\text{D}} = -30 \text{ V}$. All the data in Table 2 and Table S1 were obtained by randomly measuring 3-5 individual OTFTs for each substrate temperature.

[1] Q. Meng, J. Gao, R. Li, L. Jiang, C. Wang, H. Zhao, C. Liu, H. Li and W. Hu, *J. Mater. Chem.*, 2009, **19**, 1477.

[2] Z.H. Li, M.S. Wong, H. Fukutani and Y. Tao, *Chem. Mater.*, 2005, **17**, 5032.

[3] M.J. Frisch et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.

[4] W. C. Lee, Y. Weitao and R.G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

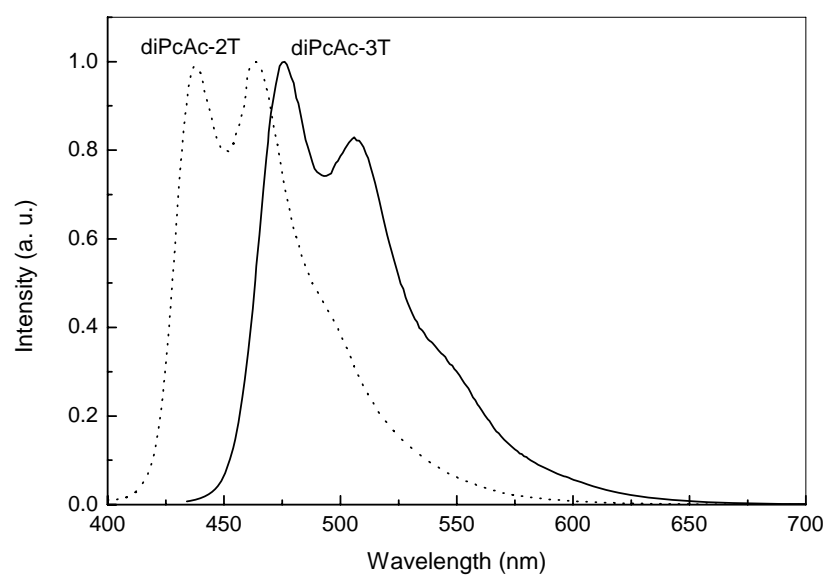
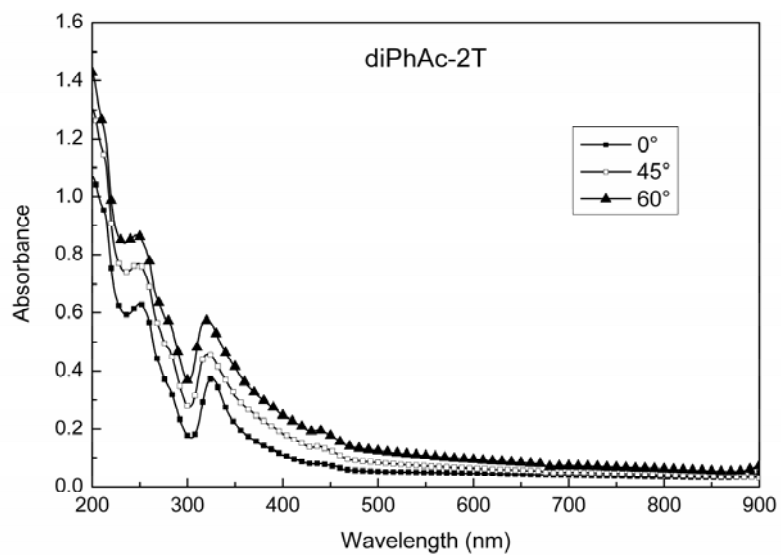


Figure S1: Emission spectra of **diPhAc-2T** and **diPhAc-3T** in CH₂Cl₂.

(a)



(b)

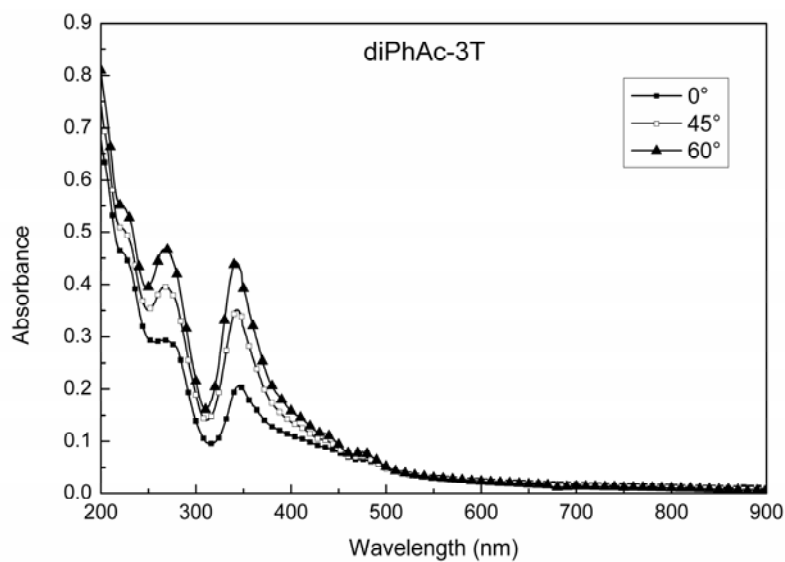
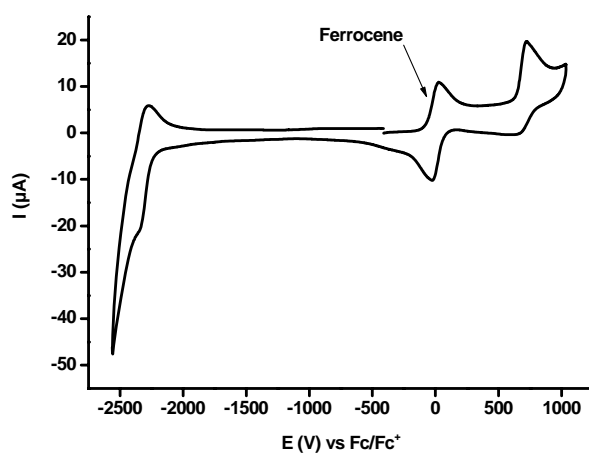


Figure S2: Incidence angles (0° , 45° and 60°) dependence of UV-Vis spectra of **diPhAc-2T** (a) and **diPhAc-3T** (b) based-thin films vacuum deposited at $T_{\text{sub}} = 50^\circ\text{C}$.

(a)



(b)

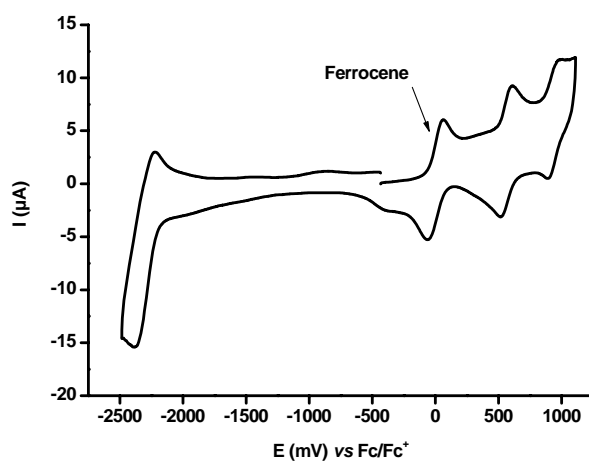
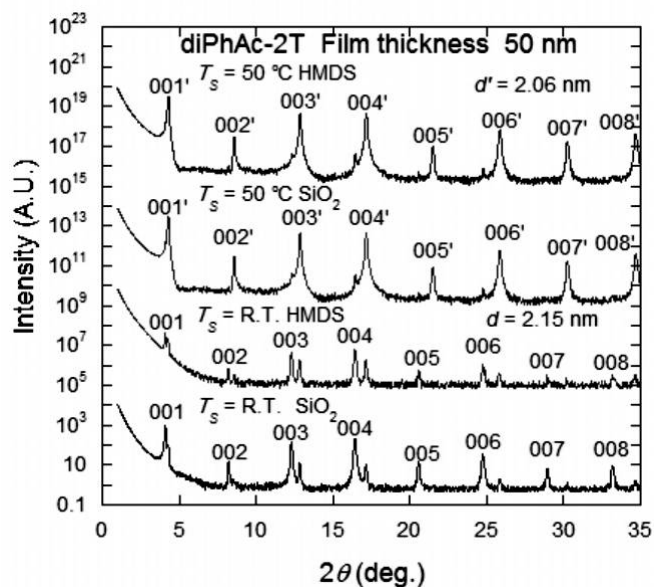


Figure S3: Cyclic voltammograms of **diPhAc-2T** (a) and **diPhAc-3T** (b) at 1.10^{-3} M in 10^{-1} M 1,2-dichlorobenzene/TBHP. $\nu = 250 \text{ mV}\cdot\text{s}^{-1}$.

(a)



(b)

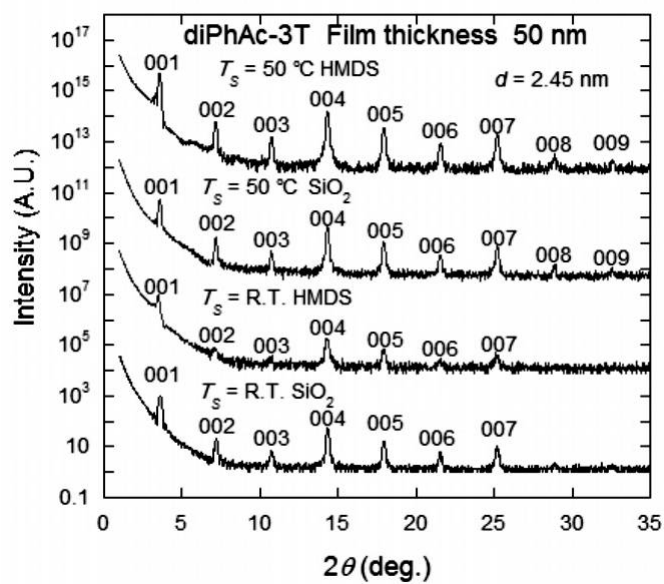
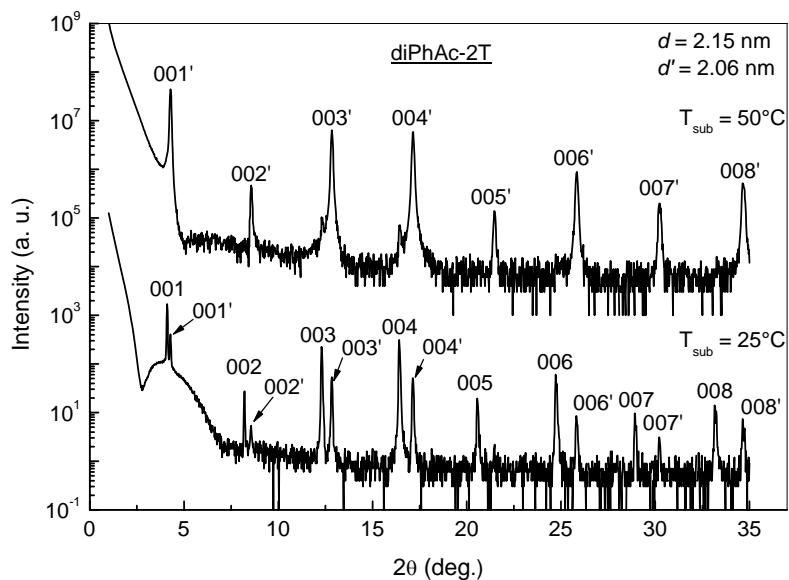


Figure S4: Comparative $\theta/2\theta$ mode of X-ray diffraction patterns of **diPhAc-2T** (a) and **diPhAc-3T** (b) based-thin film deposited at $T_{\text{sub}} = 25^\circ\text{C}$ and 50°C on bare and HMDS-treated Si/ SiO_2 with a nominal thickness of 50 nm.

(a)



(b)

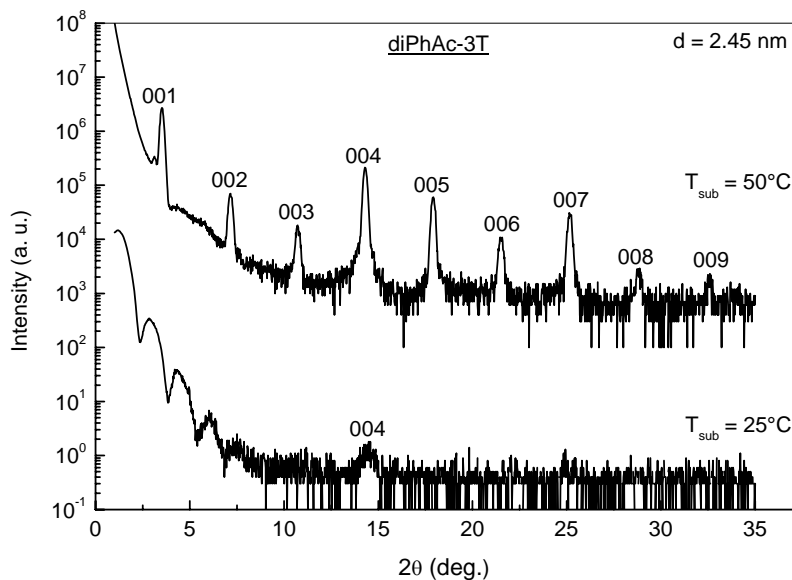
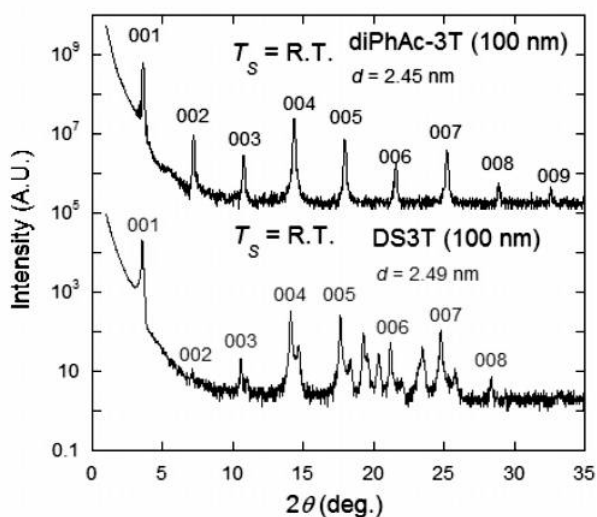


Figure S5: $\theta/2\theta$ mode of X-ray diffraction patterns of **diPhAc-2T** (a) and **diPhAc-3T** (b) based-thin film deposited at $T_{\text{sub}} = 25^\circ\text{C}$ and 50°C on bare Si/SiO₂ with a nominal thickness of 10 nm.

(a)



(b)

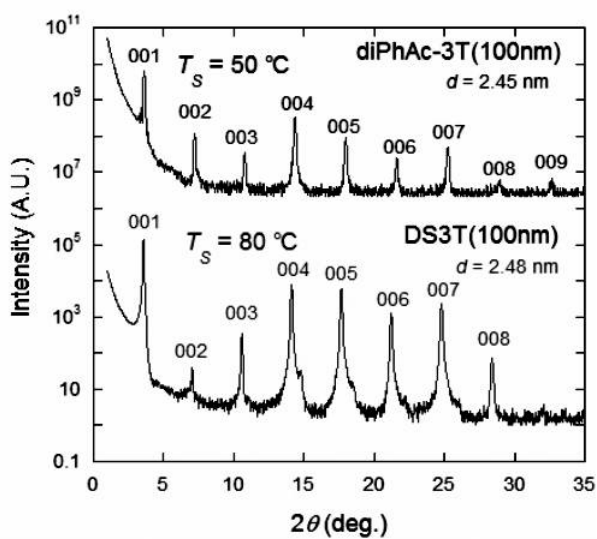
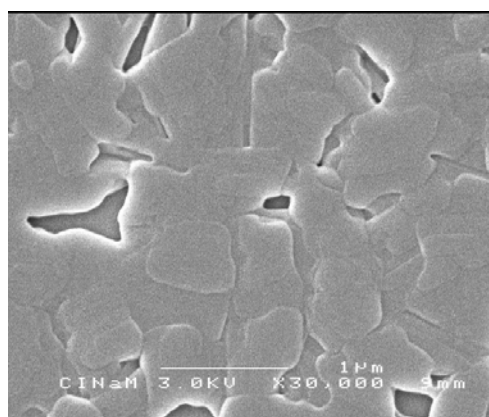
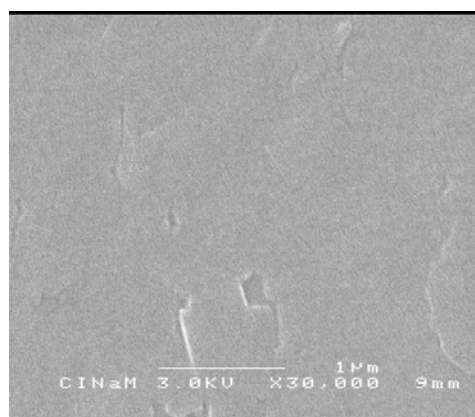


Figure S6: $\theta/2\theta$ mode of X-ray diffraction patterns of **diPhAc-3T** and **DS3T** thin film deposited at $T_{\text{sub}} = \text{RT} = 25^\circ\text{C}$ (a) and $T_{\text{sub}} = 50$ or 80°C (b) on bare Si/SiO₂ with a nominal thickness of 100 nm.



(a)



(b)

Figure S7: SEM pictures of **diPhAc-2T** (a) and **diPhAc-3T** (b) thin films deposited at $T_{\text{sub}} = 25^\circ\text{C}$ on bare Si/SiO₂ with a nominal thickness of 50 nm.

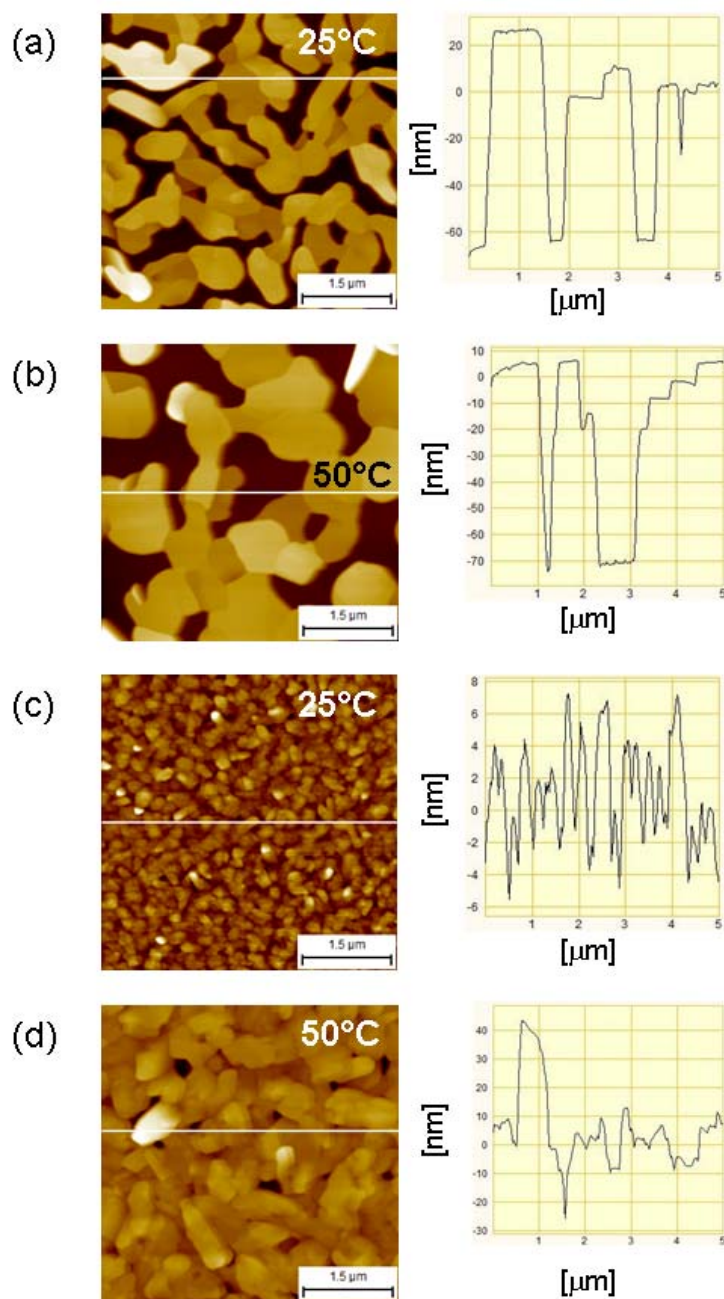


Figure S8: AFM pictures and corresponding AFM profiles of **diPhAc-2T** (a, b) and **diPhAc-3T** (c, d) thin films deposited at $T_{\text{sub}} = 25$ and 50°C on HMDS-treated Si/SiO₂ with a nominal thickness of 50 nm.

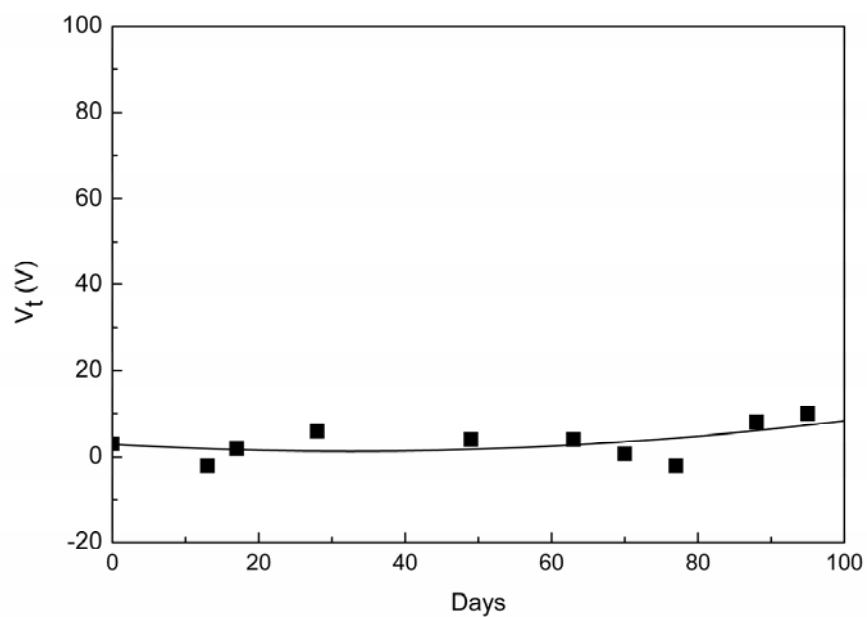


Figure S9: Plot of threshold voltage (V_t) vs storage days for **diPhAc-3T** based-OTFT on bare Si/SiO₂ substrates at $T_{\text{sub}} = 25^\circ\text{C}$.

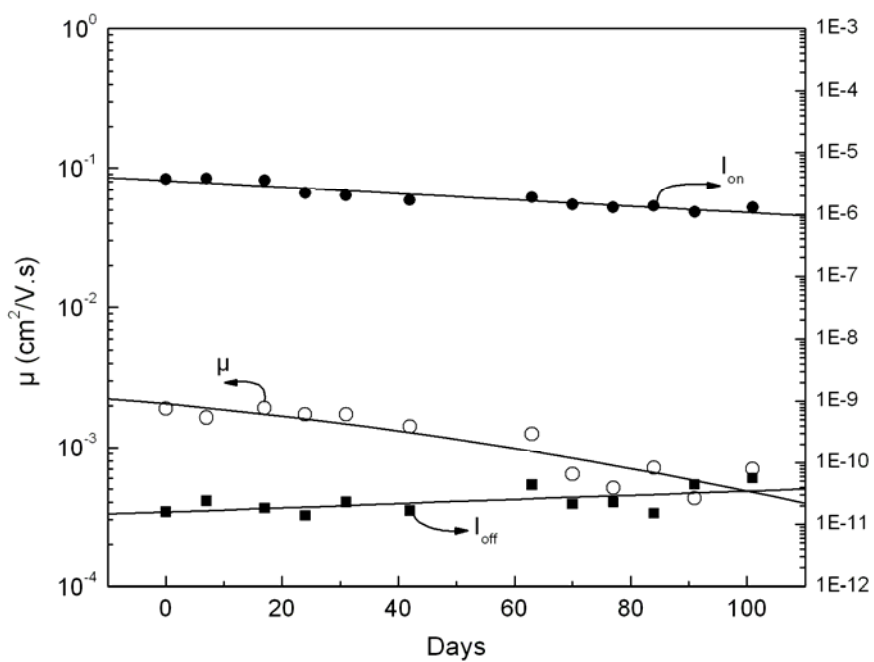


Figure S10: Plots of hole mobility (μ), on current (I_{on}) and off current (I_{off}) vs storage days for a **diPhAc-2T** based-OTFT on bare Si/SiO₂ substrates at $T_{\text{sub}} = 25^\circ\text{C}$.

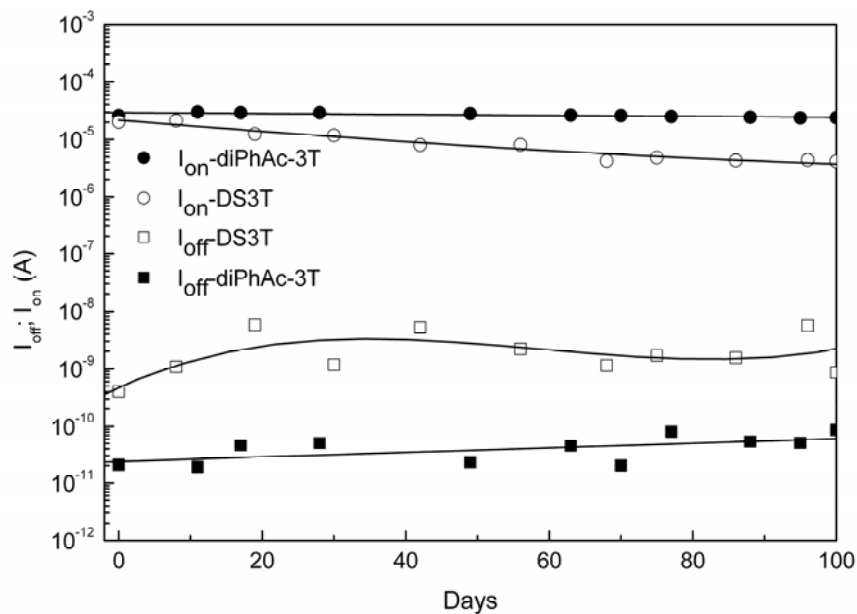


Figure S11: Plots of on current (I_{on}) and off current (I_{off}) vs storage days for **DS3T** and **diPhAc-3T** based-OTFT on bare Si/SiO₂ substrates at $T_{sub} = 25^\circ\text{C}$.

Table S1: OTFT data measured at room temperature in air for **diPhAc-2T** and **diPhAc-3T** deposited on HMDS-treated Si/SiO₂ substrates at different substrate temperatures (T_{sub}).

Oligomer	T_{sub} ($^\circ\text{C}$)	μ (cm^2/Vs)	V_t (V)	I_{on}/I_{off}	S (V/decade)
diPhAc-2T	25	$2.5-9.6 \times 10^{-3}$	(-1)-1.3	$0.5-2.2 \times 10^5$	3-6
	50	$1.4-3.5 \times 10^{-3}$	(-0.7)-8	2×10^5	2-4
	80	$0.3-1.2 \times 10^{-5}$	(-0.7)-36	$1.4-2.8 \times 10^3$	8-13
diPhAc-3T	25	$1.3-4.2 \times 10^{-2}$	1.7-5	$0.4-1 \times 10^6$	3-4
	50	$2.4-3.8 \times 10^{-2}$	(-1.3)-0.5	$4-5.6 \times 10^5$	3-4
	80	$0.8-1 \times 10^{-2}$	19-32	$1-4.7 \times 10^4$	4-6