Supporting information for

Isomerically pure electron-deficient anthradithiophenes and their acceptor performance in polymer solar cells

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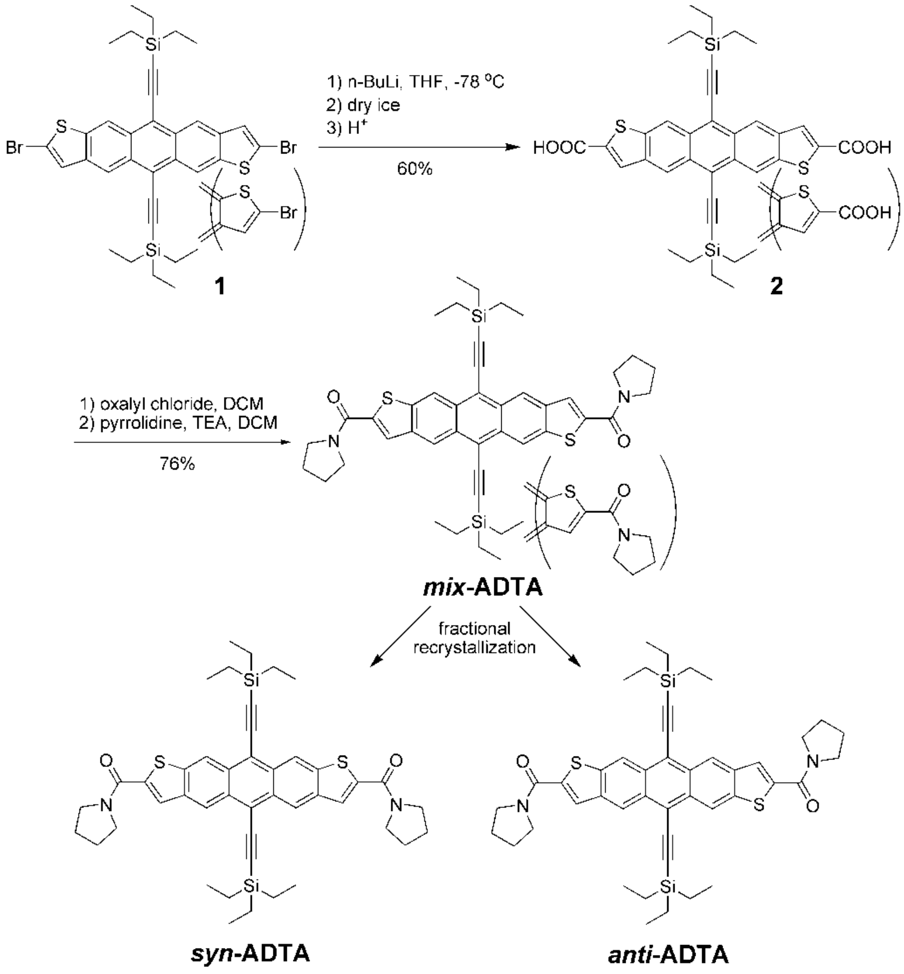
Contents of Supplementary Data

Scheme S1. The synthesis of ***syn*-ADTA** and ***anti*-ADTA**



Experimental section

General methods. Solvents were purchased from Pharmco-Aaper and used without further purification. Dry THF was purchased from Aldrich. Commercial silylacetylenes were purchased from GFS Chemicals. All other chemicals were purchased from Aldrich, Alfa Aesar, VWR, TCI or Acros and used as-received. All reactions were carried out in flame-dried glassware under N_2 atmosphere. TLC plates and Silica gel (230–400 mesh) were from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were measured on an Inova-400 NMR spectrometer (Varian) in deuterated solvents using residual solvent signals as the internal reference ($CDCl_3$ at 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C, THF-d8 at 3.58 ppm for ^{1}H and 67.57 ppm for ^{13}C). Mass spectrometry was performed by laser-desorption ionization (LDI) on a JMS-700 T Mass Spectrometer (JEOL). UV-vis spectra in dichloromethane were recorded on a Shimadzu UV-2501PC spectrophotometer at room temperature using a quartz cuvette with a path length of 1 cm. Thin films for UV-vis in solid state were prepared by spin-coating. Electrochemical analysis was performed on a BASi Epsilon potentiostat. The experiments were performed under a stream of nitrogen in a 0.1 M solution of tetra-*n*butylammonium hexafluorophosphate as a supporting electrolyte in dichloromethane (DCM). The experiments were carried out using platinum electrodes (working electrode: BASi MF-2013; auxiliary electrode: a platinum wire) at a scan rate of 100 mVs^{-1} against Ag wire as a pseudoreference electrode at room temperature. Ferrocene was used as a reference oxidation potential.

Dipole moment calculation. The molecular structures of **ADTA**s were simplified by replacing TES groups with SiH_3 groups. Density functional theory (DFT) calculations were performed in the Spartan '08 program package. The geometries of both compounds were optimized at the B3LYP level using a 3-21G* basis set in vacuum using default symmetry constraints.

Crystallographic characterization. X-ray data were collected on a Bruker-Nonius X8 Proteum CCD diffractometer using CuK(alpha) radiation. The structures were solved using SHELXS and refined using SHELXL from the SHELX-97 (Sheldrick, 2008) program package. Molecular fragment editing was performed using the XP program of SHELXTL (Sheldrick, 2008). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens were placed at calculated positions and refined using an appropriate riding model. Minor components of disordered groups required restraints and constraints to ensure proper refinement. In the case of ***anti*-ADTA,** the crystals were all twinned, but the components could be largely separated by cutting. Uncut crystals gave noticeably twinned diffraction images, but appropriately cut crystals appeared to be largely single. For the data collection crystal, there was a small piece of a second component, but it was too small to pose much of a problem beyond contributing a small amount of noise to the major component. (Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122)

Device fabrication and testing.

Planar cells. We fabricated planar-heterojunction solar cell devices with inverted architecture comprising ***syn*-ADTA** and ***anti*-ADTA**. With the planar-heterojunction architecture, we can effectively decouple the effects of phase separation, allowing us to elucidate how the isomeric structure of **ADTAs** affects device performance.[1-3] After cleaning pre-patterned ITO on glass substrates in acetone and isopropyl alcohol, a 1 wt% titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$;

Aldrich; 99.999%) in isopropyl alcohol solution was spin coated on the precleaned substrates. Hydrolysis at room temperature for 1 h and at 170 °C for 1 min yields a 40 nm electron transport layer of titania.[4,5] A 1 wt% **ADTA** solution in toluene was then spin coated directly on the titania layer at 1000 rpm for 1 min. The polymer donor layer was separately prepared and transferred onto the electron acceptor layer with the use of a poly(dimethyl siloxane), PDMS, stamp (Dow Corning Sylgard 184 formulation) according to previously published procedure.[1,6,7] Specifically, a 1.5 wt% P3HT solution in chlorobenzene was spin coated onto a UV-ozone-treated silicon wafer. A PDMS stamp was then brought into contact with P3HT. The entire assembly was then soaked in water, resulting in the transfer of P3HT onto the PDMS stamp. The transferred P3HT film was then laminated onto **ADTA** layer. Upon removal of the PDMS stamp, 100 nm gold was evaporated on the top to complete the fabrication of inverted planar-heterojunction devices. These devices were tested under AM 1.5G 100 mW/cm^2 illumination in air. *J-V* characteristics were acquired after 10 min of illumination; this photo-soaking is necessary in order to pre-fill the shallow electron trap sites in the titania layer prior to testing.[4]

BHJ Cells. Solar cells were fabricated on pre-patterned ITO coated glass substrates, which were cleaned by sonication in a mild detergent, rinsed in de-ionized water, dried in a nitrogen stream, and treated with a 10-minute UV-ozone exposure. PEDOT:PSS was filtered through a 0.45 μm PVDF syringe filter, and then deposited by spin-coating at 6000 rpm for 60 seconds. The PEDOT:PSS layer was baked on a hot-plate at 170 °C for 4 minutes to remove residual solvent. The samples were then transferred into a nitrogen-filled glovebox, in which all subsequent processing steps were carried out. P3HT and **ADTA** were dissolved in toluene at a weight ratio of 10:6 to give a total concentration of 16 mg/ml. The solutions were stirred for 2 days and then spin-coated on top of the PEDOT:PSS layer at 1000 rpm for 60 seconds. Finally, 4 Å of CsF and 400 Å of Al were thermally evaporated under high vacuum (~10^{-6} Torr) to form the cathode for the devices. A shadow mask was used in the evaporation to define a device active area of 3 mm^2. Solar cell current-voltage (I-V) curves were obtained with a Keithley 236 source-measurement-unit (SMU) under AM 1.5 100 mW/cm^2 illumination from a Solar Light 16S-002 solar simulator. Light output power was calibrated using a Newport 818P-010-12 thermopile high power detector, which has a flat response over a broad spectral range. Spectral mismatch was not taken into account in these measurements. Devices were tested as fabricated, and also after a brief thermal annealing at 120 °C for 1 minute. In general, 5 devices were tested per acceptor, and values reported here are averaged over these devices.The EQE measurement was performed using a Newport 1000 W xenon lamp coupled to an Oriel Cornerstone 260 ¼ m monochromator as the light source, a Keithley 236 SMU to measure short circuit current of the test device, and a Newport 918D-UV3-OD3 low power detector to monitor the light intensity.

The mixture of 2,8-dibromo-5,11-bis(triethylsilylethynyl)anthra[2,3-b:6,7-b'] dithiophene and 2,8-dibromo-5,11-bis(triethylsilylethynyl)anthra[2,3-b:7,6-b'] dithiophene (1) was prepared according to literature procedure.[8]

The mixture of 2,8-dicarboxy-5,11-bis(triethylsilylethynyl)anthra[2,3-b:6,7-b'] dithiophene and 2,8-dicarboxy-5,11-bis(triethylsilylethynyl)anthra[2,3-b:7,6-b'] dithiophene (2) To a pre-cooled (-78 ^{o}C) solution of **1** (6.36 g, 8.78 mmol) in dry THF (100 mL) was added 2.5 M *n*-BuLi solution in hexanes (7.38 mL, 18.4 mmol) dropwise. The purple mixture was kept at -78 ^{o}C and stirred for 30 minutes once the addition was complete. It was then poured onto freshly-crushed dry ice and allowed to warm up to room temperature with stirring. The mixture was washed with 5 % HCl, dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was then boiled in chloroform (100 mL) for 4 hours. A black solid was collected using vacuum filtration and thoroughly washed with DCM until the filtrate became slightly pink. After drying in a vacuum oven (60 ^{o}C), **2** was obtained as a black solid (3.45 g, 60 %). ^{1}H-NMR (400 MHz, THF-d8) δ 9.28 (d, J = 4 Hz, 2H), 9.20 (d, J = 4 Hz, 2H), 8.20 (s, 2H), 1.30-1.25 (m, 18H), 1.00-0.94 (m, 12H); ^{13}C-NMR (100 MHz, THF-d8) δ163.66, 142.32, 141.91, 141.24, 140.96, 139.76, 139.55, 131.87, 131.41, 131.17, 131.00, 130.71, 125.26, 125.20, 121.22, 121.14, 119.22, 117.36, 109.53, 108.97, 108.41, 103.95, 8.29, 5.48. HRMS (LDI) m/z (M+ Calc'd: 654.1749, Observed: 654.1766).

The mixture (*mix*-ADTA) of 2,8-di(1-pyrrolidinylcarbonyl)-5,11-bis(triethylsilylethynyl)anthra[2,3-b:6,7-b'] dithiophene (*syn*-ADTA) and 2,8-di(1-pyrrolidinylcarbonyl)-5,11-bis(triethylsilylethynyl)anthra[2,3-b:7,6-b'] dithiophene (*anti*-ADTA) To a suspension of **2** (3.4 g, 5.2 mmol) in DCM (200 mL) was added oxalyl chloride (2.64 g, 20.8 mmol). After stirred for 30 minutes, a few drops of DMF was added. The reaction mixture was stirred at room temperature until all solid was dissolved and a deep blue solution formed (typically after overnight stirring). The solvent was then removed by evaporation and the residue further dried in vacuum to remove excess oxalyl chloride. A deep blue solid was obtained as the crude acid chloride, which was used directly in the next step.

The as-obtained blue solid was redissolved in DCM (150 mL). To the solution was added pyrrolidine (0.81 g, 11.44 mmol) and triethylamine (2.1 g, 20.8 mmol). The blue solution turned into purple upon addition of the amines and was stirred at room temperature for 5 hours. After concentration by rotary evaporation, the residue was loaded onto a thick silica plug and eluted with 10:1 DCM/ethyl acetate to afford purified ***mix*-ADTA** as purple crystals (3.82 g, 76 %).

***mix*-ADTA** was further purified by fractional crystallization using toulene as the solvent.

***syn*-ADTA** was obtained as puple needles (1.35 g, 26.9%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 2H), 9.11 (s, 2H), 7.79 (s, 2H), 3.91 (t, J = 8 Hz, 4H), 3.74 (t, J = 8 Hz, 4H), 2.04 (m, 8H), 1.25 (t, J = 8 Hz, 9H), 1.24 (t, J = 8 Hz, 9H), 0.92 (q, J = 8 Hz, 6H), 0.91 (q, J = 8 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.98, 142.00, 139.72, 139.61, 130.55, 129.68, 125.82, 123.34, 119.85, 119.36, 116.37, 107.91, 107.33, 103.06, 102.91, 49.08, 47.46, 26.71, 24.12, 7.83, 7.79, 4.66. Elem. Anal.: Calcd for $C_{44}H_{52}N_2O_2S_2Si_2$: C, 69.43; H, 6.89; N, 3.68. Found: C, 69.09; H, 6.65; N, 3.72. HRMS (LDI) m/z (M+ Calc'd: 760.3008, Observed: 760.3011).

***anti*-ADTA** was obtained as red blocks (1.02 g, 20.3%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 4H), 7.78 (s, 2H), 3.91 (t, J = 8 Hz, 4H), 3.74 (t, J = 8 Hz, 4H), 2.07 (sextet, J = 4 Hz, 4H), 2.01 (sextet, J = 4 Hz, 4H), 1.24 (t, J = 8 Hz, 18H), 0.92 (q, J = 8 Hz, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.99, 142.23, 139.97, 139.27, 130.16, 130.07, 125.75, 123.32, 119.88, 117.85, 107.62, 102.99, 49.09, 47.46, 26.71, 24.12, 7.81, 4.66. Elem. Anal.: Calcd for $C_{44}H_{52}N_2O_2S_2Si_2$: C, 69.43; H, 6.89; N, 3.68. Found: C, 69.39; H, 6.88; N, 3.71. HRMS (LDI) m/z (M+ Calc'd:760.3008, Observed: 760.3004).

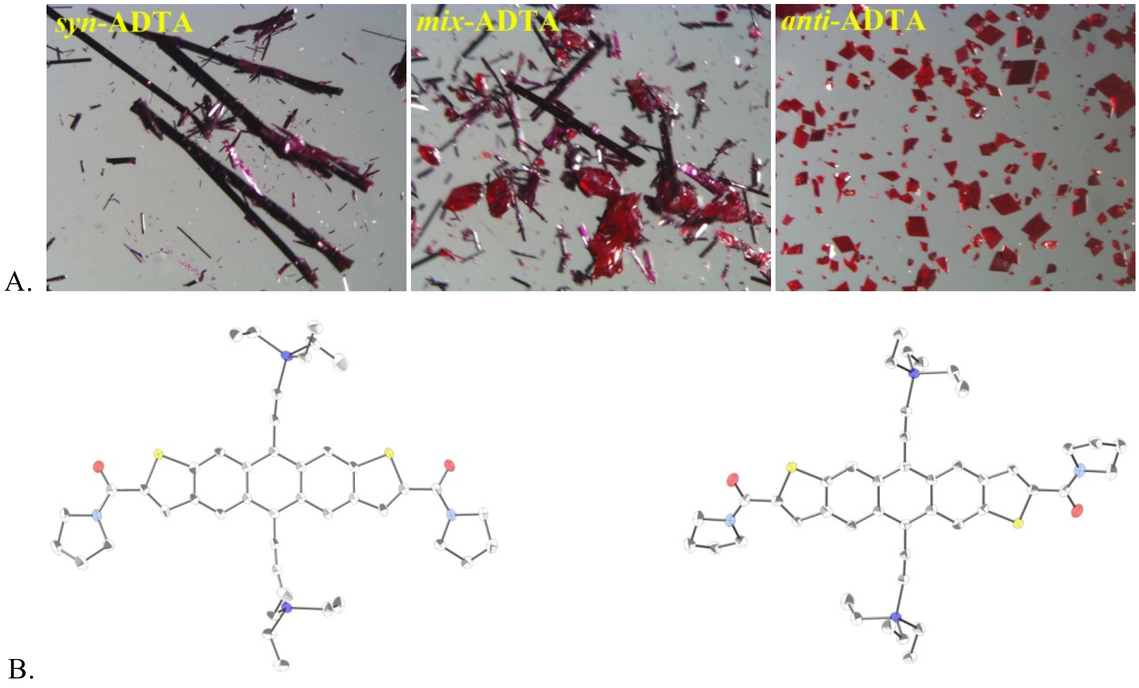
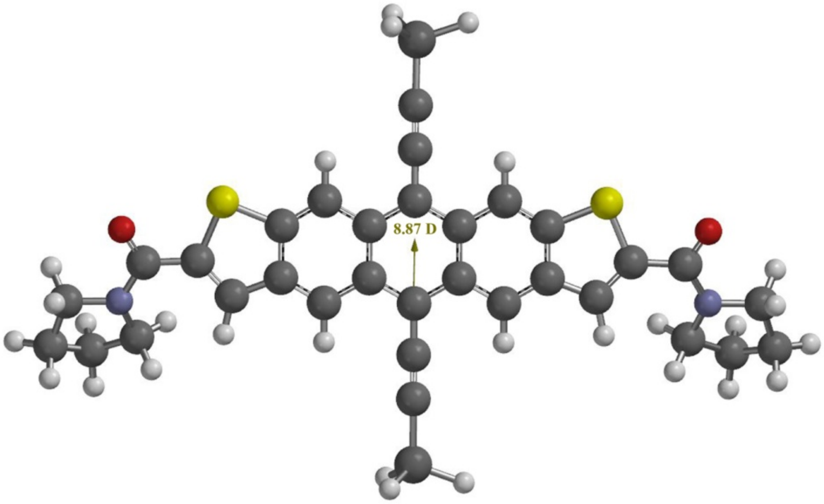
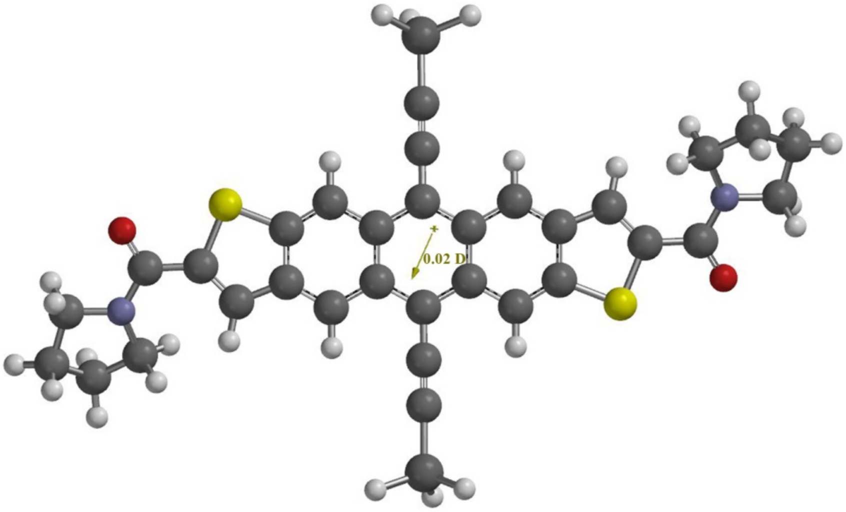


Fig. S1. (A). Optical images of **ADTA** single crystals obtained from toluene solution. Left: *syn*; middle, *mix*; right: *anti*. (B). Thermal ellipsoid (50% probability) plot of **ADTA**s, hydrogen atoms omitted for clarity. C atoms are showed in black, O in red, N in cyan, S in yellow and Si in blue. Left: *syn*; right: *anti*.



A.



B.

Fig. S2. Calculated geometries and dipole moments of ***syn*-SiH3 ADTA** (A) and ***anti*-SiH3 ADTA** (B).

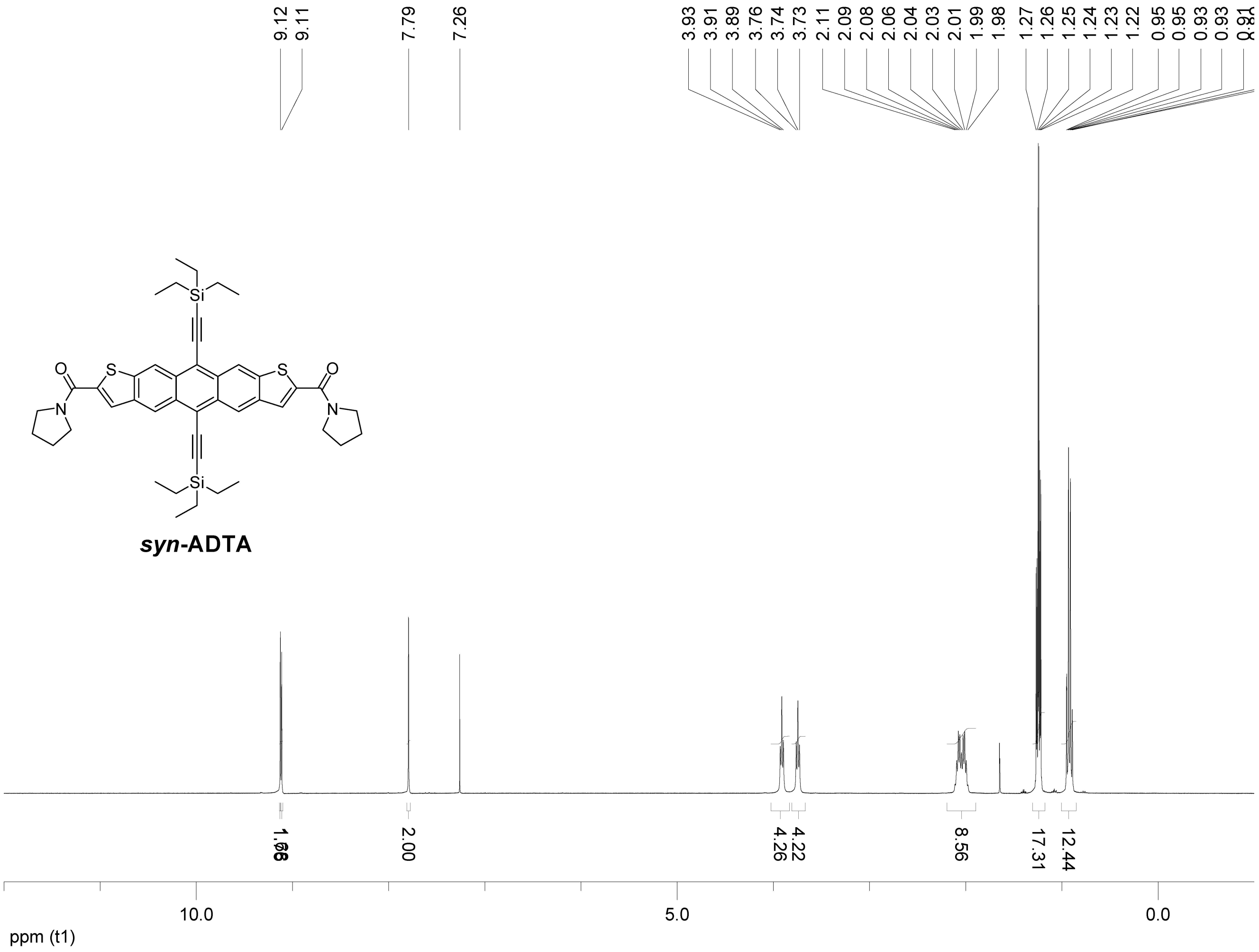


Fig. S3. ^{1}H NMR spectrum of ***syn*-ADTA**.

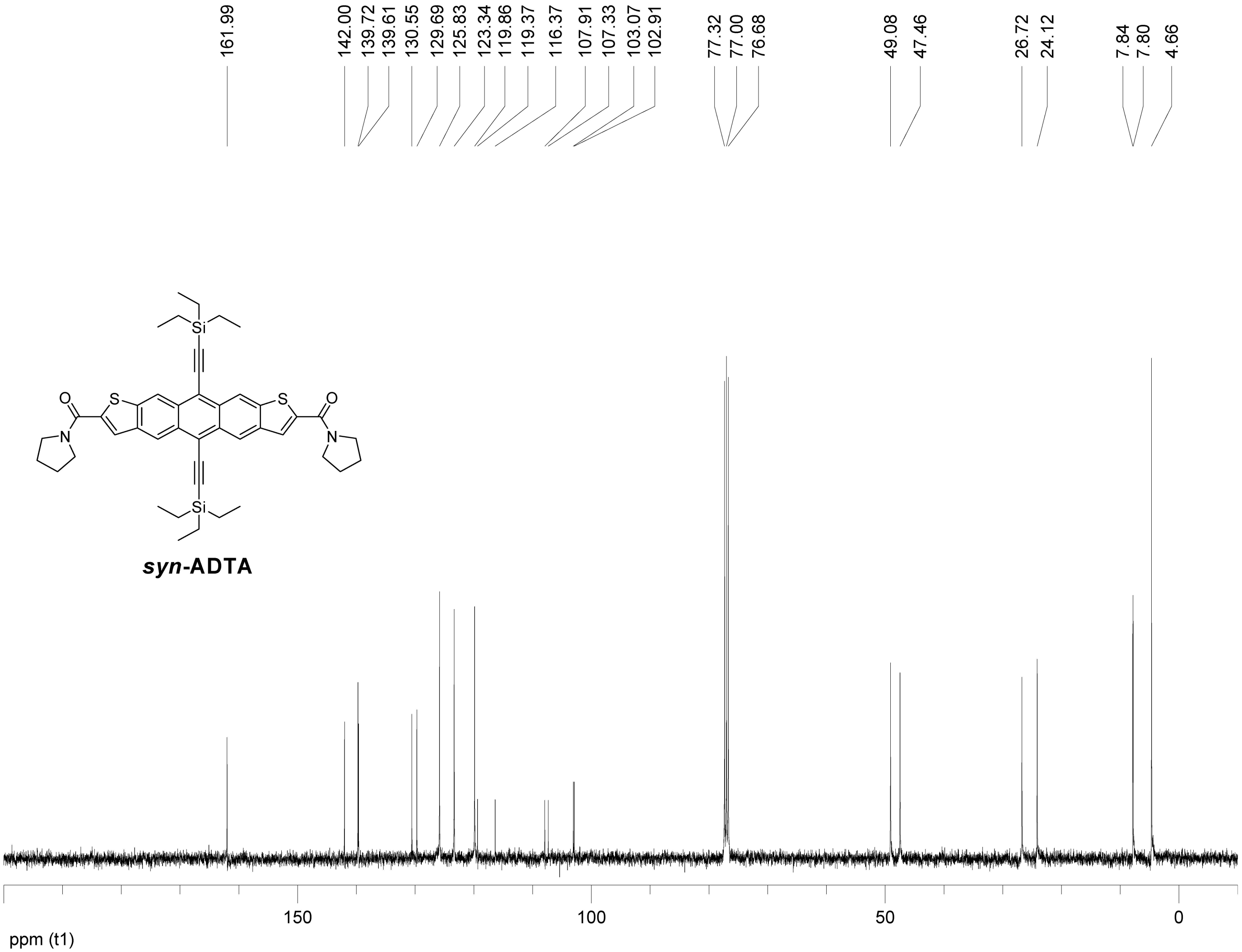


Fig. S4. ^{13}C NMR spectrum of ***syn*-ADTA**.

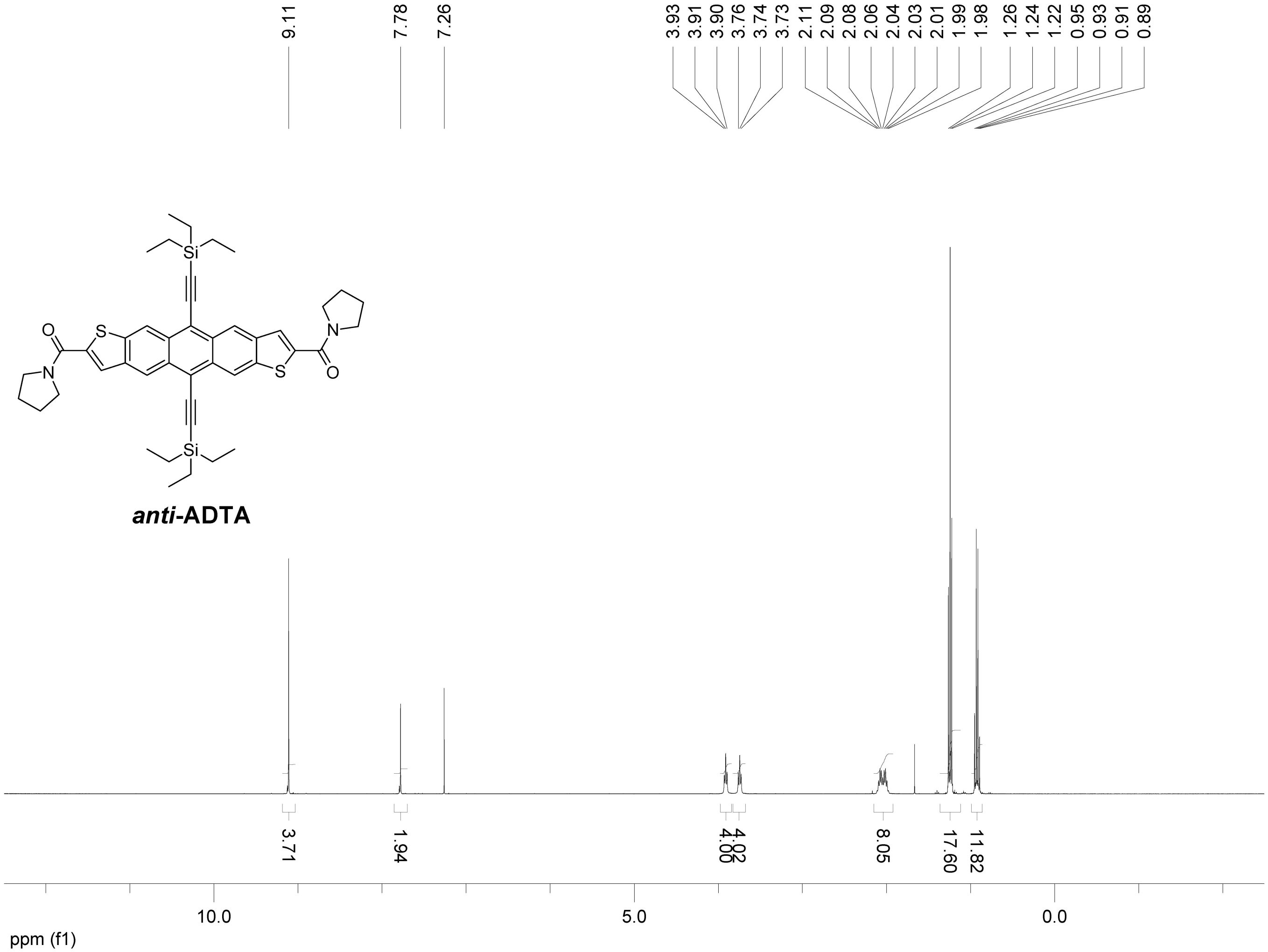


Fig. S5. ^{1}H NMR spectrum of ***anti*-ADTA**.

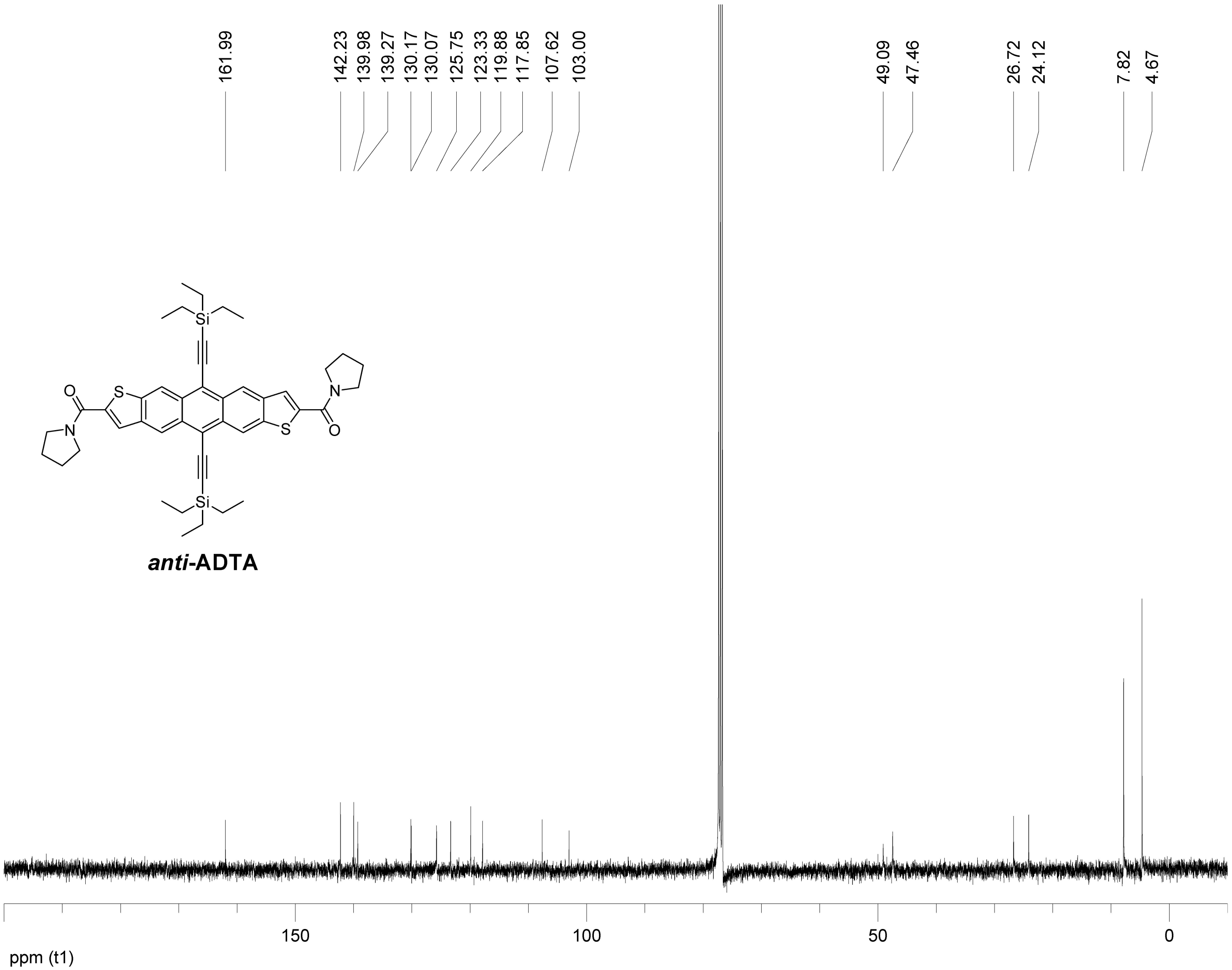


Fig. S6. ^{13}C NMR spectrum of ***anti*-ADTA**.

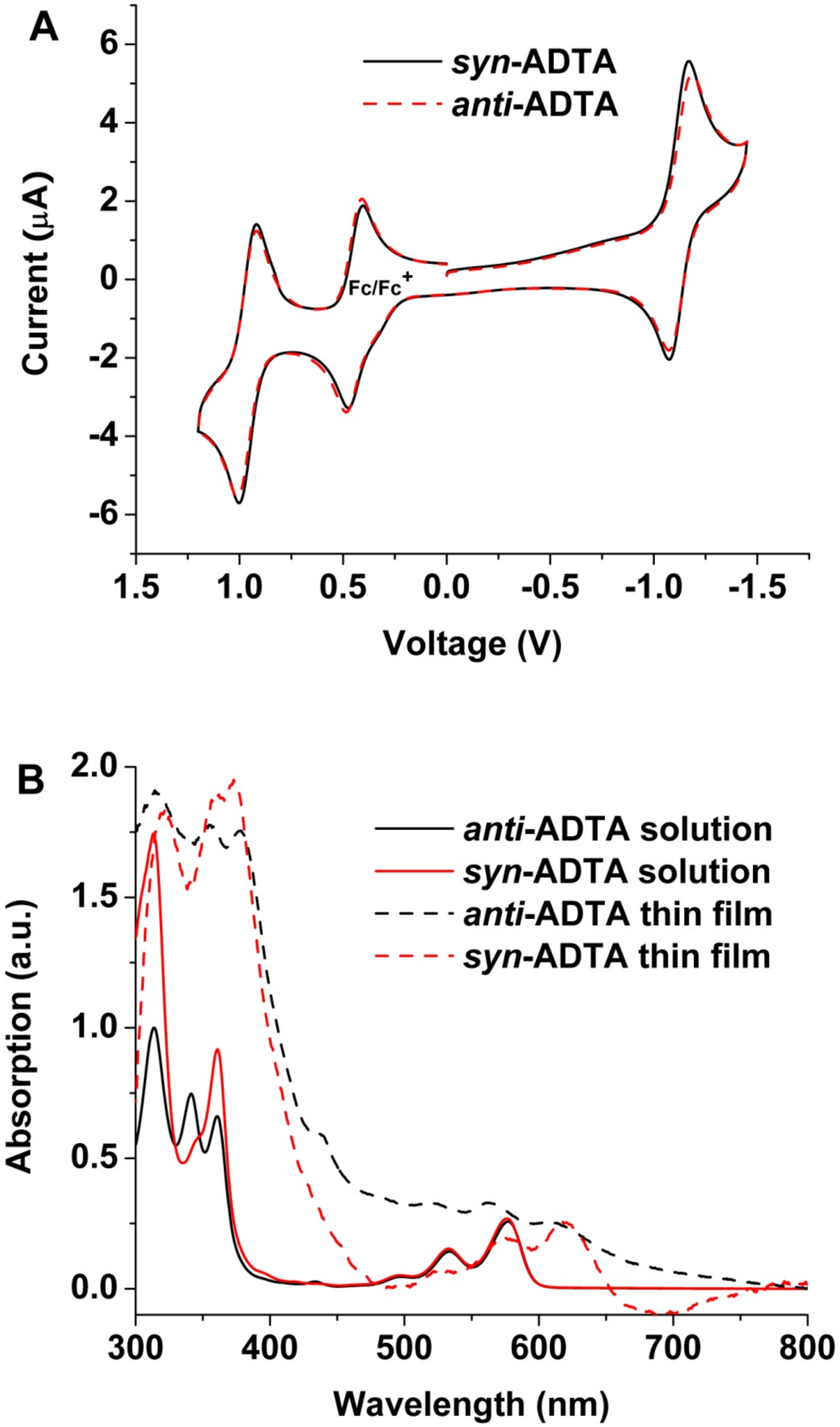


Fig. S7. Cyclic voltammetry (A) and absorption spectra (B) of ***syn-*** and ***anti*-ADTA**s.

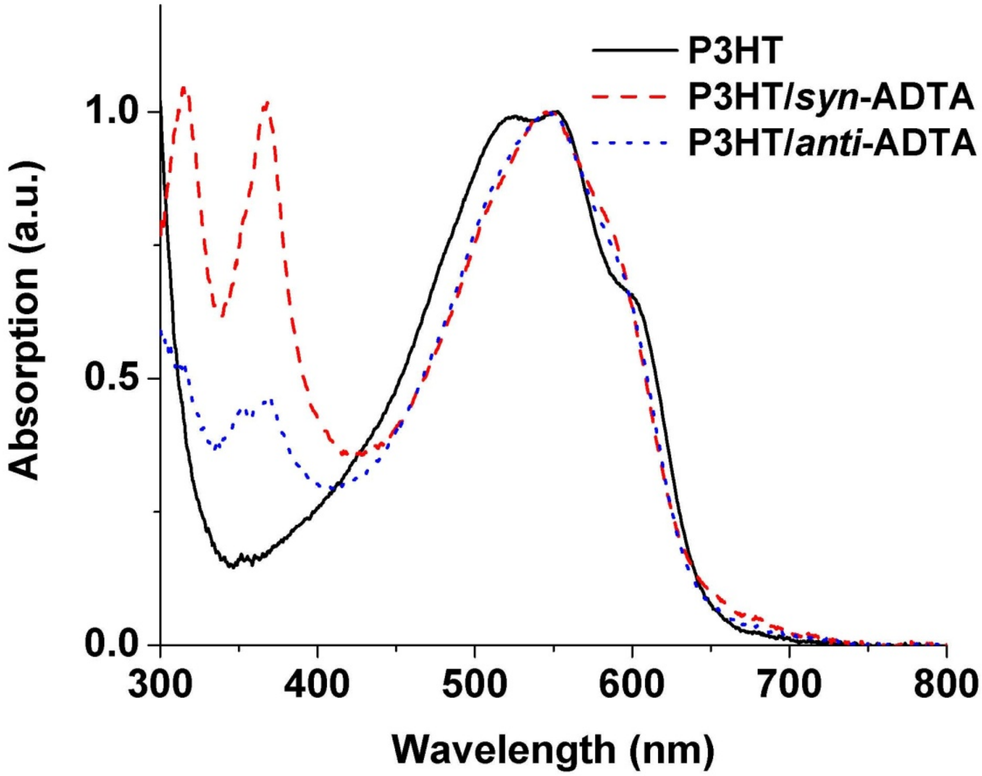


Fig. S8. Absorption spectra of the thin films of P3HT, P3HT/***syn*-ADTA** and P3HT/***anti*-ADTA**.

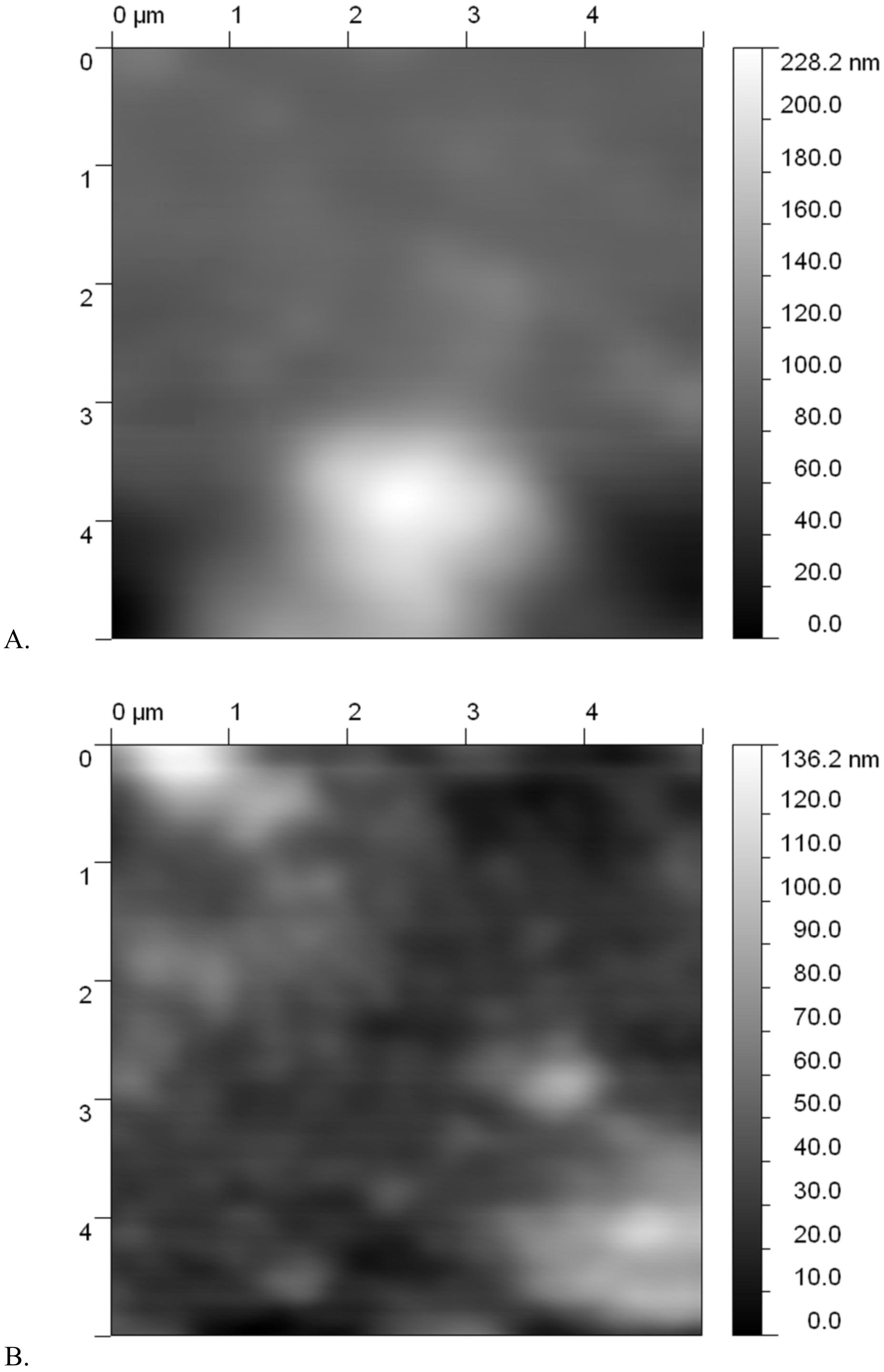


Fig. S9 AFM images of the blend films from P3HT/***anti*-ADTA** (A) and P3HT/***syn*-ADTA** (B).

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