Semiconducting polymer thin films by surface-confined stepwise click polymerization

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Supporting Information

I. Additional figures.

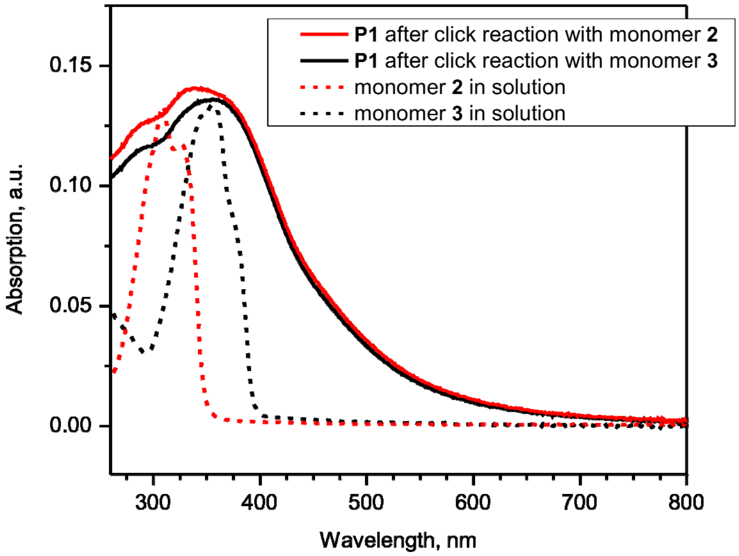


Figure S1. Alternating bathochromic and hypsochromic shifts in the growing film of polymer **P1** absorption maximum during stepwise click polymerization (steps 33 and 34 shown). Dashed traces show absorption spectra of the monomer compounds **2** and **3** in solution.

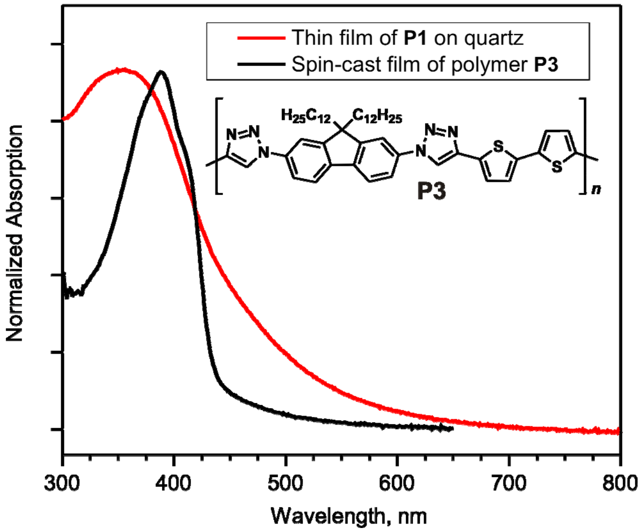


Figure S2. Comparison of absorption spectra of a thin film of **P1** and of a spin-cast film of the soluble model polymer **P3** (spin-cast from $CHCl_3$ solution).

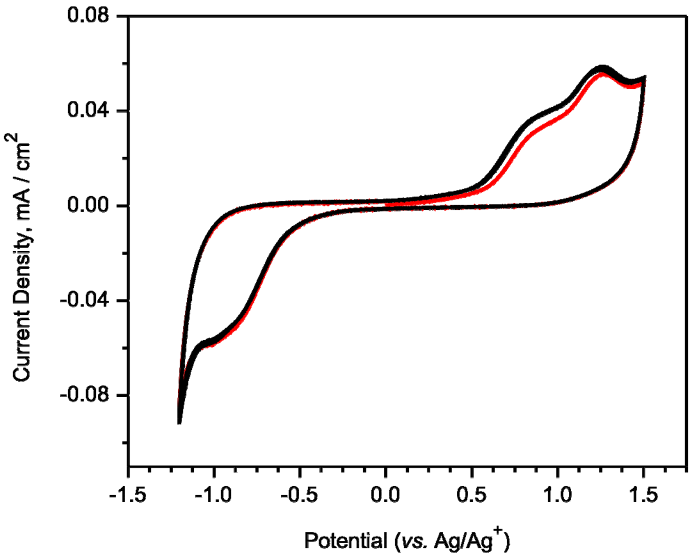


Figure S3. Cyclic voltammogram of a surface-immobilized polymer **P1** thin film on ITO. Four consecutive CV scans are shown (red trace – first scan). Experimental conditions: 0.1 M Bu_4NPF_6 in CH_3CN, sweep rate 0.1 V/s. Following the literature procedure,[1] energy level of HOMO (E_{HOMO}) was estimated at –5.28 eV. The HOMO-LUMO gap energy (E_g) was estimated from the onset wavelength of the UV/vis absorption spectrum of **P1** on ITO. Based on the estimated E_g of 2.52 eV, LUMO energy level (E_{LUMO}) was approximated at –2.76 eV.

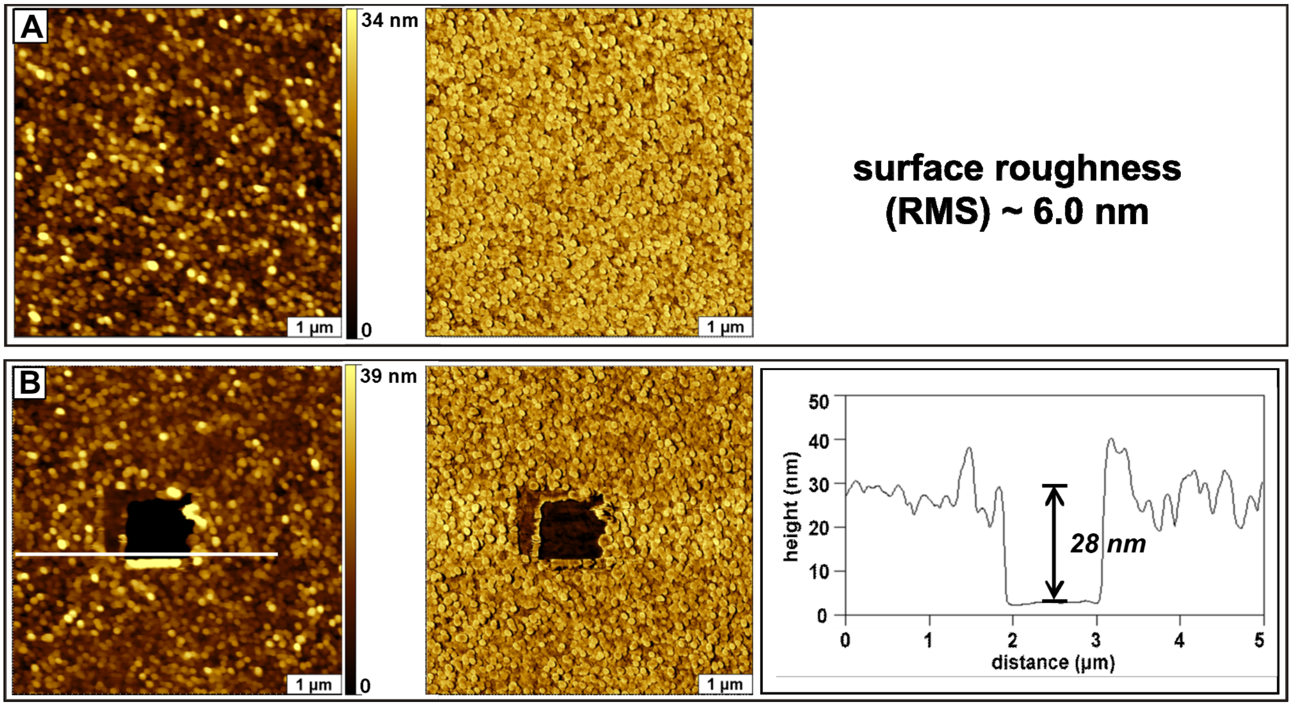


Figure S4. (A) AFM surface morphology of a surface-immobilized thin film of **P1**; (B) Determination of the **P1** film thickness by “nanoshaving” to reference the quartz substrate as a baseline.

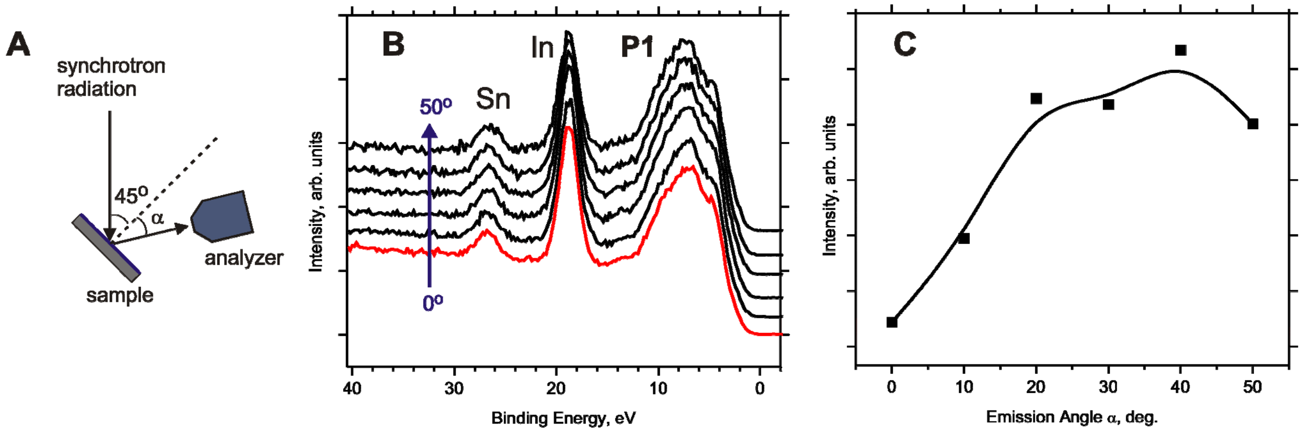


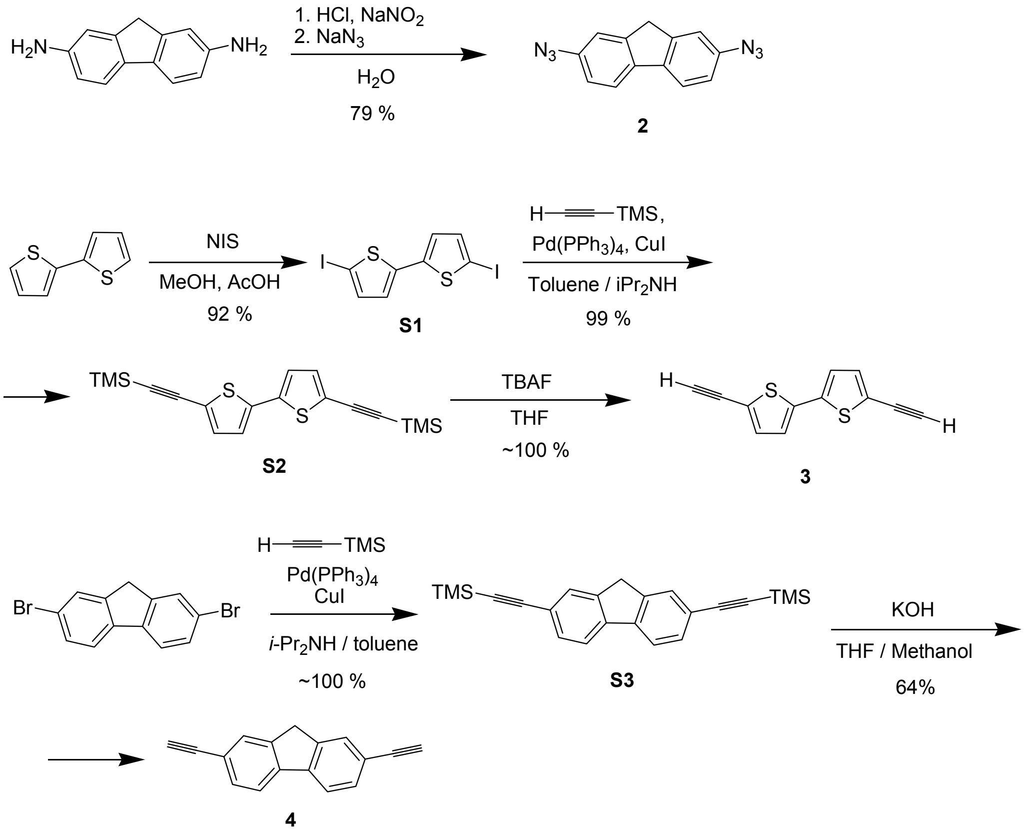
Figure S5. (A) Experimental setup for emission angle-dependent UPS spectroscopy utilizing (s+p)-polarized incident light; (B) Angular-dependent UPS spectra of the polymer **P1** on ITO/glass surface collected for (s+p)-polarized incident light (beam energy 85 eV, the emission angle α was changed in 10° increments from 0 to 50°); (C) Intensity of the polymer **P1** valence band maximum (at ~ 7 eV binding energy) *vs.* emission angle α.

II. Experimental Section.

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. Melting points were determined in open capillaries and are uncorrected. Column chromatography was performed on silica gel (Sorbent Technologies, 60 Å, 40-63 μm) slurry packed into glass columns. Tetrahydrofuran (THF), dichloromethane, toluene, and acetonitrile were dried by passing through activated alumina using a PS-400 Solvent Purification System from Innovative Technology, Inc. The water content of the solvents was periodically controlled by Karl Fischer titration (using a DL32 coulometric titrator from Mettler Toledo). All other solvents (HPLC or anhydrous grade) were purchased from Aldrich and used as received. All reagents were obtained from Aldrich, Acros Organics, and Alfa Aesar and used without further purification. Indium tin oxide (ITO) coated glass slides with 8-12 Ohm/sq. surface resistivity were purchased from Delta Technology. 75 x 25 mm^2 sized rectangular quartz slides were purchased from Chemglass. ^{1}H NMR spectra were recorded at 400 or 250 MHz, and are reported in ppm downfield from tetramethylsilane. UV-visible spectra were recorded on Varian Cary 50 UV-Vis spectrophotometer. GPC analysis of polymer samples was performed with Agilent 1100 chromatograph equipped with two PLgel 5 μm MIXED-C and one PLgel 5 μm 1000 Å columns connected in series, using THF as a mobile phase, and calibrated against polystyrene standards. All electrochemical experiments were performed using Autolab PGSTAT 302 potentiostat from Eco Chemie.

Synthetic details.

Scheme S1. Synthesis of monomer **2**, **3**, and **4.**



2,7-Diazido-9H-fluorene (2) was synthesized through a modified literature procedure.[2] A solution of 0.2 g (1.0 mmol) of 9H-fluorene-2,7-diamine, 0.2 g (3.0 mmol) of $NaNO_2$, and 2 ml of conc. HCl in 6 ml of water was stirred at 0 °C for 2 h. Then the reaction mixture was allowed to warm to room temperature, and a solution of 0.2 g (3.0 mmol) of NaN_3 in 2 ml of water was added dropwise. After stirring for an additional 1 h at the same temperature, the mixture was poured into water, extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. Concentration in vacuo gave a crude product, which was purified by column chromatography on Florisil (eluent ethyl acetate – hexane 1:10, R_f 0.20) to give 0.17 g (79 %) of **2** as a brown solid. The characterization was in agreement with the literature data.[2] ^1H NMR ($CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.19 (s, 2H), 7.03 (dd, J_1 = 8.2, J_1 = 2.0 Hz, 2H).

5,5'-Diiodo-2,2'-bithiophene (S1) was prepared following a modified literature procedure.[3] A mixture of 4.0 g (24.0 mmol) of 2,2'-bithiophene, 13.5 g (60.0 mmol) of *N*-iodosuccinimide, and 4 ml of acetic acid in 360 ml of methanol was stirred for 2 h at room temperature. The precipitate was filtered and washed with copious amount of cold methanol to yield 9.23 g (92 %) of **S1** as a green solid. The characterization was in agreement with the literature data.[3] ^{1}H NMR ($CDCl_3$) δ 7.15 (d, *J* = 3.8 Hz, 2H), 6.78 (d, *J* = 3.8 Hz, 2H).

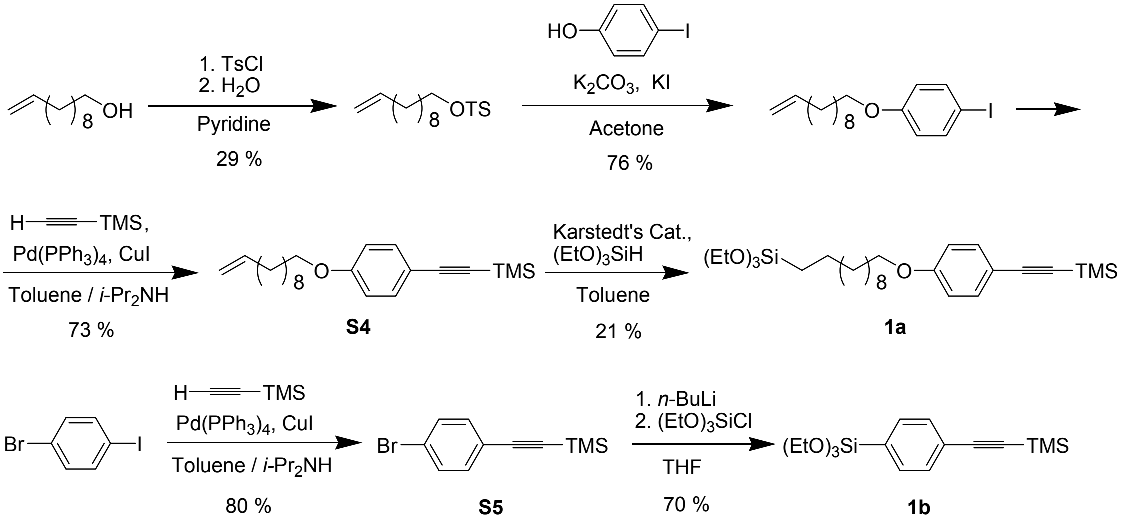
5,5'-bis((Trimethylsilyl)ethynyl)-2,2'-bithiophene (S2) was prepared following a modified literature procedure.[3] A solution of 1.0 g (2.4 mmol) of **S1**, 0.56 g (0.81 ml, 5.8 mmol) of trimethylsilylacetylene, 0.138 g (0.12 mmol) of $Pd(PPh_3)_4$, and 46 mg (0.24 mmol) of CuI in 10 ml of toluene – diisopropylamine mixture (7:3) was stirred at room temperature in a sealed flask for 2 days. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (eluent CH_2Cl_2 – hexane 1:4, R_f 0.30) to give 0.85 g (99 %) of **S2** as a yellow solid. The characterization was in agreement with the literature data.[3] ^{1}H NMR ($CDCl_3$) δ 7.11 (d, *J* = 3.8 Hz, 2H), 7.00 (d, *J* = 3.8 Hz, 2H), 0.25 (s, 18H).

5,5'-Diethynyl-2,2'-bithiophene (3) was prepared following a modified literature procedure.[3] A solution of 0.65 g (11.7 mmol) of KOH in 5 ml of methanol was added to a stirred solution of 0.7 g (2.0 mmol) of **S2** in 10 ml of THF. After stirring for 1 h at room temperature, the mixture was poured into water, extracted with $CHCl_3$, washed with water and brine, and dried over Na_2SO_4. Concentration in vacuo gave a crude product, which was purified by flash column chromatography on silica gel (eluent CH_2Cl_2 – hexane 1:4, R_f 0.30) to give quantitative yield (0.43 g) of **3** as a brown solid. The characterization was in agreement with the literature data.[3] ^{1}H NMR ($CDCl_3$) δ 7.18 (d, *J* = 3.8 Hz, 2H), 7.04 (d, *J* = 3.8 Hz, 2H), 3.41 (s, 2H).

2,7-bis((Trimethylsilyl)ethynyl)-9H-fluorene (S3) was prepared following the procedure described for the compound **S2**. A reaction of 2.0 g (6.3 mmol) of 2,7-dibromo-9H-fluorene, 1.48 g (2.11 ml, 15.1 mmol) of trimethylsilylacetylene, 0.138 g (0.12 mmol) of $Pd(PPh_3)_4$, and 46 mg (0.24 mmol) of CuI in 20 ml of 7:3 mixture of toluene and diisopropylamine afforded the crude product which was purified by column chromatography on silica gel (eluent $CHCl_3$ – hexane 2:1, R_f 0.89) to produce quantitative yield (2.3 g) of **S3** as a white solid, mp 139 - 141 °C. ^{1}H NMR ($CDCl_3$) δ 7.69 (s, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 0.27 (s, 18H).

2,7-Diethynyl-9H-fluorene (4) was prepared following the procedure described for the compound **3**. A reaction of 1.00 g (2.8 mmol) of **S3** in 20 ml of THF, and 0.93 g (16.8 mmol) of KOH in 15 ml of methanol afforded the crude product which was purified by flash column chromatography on silica gel (eluent $CHCl_3$ – hexane 2:1, R_f 0.90) to yield 0.38 g (64 %) of **3** as a white solid, mp 133 - 135 °C. ^{1}H NMR ($CDCl_3$) δ 7.73 (s, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 3.12 (s, 2H).

Scheme S2. Synthesis of surface initiators **1a** and **1b.**



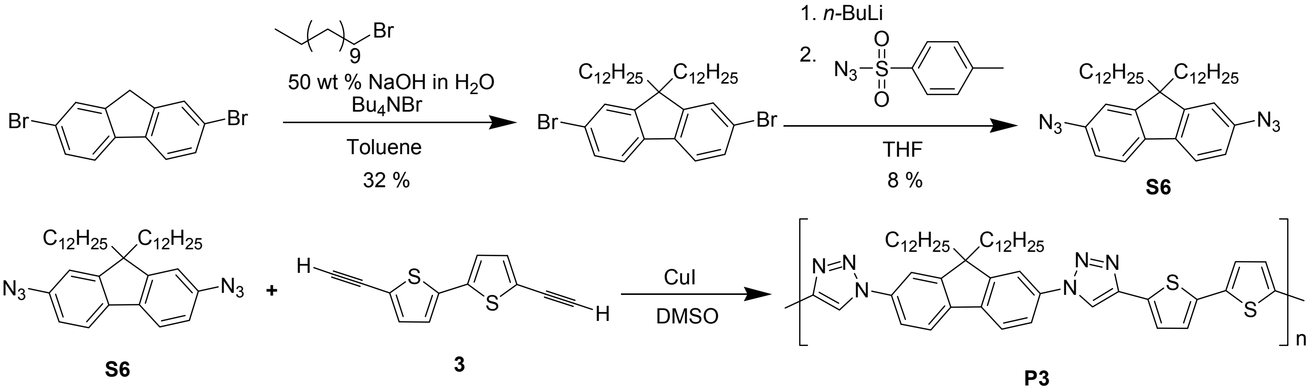
1-(Trimethylsilyl)-2-(4-(undec-10-enyloxy)phenyl)acetylene (S4) was synthesized following the literature procedures.[4]

Triethoxy-(11-(4-((trimethylsilyl)ethynyl)phenoxy)undecyl)silane (1a). A solution of 0.50 g (1.46 mmol) of **S4** and 1.5 ml of Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex (Karstedt's catalyst, 0.1 M solution in poly(dimethylsiloxane)) in 10 ml of toluene was stirred for 10 min at room temperature, followed by addition of 1.68 g (3 ml, 16 mmol) of triethoxysilane. The reaction mixture was stirred for 2 days at room temperature, and concentrated in vacuo. Purification by column chromatography on silica gel (eluent $CHCl_3$) afforded 0.16 g (21 %) of **1a** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.39 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 7.8 Hz, 2H), 3.94 (t, J = 6.2 Hz, 2H), 3.82 (q, J = 7.0 Hz, 6H), 1.76 (pentet, J = 6.6 Hz, 2H), 1.54 – 1.24 (m, 25H), 0.66 (t, J = 6.2 Hz, 2H), 0.23 (s, 9H).

((4-Bromophenyl)ethynyl)trimethylsilane (S5) was prepared following the procedure for compound **S2**. A reaction of 10.0 g (35.4 mmol) of 1-bromo-4-iodobenzene, 4.16 g (5.94 ml, 42.4 mmol) of trimethylsilylacetylene, 0.456 g (0.65 mmol) of $Pd(PPh_3)_4$, and 38 mg (0.2 mmol) of CuI in 150 ml of 7:3 mixture of toluene and diisopropylamine afforded the crude product which was purified by column chromatography on silica gel (eluent hexane, R_f 0.50) to yield 7.7 g (86 %) of **S5** as a white solid, mp 51 - 53 °C. ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 0.24 (s, 9H).

Triethoxy(4-((trimethylsilyl)ethynyl)phenyl)silane (1b). A solution of n-BuLi (1.25 ml of 1.6 M solution in hexanes, 2.0 mmol) was added dropwise to a stirred at -78 °C solution of 0.51 g (2.0 mmol) of **S5** in 7 ml of THF. The reaction mixture was stirred for 3 h at the same temperature, followed by dropwise addition of 0.43 ml (2.2 mmol) of $(EtO)_3SiCl$. The resulting solution was stirred at -78 °C for 1 h. After allowing to warm to room temperature, the reaction mixture was concentrated in vacuo, and purified by column chromatography on silica gel (eluent $CHCl_3$, R_f 0.46) to yield 48 mg (7 %) of **1b** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.60 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 3.85 (q, J = 7.0 Hz, 6H), 1.23 (t, J = 7.0 Hz, 9H), 0.25 (s, 18H).

Scheme S3. Synthesis of soluble model polymer **P3**.



2,7-diazido-9,9-didodecyl-9H-fluorene (S6) was prepared following the literature procedures.[5]

Polymer P3. A mixture of 16.8 mg (0.03 mmol) of **S6**, 6.4 mg (0.03 mmol) of **3**, and 0.5 mg (0.003 mmol) of CuI in 3 ml of DMSO was stirred for 2 days at 50 °C. To remove DMSO, the reaction mixture was poured into water, and precipitate was washed with copious amount of methanol. The crude precipitated polymer was redissolved in THF and re-precipitated into acetone; and the precipitate was dried in vacuo. This afforded 3.0 mg (13 %) of **P3** as a dark brown solid material. GPC (vs. polystyrene standard) M_n 18,800 g/mol, PDI 1.6.

Experimental Details.

(1) Electrochemical measurements.

These were performed using an Autolab PGSTAT 302 potentiostat from Eco Chemie. All experiments were carried out in nitrogen atmosphere using a three-electrode system with either a Pt button electrode (diameter 2 mm, CH Instruments, Inc.) or an ITO-covered glass working electrode with surface-immobilized polymer thin film, a Ag/$AgNO_3$ non-aqueous reference electrode, and a Pt gauze counter electrode. The reference electrode was checked against a ferrocene standard before and after each experiment was performed. All the experiments were carried out in a 0.1 M Bu_4NPF_6 solution in CH_3CN as supporting electrolyte.

(2) Atomic Force Microscopy.

Topography images were acquired with an Agilent 5500 (PicoPlus) system with PicoScan v5.3.3 acquisition software. Digital images were processed with Gwyddion open source software (version 2.9), which is supported by the Czech Metrology Institute.[8] Silicon nitride tips with an average force constant of 0.5 N m^{-1} were used for contact mode AFM in air (Veeco Probes, Camarillo, CA). To measure film thickness, an area of the surface was nanoshaved. A high force (20-50 nN) was applied to the AFM tip while scanning a selected region to sweep away the molecules under the tip. The areas were scanned consecutively for six passes under high force. The molecules that were removed were either displaced to other areas of the surface or remain at the edges of the patterns. Nanoshaving is accomplished by applying mechanical force to the AFM probe during scans; essentially small areas of the SAM are "shaved" away by the action of a scanning AFM tip. Information about the thickness of molecular layers on surfaces can be obtained using the height profiles of nanoshaved areas as a baseline for cursor measurements. Unlike spatially-averaged techniques such as ellipsometry, which incorporate measurements of the surface defects and roughness over wide areas from millimeters to centimeters, nanoshaving furnishes highly-local measurements of film thickness for selected nanometer-sized areas. The AFM tips used for nanoshaving and contact-mode AFM were standard silicon nitride probes with an average force constant of 0.5 N m^{-1}.

(3) Ultraviolet Photoelectron Spectroscopy (UPS).

The UPS measurements were performed at the LSU Center for Advanced Microstructures and Devices (CAMD) using the 3 m toroidal grating monochromator (3 m TGM) beamline. The UHV chamber was equipped with an energy analyzer with an angular acceptance of ±1° and a combined (including the monochromator) energy resolution of 150 meV or better. The base pressure of the UPS chamber was $\sim 5 \times 10^{-10}$ mbar. All the photoemission spectra were taken with incident photon energy of 85 eV. The emitted photoelectrons were collected with an analyzer movable in-plane with surface normal and the incident photon beam. The Fermi level position was established from a copper piece in electrical contact with the sample. The valence band features are reported with respect to this Fermi level. All the measurements were carried out at ambient temperature.

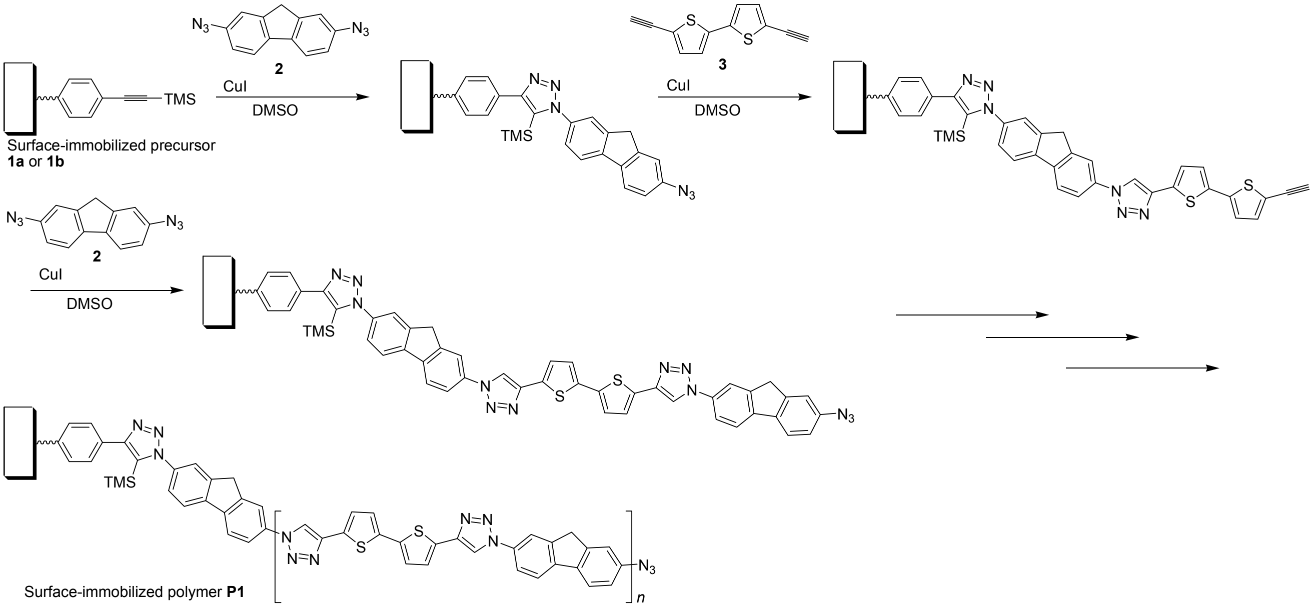
(4) Activation of Substrates.

Activation of ITO-glass substrates. Rectangular ITO-covered glass slides (approx. 1.1×2.5 cm) were ultrasonicated in CH_2Cl_2 for 20 min, followed by rinsing with acetone and deionized water. The pre-cleaned slides were subjected to an RCA-type cleaning procedure by keeping in the mixture of water – 30% H_2O_2 – 30% aqueous NH_3 (5:1:1) at 70 °C for 1 hour. The substrates were then rinsed with copious amount of deionized water and dried in N_2 flow at room temperature for 4 h, and then activated using O_2 plasma for 10 min.

Activation of quartz substrates. Rectangular quartz slides (approx. 1.1×2.5 cm) were ultrasonicated sequentially for 10 min in $CHCl_3$, methanol, and deionized water. The pre-cleaned slides were placed into a Piranha solution (a mixture of conc. H_2SO_4 and 30 % H_2O_2 (7:3)) and ultrasonicated for 30 min. After rinsing with copious amount of deionized water, substrates were dried in N_2 flow at room temperature for 4 h, and then activated using O_2 plasma for 10 min. ***NOTE:*** *extreme care must be taken when dealing with piranha solutions as they can detonate when contacted with organic compounds!*

(5) Deposition of Surface-Immobilized Thin Films by Stepwise Click Polymerization.

Scheme S4. Preparation of a surface-immobilized organic semiconducting polymer thin film through stepwise click polymerization.



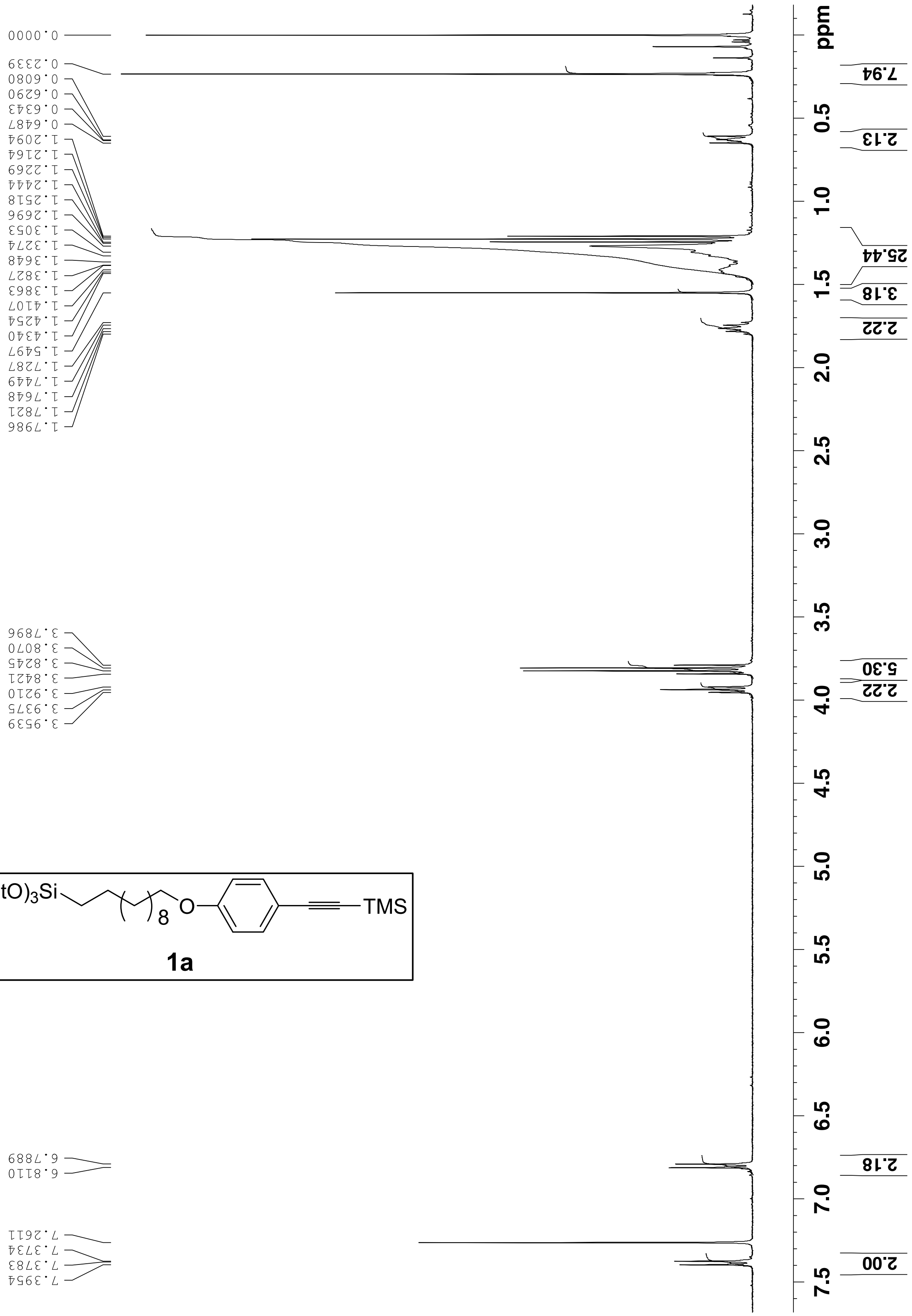
Preparation of surface-immobilized initiator monolayer. Activated quartz or ITO substrates were immersed into a 10 mM solution of an initiator (**1a** or **1b**) in toluene and kept at 60°C for 3 days. To obtain optimal results, immobilization was performed inside a glovebox. After deposition, the substrates were ultrasonicated in $CHCl_3$ (2 times for 10 min), and dried under N_2 flow for 2 h.

Surface-immobilized thin films of semiconducting polymers P1 and P2. Substrates modified with a monolayer of initiator (**1a** or **1b**) were immersed into a 10 mM solution of the bis-azide monomer **2** in 50 ml of DMSO containing 9 mg (0.05 mmol) of CuI at 40 °C and kept there for 1 h at gentle stirring. After completing the click step, the substrates were rinsed twice with copious amount of $CHCl_3$ followed by 10 min ultrasonication in $CHCl_3$. Then the substrates were placed into a 10 mM solution of the bis-acetylene monomer **3** (for **P1**, or **4** for **P2**) in 50 ml of DMSO containg 9 mg (0.05 mmol) of CuI at 40 °C and kept there for 1 h, followed by rinsing and ultrasonication in $CHCl_3$. This sequence was repeated for the required number of steps.

References:

1. J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang and Y. F. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4911-4916.
2. S. Nimura, O. Kikuchi, T. Ohana, A. Yabe, S. Kondo and M. Kaise, *J. Phys. Chem. A*, 1997, **101**, 2083-2088.
3. T. Cardolaccia, A. M. Funston, M. E. Kose, J. M. Keller, J. R. Miller and K. S. Schanze, *J. Phys. Chem. B*, 2007, **111**, 10871-10880.
4. J. R. Acharya, H. Zhang, X. Li and E. E. Nesterov, *J. Am. Chem. Soc.*, 2009, **131**, 880-881.
5. D. van Steenis, O. R. P. David, G. P. F. van Strijdonck, J. H. van Maarseveen and J. N. H. Reek, *Chem. Commun.*, 2005, 4333-4335.
6. Gwyddion, (2010) Czech Metrology Institute, http://gwyddion.net/.

^{1}H NMR spectra of the selected compounds.



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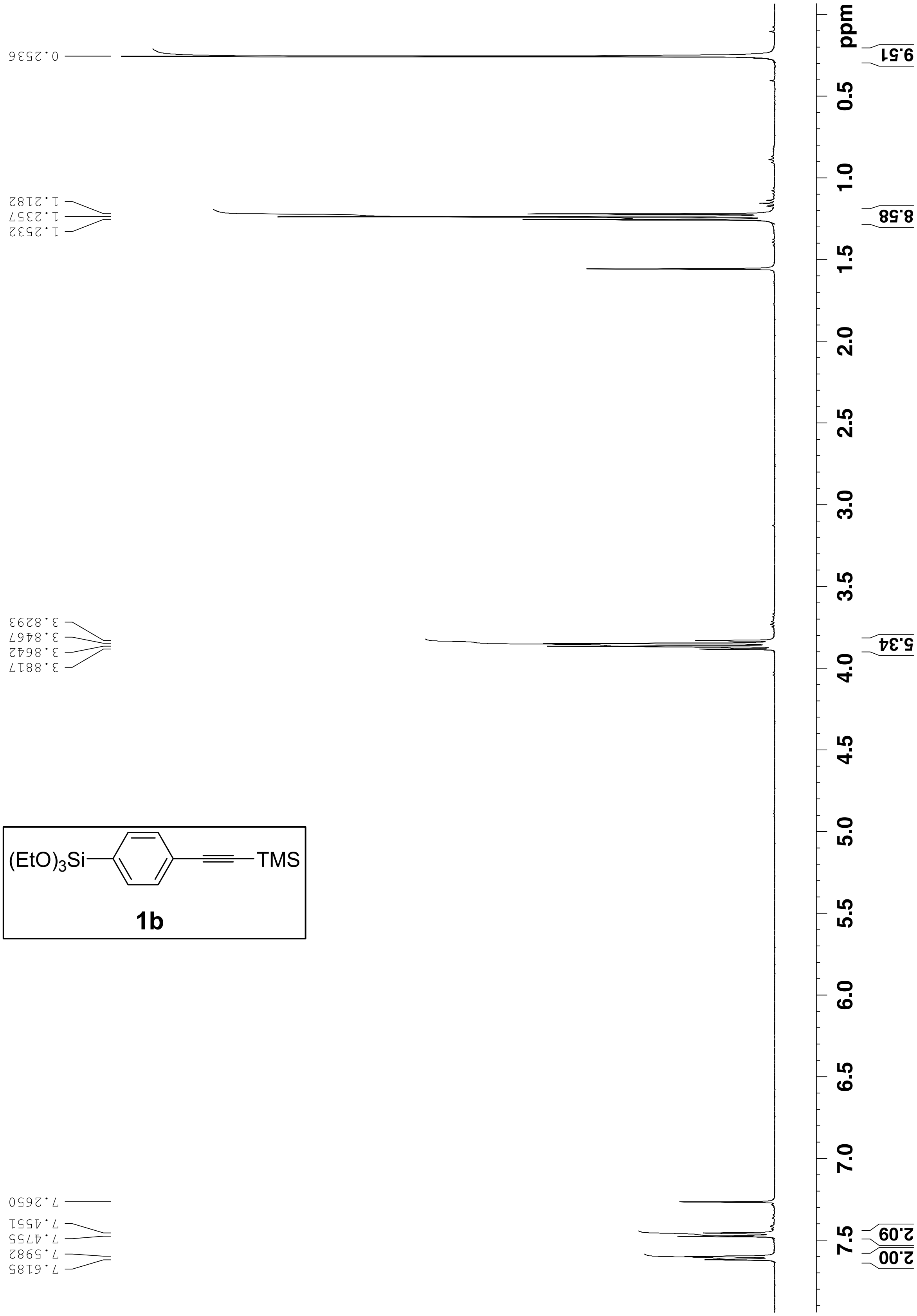
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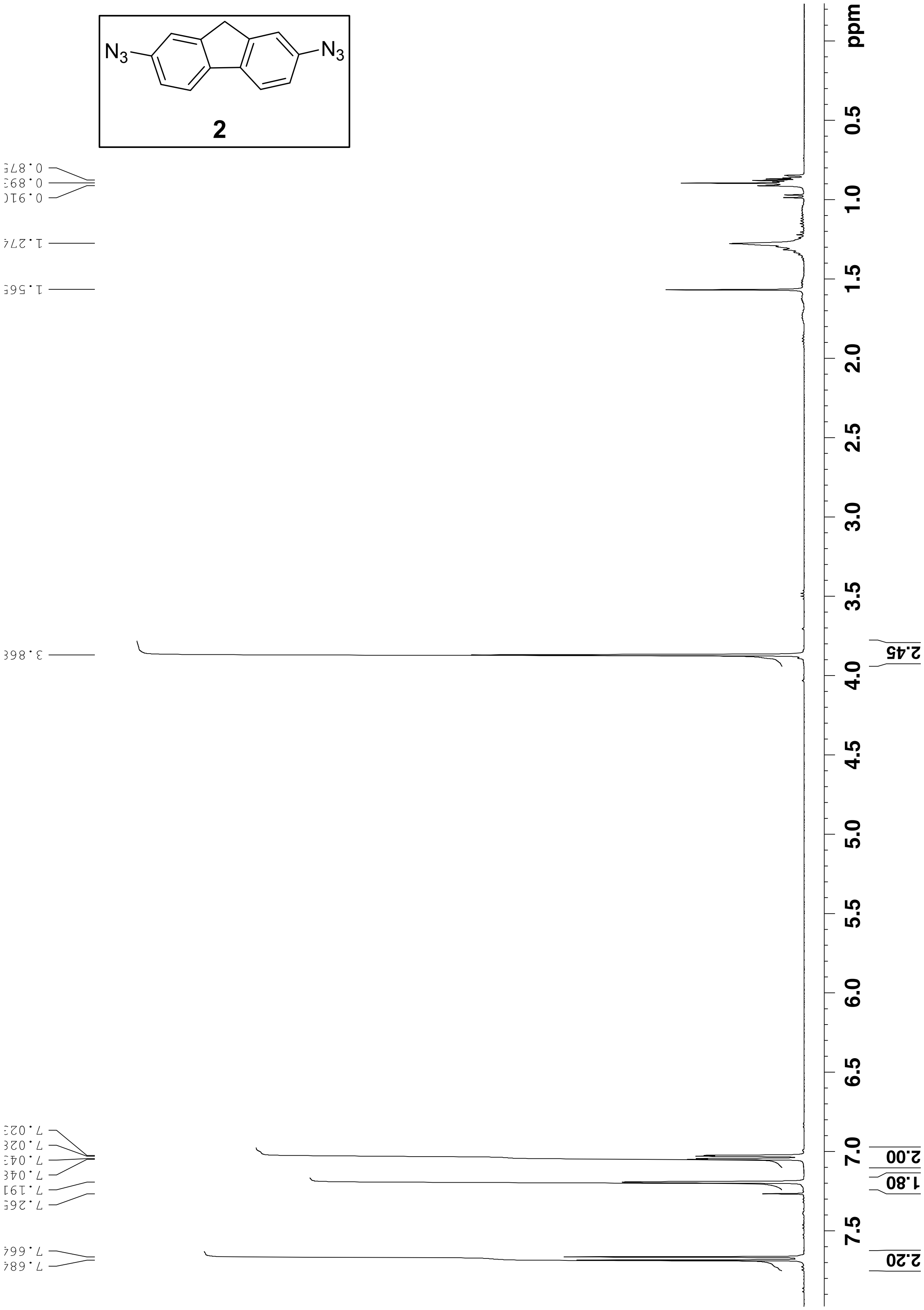
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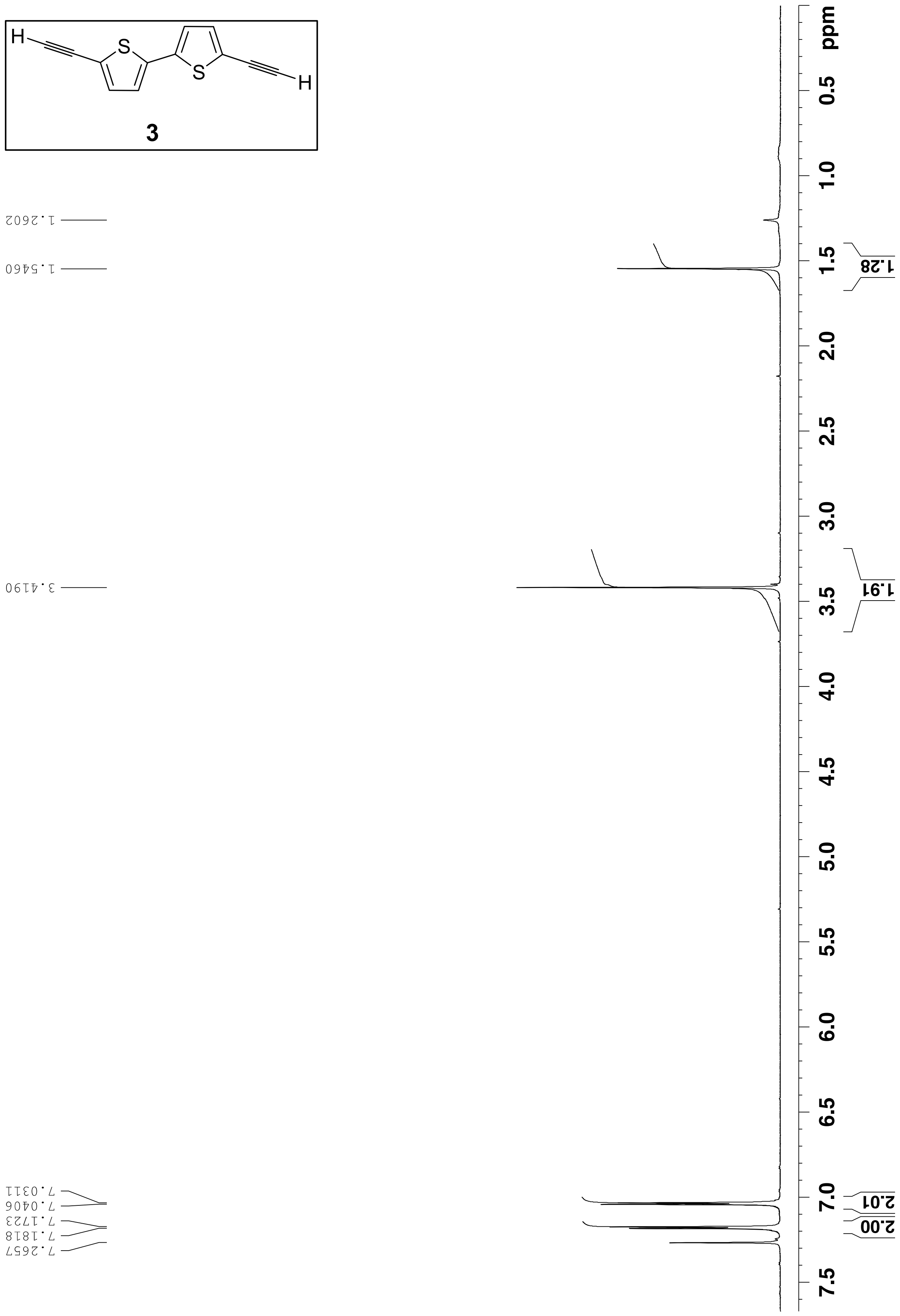
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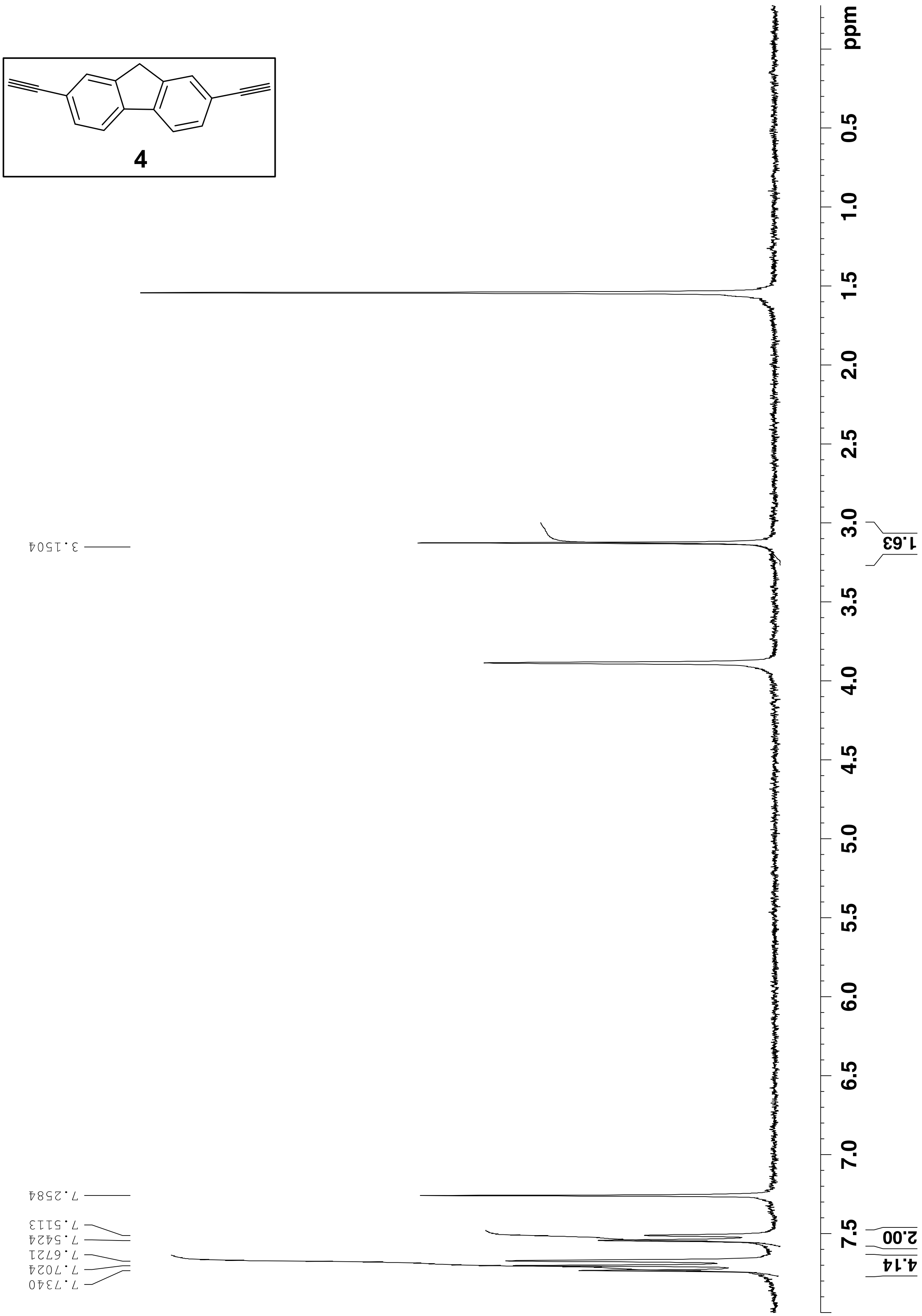

4

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