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Controlling the Functional Properties of Oligothiophene Crystalline Nano/Micro-Fibers *via* Tailoring of the Self-Assembling Molecular precursors

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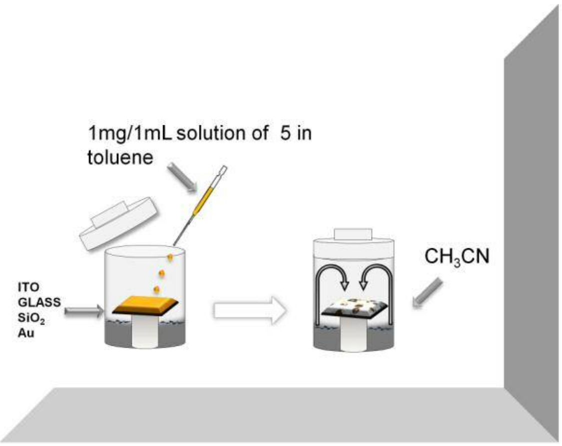
SUPPLEMENTARY INFORMATION

I. Methods

Synthesis. TLC was carried out with 0.2-mm thick of silica gel 60 F_{254} (Sigma). Preparative column chromatographies were carried out on glass columns with silica gel 60 (particle sizes 0.040-0.063 mm, Sigma). 3-bromothiophene, 2-thienylboronic acid, 2-bromo-5-nitrothiophene, 4-bromo-2,1,3-benzothiadiazole, 2-thiophenecarboxaldehyde, 2-bromo-5-nitrothiophene, 5-bromo-1- benzothiophene, *N*-bromosuccinimide, Manganese(IV) oxide, bromine, sodium bicarbonate, *n*-butyllithium 2.5 M solution in hexane, potassium tert-butoxide, 1-bromohexane 98%, palladium(II)chloride dichloromethane complex ($PdCl_2dppf$), 1,1′-bis(diphenylphosphino) ferrocene, 3-Chloroperbenzoic acid, were purchased from Sigma-Aldrich Co; sulfur sublimed washed winnowed 99.5% from Carlo Erba; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, bis(pinacolato)diboron from Alfa Aesar GmbH & Co KG. All reagents and solvents were used as received. Organic solvents were dried by standard procedures.

Microwave experiments were carried out in a CEM Discover SP-Microwave Synthesizer reactor in a closed vessel (230W, fixed temperature at 80°C, air, high stirring rate). Reactions with ultrasound were performed in a FALC LBS1 50KHz Ultrasonic bath at room temperature. Melting points were determined on Kofler bank apparatus and are uncorrected. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400/500 spectrometer equipped with a 5-mm probe. Chemical shifts were calibrated using the internal $CDCl_3$ resonance which were referenced to TMS. Mass spectra were collected on a Thermo Scientific TRACE 1300 gas chromatograph.

Fibers growth. The sketch below illustrates the preparation of the fibers of **1-5** according to the solvent-exchange in solution (or vapour diffusion method), in which the molecules move from a good solvent (toluene) into a poor solvent (acetonitrile).



The solutions employed were in the range 10^{-3}-10^{-5} M of **1-5** in toluene. Freshly distilled toluene and acetonitrile were employed. Once formed on the appropriate substrate, the desired measurements were directly carried out on the instrument chosen without further modifications.

Scanning Electron Microscopy. SEM images were collected with a SEM-FEG Zeiss LEO 1530 operating at Vacc = 5 keV. The fibers of **1-5** were grown on Si/SiO_2 wafers and sampled with no further treatment.

Photophysical characterization. Absorption spectra were recorded on air equilibrated solutions at room temperature with a Agilent Cary 100 UV-Vis spectrophotometer, using quartz cells with path length of 1.0 cm. Absorption spectra of films on glass (drop-cast and fibers) were recorded in transmission mode at room temperature with a Perkin Elmer Lambda 650 spectrophotometer. Emission spectra of solutions and films on glass were recorded on a Perkin Elmer LS50B fluorescence spectrofluorometer. Emission lifetime measurements were performed on a Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a a LDH-P-C-405 pulsed diode laser. Longer lifetimes were measured by the PerkinElmer LS-50. Emission quantum yields were measured following the method of Demas and Crosby[1] (standard used: $[Ru(bpy)_3]^{2+}$ in aqueous solution, Φ=0.04).[2] For solid samples, emission quantum yield was calculated from corrected emission spectra registered by an Edinburgh FLS920 spectrofluoremeter equipped with a LabSphere barium sulfate coated integrating sphere (4 in.), a 450W Xe lamp (excitation wavelength tunable by a monochromator supplied with the instrument) as light source, and a R928 photomultiplayer tube, following the procedure described by De Mello *et al*.[3] The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime, 10% on the emission quantum yield in solution, and 20% on the emission quantum yield in solid.

(1) Crosby, G.; Demas, J. *J. Phys. Chem.* **1971**, *75* (8), 991. (2) Suzuki, K.; Kobayashi, A.; Kaneko, S.;Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11* (42), 9850. (3) de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9* (3), 230.

Cyclic Voltammetry. The cyclic voltammetries (CV) were performed with the AMEL electrochemical system model 5000 controlled by the software Corrwere 2.9 for Windows using a home-made three-compartments cell at room temperature under Ar pressure. The working electrode was a Pt disk (⌀ 1 mm), for the experiments in solution, and indium-tin-oxide/glass modified electrodes [ITO, Balzers, 23 ohm/square, area (12 x 12) mm^2] for the experiments on the fibers or amorphous films. The auxiliary electrode was a Pt wire and the reference electrode was an aqueous KCl Saturated Calomel Electrode (SCE) connected to the working compartment with a liquid bridge. The supporting electrolytes, purged with Ar before the experiments, were CH_2Cl_2 (Aldrich HPLC grade., distilled on P_2O_5 and stored under Ar pressure) 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ (Aldrich, puriss. vacuum dried) to dissolve the compounds, and propylene carbonate (Aldrich anhydrous, stored under Ar pressure) 0.1 mol L^{-1} $(C_2H_5)_4NBF_4$ (Aldrich, puriss. vacuum dried) for film and fibers testing. Where possible, the energy gaps of the molecules ware evaluated as the difference of the reduction and oxidation standard potentials for the compound in solutions, and as the differences of the reduction and oxidation onset potentials, for the solid samples.

DFT calculations. Ground-state calculations and geometry optimizations have been performed with the TURBOMOLE program package [1,2] using the BLOC exchange-correlation [3-5] functional and the multipole accelerated resolution of identity approximation [6]. For isolated molecules a def2-TZVP basis set [7] was employed. For the dimers, the optimal strucutres have been identified performing a preliminary screening, via geometry optimizations at the BLOC/de2-SV(P) level of theory [3-5,8], on a large number (about 100) of guess structures generated by random displacements of two monomers. Subsequently, the 20 best candidates have been optimized at the BLOC/def2-TZVP level to identify the most stable configuration.
The NCI indicator [9,10] investigation has been carried out using the NCI PLOT program [11].

(1) TURBOMOLE, V7.1; TURBOMOLE GmbH: Karlsruhe, Germany, **2011**. http://www.turbomole.com. (2) Furche, F.; Ahlrichs, R.; Hättig, C.; Klopper, W.; Sierka, M.; Weigend, F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, *4*, 91-100. (3) Constantin, L. A.; Fabiano, E.; Della Sala, F. *J. Chem. Theory Comput*. **2013**, *9*, 2256-2263.
(4) Constantin, L. A.; Fabiano, E.; Della Sala, F. *Phys.Rev.B* **2012**, *86*, 035130. (5) Constantin, L. A.; Fabiano, E.; Della Sala, F. *Phys. Rev. B* **2013**, *88*, 125112. (6) Sierka, M.; Hogekamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *118*, 9136. (7) Weigend, F.; Haser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett*. **1998**, *294*, 143-152. (8) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys*. **1992**, *97*, 2571. (9) Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W. *J. Am. Chem. Soc.* **2010**, *132*, 6498-6506. (10) Contreras-Garcia, J.; Yang, W.; Johnson, E. R. *J. Phys. Chem. A* **2011**, *115*, 12983-12990. (11) Contreras-Garcia, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J. P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.* **2011**, *7*, 625-632.

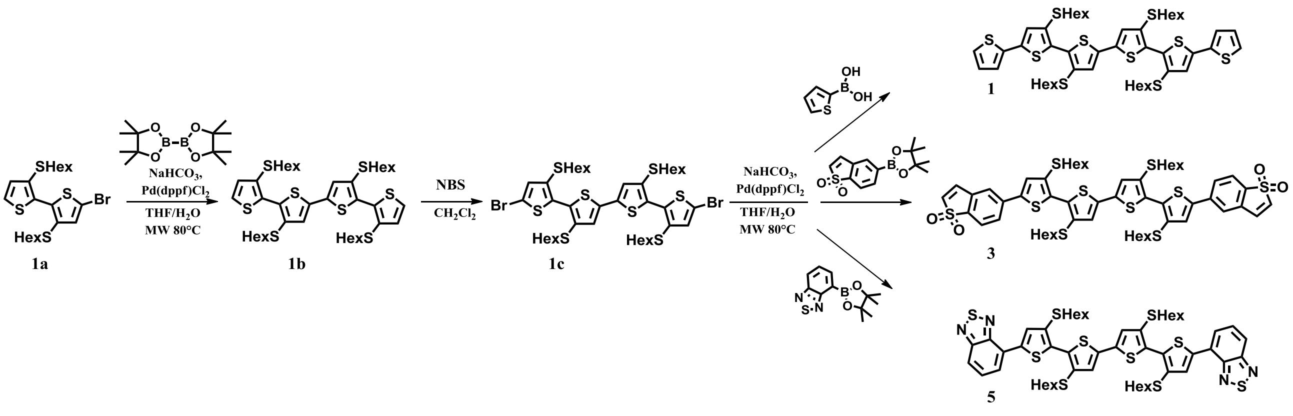
X-ray diffraction. X-ray diffraction analysis was performed using a PANalytical X'Pert diffractometer equipped with a copper anode (λmean = 0.15418 nm) and a fast X'Celerator detector. Films directly grown on glass cover slips were analyzed as prepared.

Photoconductivity. *Samples fabrication*: Gold electrodes were defined by photolithography and evaporation on an electronic-grade glass substrate (Corning 1737F). The defined active area is 2 mm wide and 20 µm long. The fibers were grown on top of the electrodes. *Measurements*: The samples were measured in a nitrogen atmosphere (< 0.1 ppm H2O and O2) with an Agilent SPA B1500A.

KPFM. KPFM measurements were obtained in air by employing a commercial microscope Multimode 8 (Bruker). In order to obtain a sufficiently large and detectable mechanical deflection, we used (k = 2.8 N/m) Pt/Ir coated cantilever silicon tips (SCM, Bruker) with oscillating frequencies in the range between 60 - 90 KHz. AFM and KPFM images are acquired in the same measurement; a topographic line scan is first obtained by AFM operating in Tapping Mode and then that same line is rescanned in Lift Mode with the tip raised to a lift height of 50 nm using the Frequency Modulation (FM) mode. KPFM provides a voltage resolution of about 5 mV, while the lateral resolution amounts to a few tens of nanometers.

II. Materials

Scheme S1



General synthesis of compounds 1,3,5: A mixture of **1c** (1 mmol), prepared from 3,3',3''',4''-tetrakis-(hexylthio)-2,2':5',2'':5'',2'''-quaterthiophene (1b) according to ref 2, thienylboronic ester or **5c** or 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (6 mmol), $PdCl_2dppf$ (0.1 mmol), $NaHCO_3$ (4 mmol) in THF/water 2:1 (3 mL) was irradiated with microwaves at 80°C for 15 min. The reaction mixture was brought to room temperature and the solvent was evaporated under reduced pressure. All compounds were purified by flash chromatography.

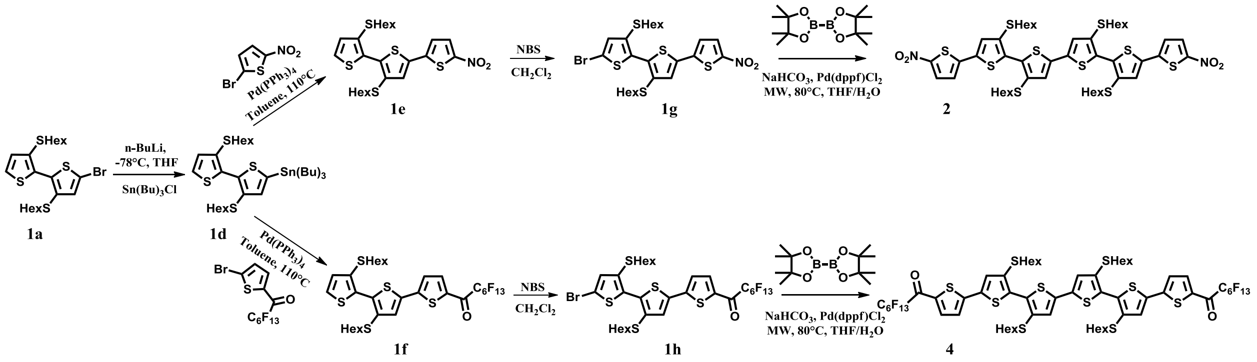
3'',3'''',4',4'''-tetrakis(hexylthio)-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene (1) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 80%. Orange solid; mp=54-56°C. EI-MS *m/z* 958 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.37 (d, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz, 2H), 7.34 (d, $^3J = 5.2$ Hz, $^3J = 1.2$ Hz, 2H), 7.14 (s, 2H), 7.13 (s, 2H), 7.06 (dd, $^3J = 3.6$ Hz, $^3J = 5.2$ Hz, 2H), 2.90–2.85 (m, 8H), 1.65–1.59 (m, 8H), 1.41–1.38 (m, 8H), 1.30–1.25 (m, 16H), 0.88–0.85 (m, 12H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 137.2, 136.5, 136.1, 132.5, 132.46, 132.0, 131.2, 127.9, 127.4, 127.0, 125.0, 124.2, 43.5, 36.4, 36.3, 31.4, 30.2, 29.7, 29.5, 28.4, 22.6, 14.0. UV/Vis: λ_{max} 421 nm (ε 34700 $cm^{-1}M^{-1}$), $\lambda_{em.}$ 538 nm in CH_2Cl_2.

5,5'-(3,3',3''',4''-tetrakis(hexylthio)-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)bis (benzo[b]thiophene 1,1-dioxide) (3) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2/AcOEt, 70:25:5). Yield 95%. Dark orange solid; mp=54-56°C. ^1H NMR (500 MHz, CD_2Cl_2, TMS/ppm): δ 7.80 (d, *J*=8 Hz, 2H), 7.75 (d, *J*=8 Hz, 2H), 7.65 (s, 2H), 7.48 (s, 2H), 7.32 (d, *J*=7 Hz, 2H) 7.28 (s, 2H) 6.82 (d, *J*=7 Hz, 2H), 2.93 (t, 8H), 1.68–1.61 (m, 8H), 1.45–1.38 (m, 8H), 1.33–1.28 (m, 16H), 0.90–0.86 (m, 12H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 140.8, 139.0, 136.4, 135.2, 134.1, 133.2, 133.18, 132.4, 131.8, 131.6, 131.4, 128.9, 127.4, 127.3, 122.1, 122.0, 36.4, 36.37, 31.3, 29.4, 28.4, 22.5, 14.0. UV/Vis: λ_{max} 431 nm (ε 38500 $cm^{-1}M^{-1}$), $\lambda_{em.}$ 575 nm in CH_2Cl_2.

4,4'-(3,3',3''',4''-tetrakis(hexylthio)-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)bis (benzo[c][1,2,5]thiadiazole) (5) → The residue was isolated by flash chromatography

(Cyclohexane/CH_2Cl_2/AcOEt, 80:18:2). Yield 75%. Dark red solid; mp=124-126°C. EI-MS *m/z* 1062 (M$^+$). ^{1}H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 8.20 (s, 2H), 7.95 (d, ^3J = 8.4 Hz, 2H), 7.87 (d, ^3J = 7.2 Hz, 2H), 7.64 (dd, ^3J = 6.8 Hz, ^3J = 8.4 Hz, 2H), 7.23 (s, 2H), 2.97–2.89 (m, 8H), 1.68–1.62 (m, 8H), 1.45–1.26 (m, 24H), 0.88–0.83 (m, 12H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 155.5, 152.0, 138.8, 136.6, 133.5, 132.9, 132.8, 131.9, 131.6, 129.6, 127.5, 126.7, 125.3, 120.5, 36.4, 31.4, 31.39, 29.56, 29.51, 28.5, 28.4, 22.6, 22.57, 14.1, 14.0.

Scheme S2



General synthesis of compounds 2, 4: A mixture of 5-bromo-3,3'-bis(hexylthio)-5''-nitro-2,2':5',2''-terthiophene (**1g**) or 1-(5''-bromo-3'',4'-bis(hexylthio)-[2,2':5',2''-terthiophen]-5-yl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-one (**1h**) (1 mmol), bis(pinacolato)diboron (0.6 mmol), $PdCl_2$dppf (0.05 mmol), $NaHCO_3$ (2 mmol) in THF/water 2:1 (3 mL) was irradiated with microwaves at 80°C for 30 min. The reaction mixture was brought to room temperature and the solvent was evaporated under reduced pressure. All compounds were purified by flash chromatography.

3'',3'''',4',4'''-tetrakis(hexylthio)-5,5'''''-dinitro-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene (2) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 80%. Dark blue solid; mp=147-149°C. EI-MS *m/z* 1048 (M$^+$).^{1}H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.88 (d, *J*=4 Hz, 2H), 7.33 (s, 2H), 7.22 (s, 2H), 7.14 (d, *J*=4 Hz, 2H), 2.92–2.88 (m, 8H), 1.66–1.60 (m, 8H), 1.44–1.40 (m, 8H), 1.30–1.28 (m, 16H), 0.90–0.87 (m, 12H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 149.7, 144.0, 136.5, 134.8, 134.2, 133.5, 133.4, 131.4, 129.8, 129.7, 127.7, 122.7, 36.5, 36.48, 31.3, 29.5, 29.4, 28.4, 22.5, 14.0. UV/Vis: λ_{max} 480 nm (ε 41300 cm^{-1}M^{-1}), $\lambda_{em.}$ 657 nm in CH_2Cl_2.

1,1'-(3'',3'''',4',4'''-tetrakis(hexylthio)-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene] -5,5'''''-diyl)bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-one) (4) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 60%. Dark purple solid; mp=136-138°C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.91 (d, *J*=4 Hz, 2H), 7.40 (s, 2H), 7.31 (d, *J*=4 Hz, 2H), 7.22 (s, 2H), 2.92–289 (m, 8H), 1.64–1.58 (m, 8H), 1.42-1.41 (m, 8H), 1.29–1.27 (m, 16H), 0.89–0.87 (m, 12H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 174.9, 149.4, 137.8, 136.5, 135.9, 135.0, 134.4, 133.5, 133.4, 131.4, 130.3,127.7, 125.3, 36.5, 36.4, 31.3, 29.7, 29.5, 29.4, 28.4, 22.7, 22.6, 14.03, 14.01. UV/Vis: λ_{max} 482nm (ε 40200 $cm^{-1}M^{-1}$), $\lambda_{em.}$ 667 nm in CH_2Cl_2.

General synthesis of compounds 1e, 1f: A mixture of 1-(5-bromothiophen-2-yl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-one prepared according to ref. (1) or 2-bromo-5-nitrothiophene (1 mmol), (3,3'-bis(hexylthio)-[2,2'-bithiophen]-5-yl)tributylstannane (**1d**) (1 mmol), $Pd(PPh_3)_4$ (0.05 mmol) in Toluene (10 mL) was refluxed for 24 h. The reaction mixture was brought to room temperature and the solvent was evaporated under reduced pressure. The title compound was isolated by flash chromatography on silica gel.

3,3'-bis(hexylthio)-5''-nitro-2,2':5',2''-terthiophene (1e) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 60%. Red solid. EI-MS *m/z* 290(M^+). ^1H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.87 (d, *J*=5 Hz, 1H), 7.43 (d, *J*=5 Hz, 1H), 7.32 (s, 1H), 7.11 (d, *J*=5 Hz, 2H), 2.86–2.82 (m, 4H), 1.62–1.55 (m, 4H), 1.39–1.23 (m, 12H), 0.89–0.85 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 149.6, 144.2, 135.0, 134.1, 133.5, 132.8, 131.2, 130.7, 129.7, 129.6, 126.7, 122.6, 36.2, 36.1, 31.35, 31.32, 29.5, 29.4, 28.4, 28.3, 22.55, 22.52, 14.01.

1-(3'',4'-bis(hexylthio)-[2,2':5',2''-terthiophen]-5-yl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro heptan-1-one (1f) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 62%. Orange oil. EI-MS *m/z* 592 (M^+). ^1H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.89 (d, *J*=5 Hz, 1H), 7.42 (d, *J*=5 Hz, 1H), 7.39 (s, 1H), 7.29 (d, *J*=5 Hz, 1H), 7.12 (d, *J*=5 Hz, 1H), 2.86-2.83 (m, 4H), 1.62–1.55 (m, 4H), 1.40–1.26 (m, 12H), 0.89–0.85 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 174.8, 149.6, 137.7, 135.8, 135.3, 134.4, 133.6, 132.8, 131.3, 130.7, 130.6, 130.1, 126.4, 125.9, 125.2, 36.2, 36.1, 35.8, 31.4, 29.53, 28.4, 22.5, 13.9.29.

General synthesis of compounds 1g, 1h: To a solution of **1e**, **1f** (1 mmol) in CH_2Cl_2, 1 mmol of NBS were added. The reaction mixture was sonicated for 15 min at room temperature. The solvent was removed and the products were purified by flash chromatography.

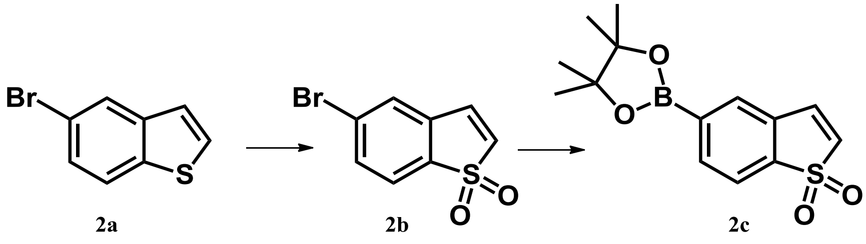
5-bromo-3,3'-bis(hexylthio)-5''-nitro-2,2':5',2''-terthiophene (1g) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 90%. Dark red oil. EI-MS *m/z* 370 (M^+). ^1H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.86 (d, *J*=4 Hz, 1H), 7.29 (s, 1H), 7.11 (d, *J*=4 Hz, 1H), 7.06 (s, 1H), 2.86–2.82 (m, 4H), 1.62–1.56 (m, 4H), 1.39–1.26 (m, 12H), 0.90–0.87 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 149.8, 143.9, 134.5, 134.2, 133.4, 133.1, 132.9, 132.8, 129.8, 129.6, 122.7, 114.1, 36.5, 31.3, 29.44, 29.41, 28.4, 28.3, 22.5, 14.02, 14.01.

1-(5''-bromo-3'',4'-bis(hexylthio)-[2,2':5',2''-terthiophen]-5-yl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-one (1h) → The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Yield 99%. Dark red oil. EI-MS *m/z* 670 (M^+). ^1H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 7.89 (d, *J*=4 Hz, 1H), 7.36 (s, 1H), 7.29 (d, *J*=4 Hz, 1H), 7.06 (s, 1H), 2.87–2.83 (m, 4H), 1.63–1.56 (m, 4H), 1.42–1.24 (m, 12H), 0.90–0.85 (m, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 175.0, 149.3, 137.7, 136.0, 134.7, 134.5, 133.4, 133.1, 132.9, 132.8, 130.3, 125.4, 114.0, 36.4, 31.3, 29.43, 29.40, 28.3, 26.9, 22.5, 14.0, 13.9.

General synthesis of tributyl stannane derivatives: To a solution of brominated derivative (5-bromo-3,3'-bis(hexylthio)-2,2'-bithiophene (**1a**)(2), or 2-bromo-3-(hexylthio)thiophene(2) (**2b**) (1 mmol) in anhydrous THF (5 mL) at room temperature, n-BuLi (1 mmol or 2 mmol) was added. After 1.5h, Bu_3SnCl (1mmol or 2 mmol) was added and the reaction was stirred for 12h at room temperature. The mixture was extracted with water and then the organic phase was evaporated under reduced pressure.

(3,3'-bis(hexylthio)-[2,2'-bithiophen]-5-yl)tributylstannane (1d) → Yield 60%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.33 (d, *J*=5.2 Hz, 1H), 7.08 (s, 1H), 7.06 (d, *J*=5.2 Hz, 1H), 2.79–2.74 (m, 4H), 1.62–1.49 (m, 12H), 1.37–1.09 (m, 22H), 0.93–0.83 (m, 15H)

Scheme S3



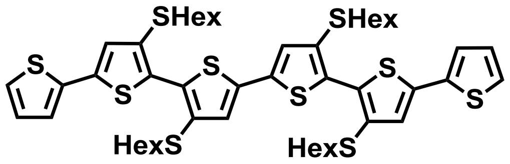
2a 2b 2c

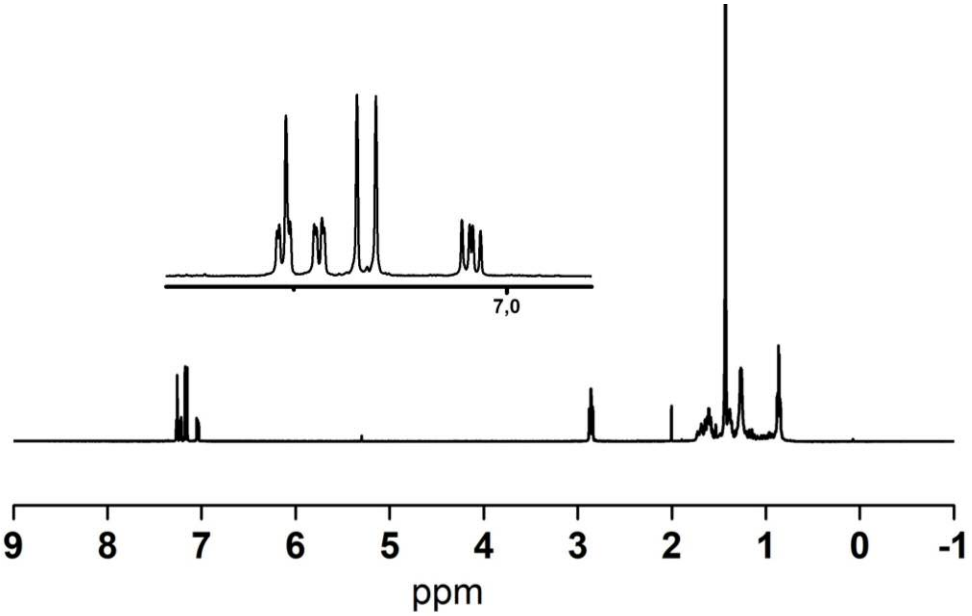
Synthesis of 5-bromobenzo[b]thiophene 1,1-dioxide (2b): To a solution of **2a** (1 mmol) in CH_2Cl_2, 3 mmol of meta-chloroperoxybenzoic acid (mCPBA) were added. The reaction mixture was sonicated in an ultrasonic bath. The solvent was removed and the product was purified by flash chromatography (Cyclohexane/CH_2Cl_2/AcOEt, 70:25:5). →Yield 95%. White solid; EI-MS *m/z* 245(M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.66 (d, *J*=8 Hz, 1H), 7.59 (d, *J*=8 Hz, 1H), 7.51 (s, 1H), 7.20 (d, *J*=6.8 Hz, 1H), 6.77 (d, *J*=6.8 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): 135.4, 133.6, 133.1, 132.0, 131.3, 128.6, 128.1, 122.6.

Synthesis of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[b]thiophene 1,1-dioxide (2c): A solution of **2b** (1mmol.), Bis(pinacolato)diboron (1.2 mmol), CH_3COOK (3 mmol.) in anhydrous dioxane (3 mL) was first purged with nitrogen for 20 min and then, after addition of Pd(dppf)Cl_2, refluxed at 110°C for 20 h. The cooled mixture was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. The crude product was purified by distillation under vacuum (1.5 mmHg) collecting the fraction boiling at 120°C. Yield 96%. Pale yellow solid; EI-MS *m/z* 292(M^+); ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.90 (d, *J*=7.2 Hz, 1H), 7.23 (s, 1H), 7.65 (d, *J*=7.2 Hz, 1H), 7.18 (d, *J*=6.8 Hz, 1H), 6.67 (d, *J*=6.8 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$): 138.7, 137.4, 132.7, 131.3, 130.4, 130.3, 120.5, 84.6, 25.0, 24.9, 24.6.

(1) *J. Am. Chem. Soc.*, **2005**, 127, 1348 -1349. (2) *J. Am. Chem. Soc.*, **2011**, 133, 8654-866. (3) *Tetrahedron*, **1997**, 53, 9401-9406.

III. ^{1}H and ^{13}C NMR spectra





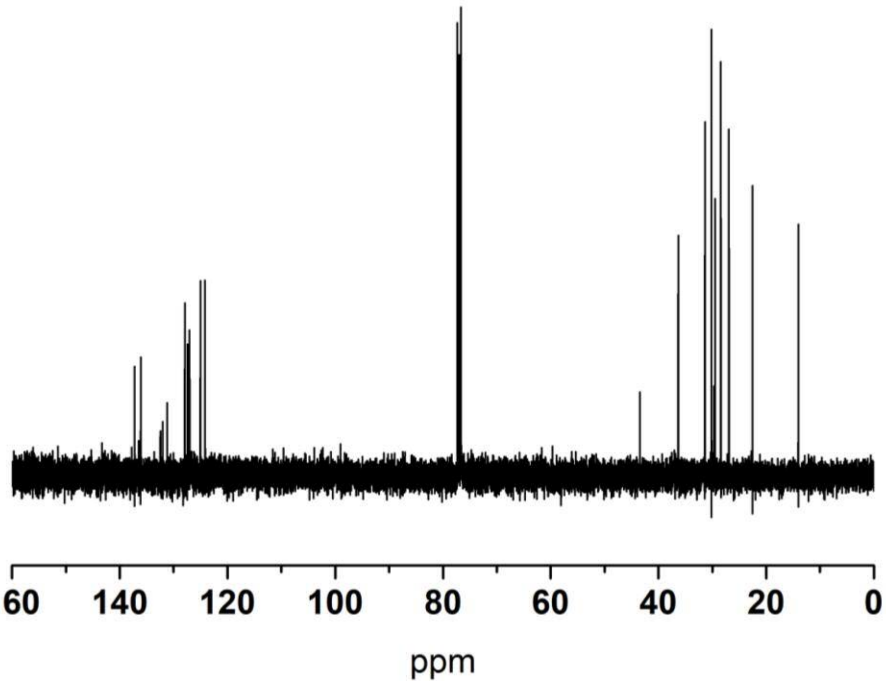


Figure S1. ^{1}H and ^{13}C NMR spectra of compound **1**.

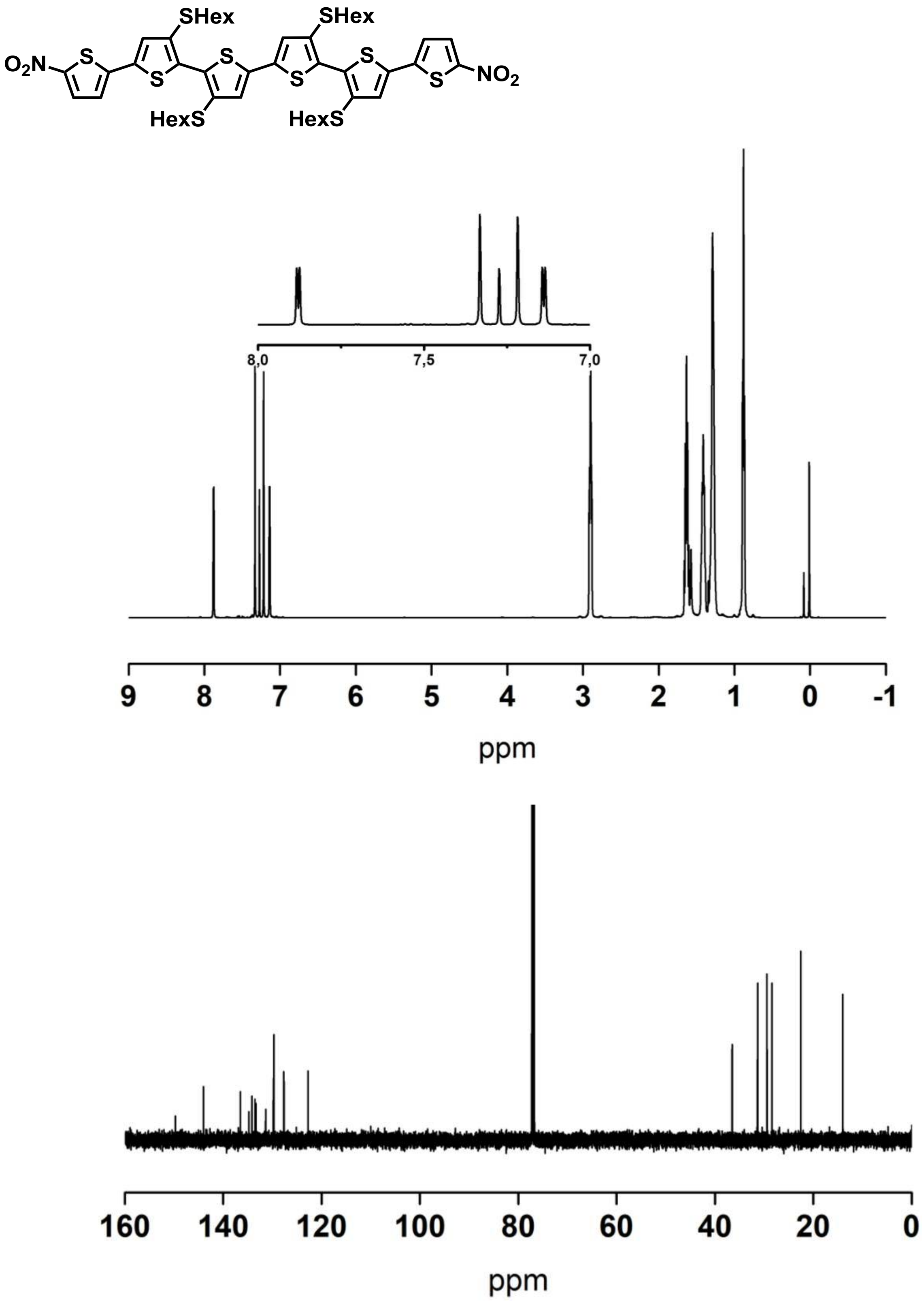


Figure S2. ^{1}H and ^{13}C NMR spectra of compound **2**.

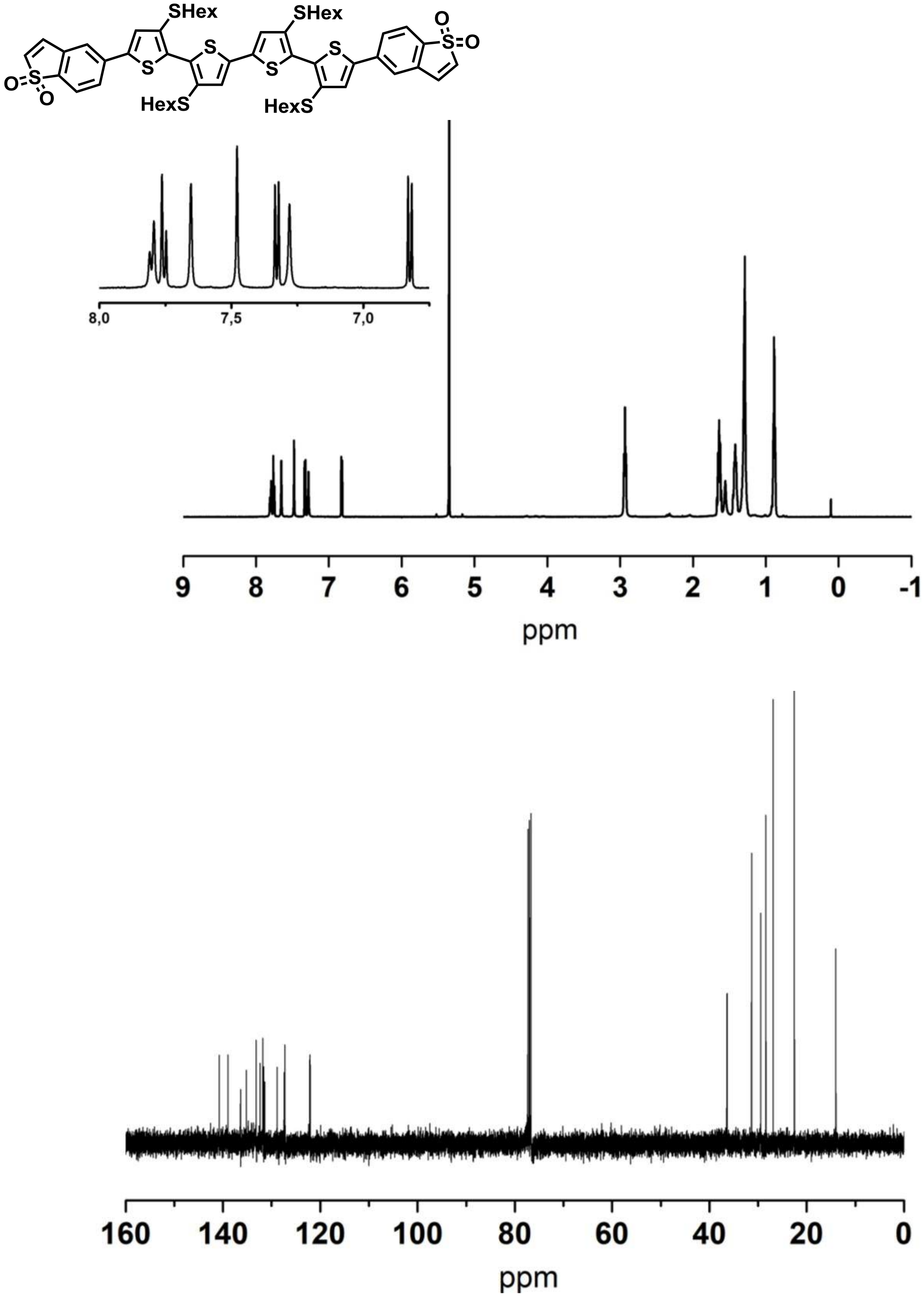


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **3**.

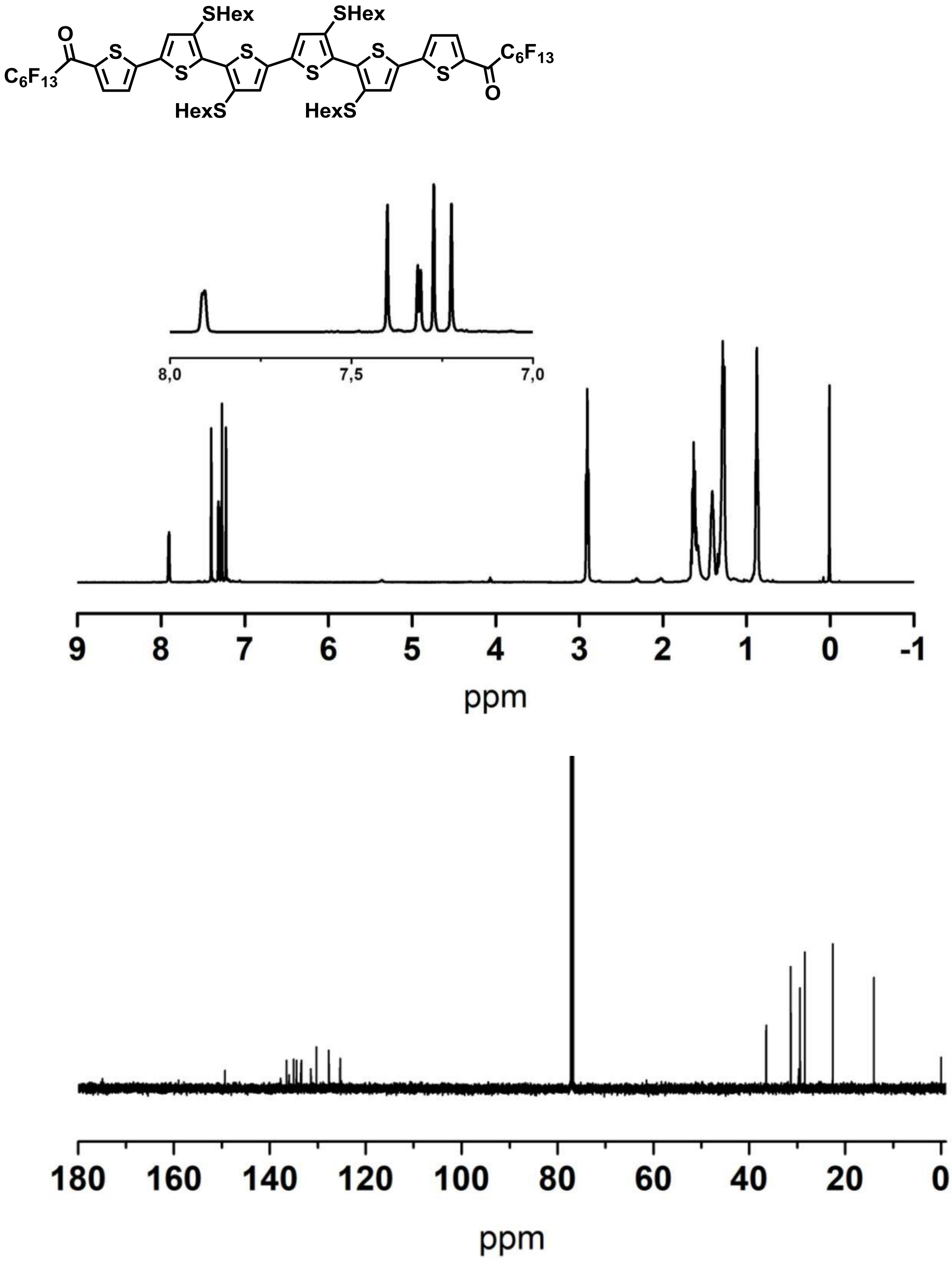


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **4**.

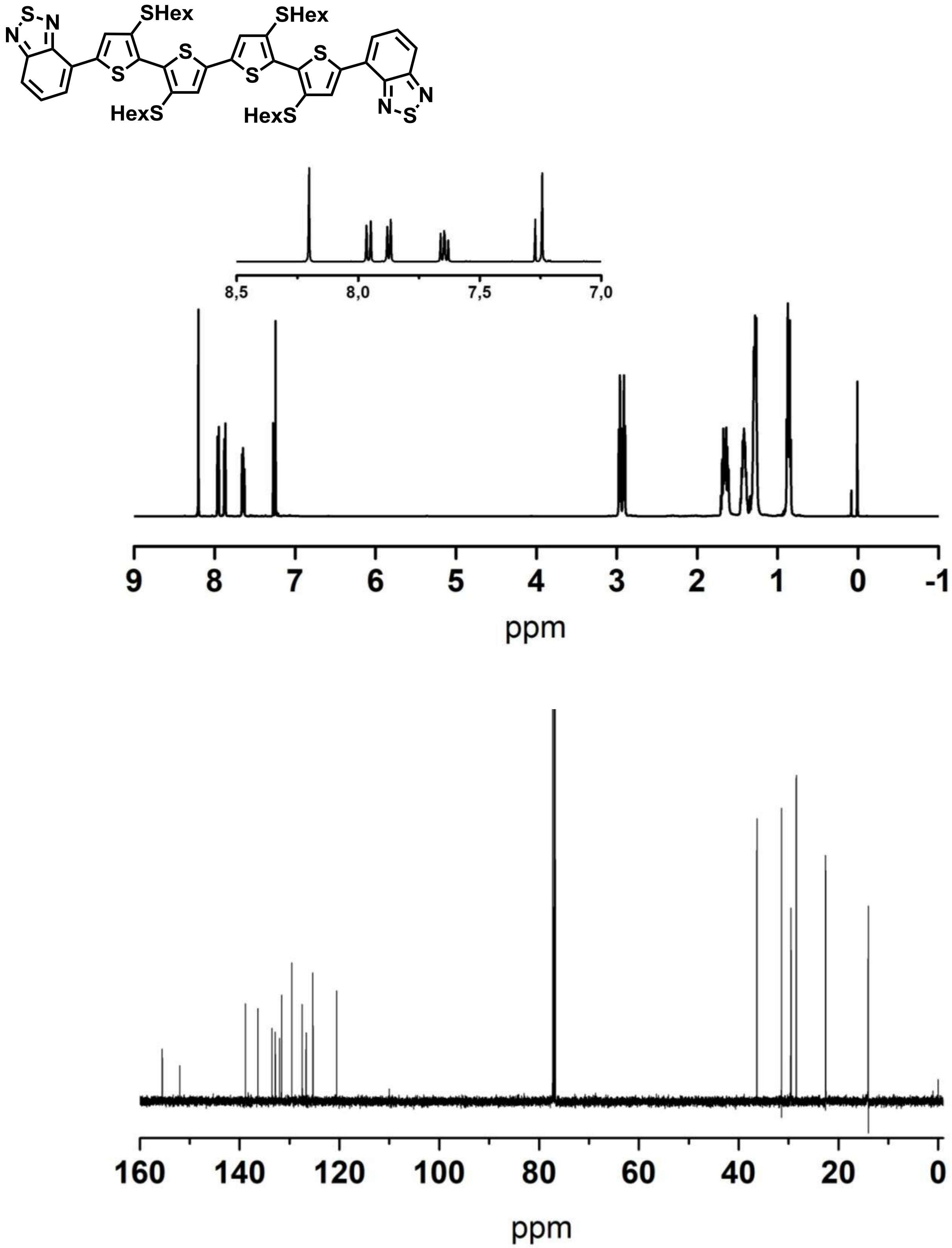


Figure S5. ^{1}H and ^{13}C NMR spectra of compound **5**.

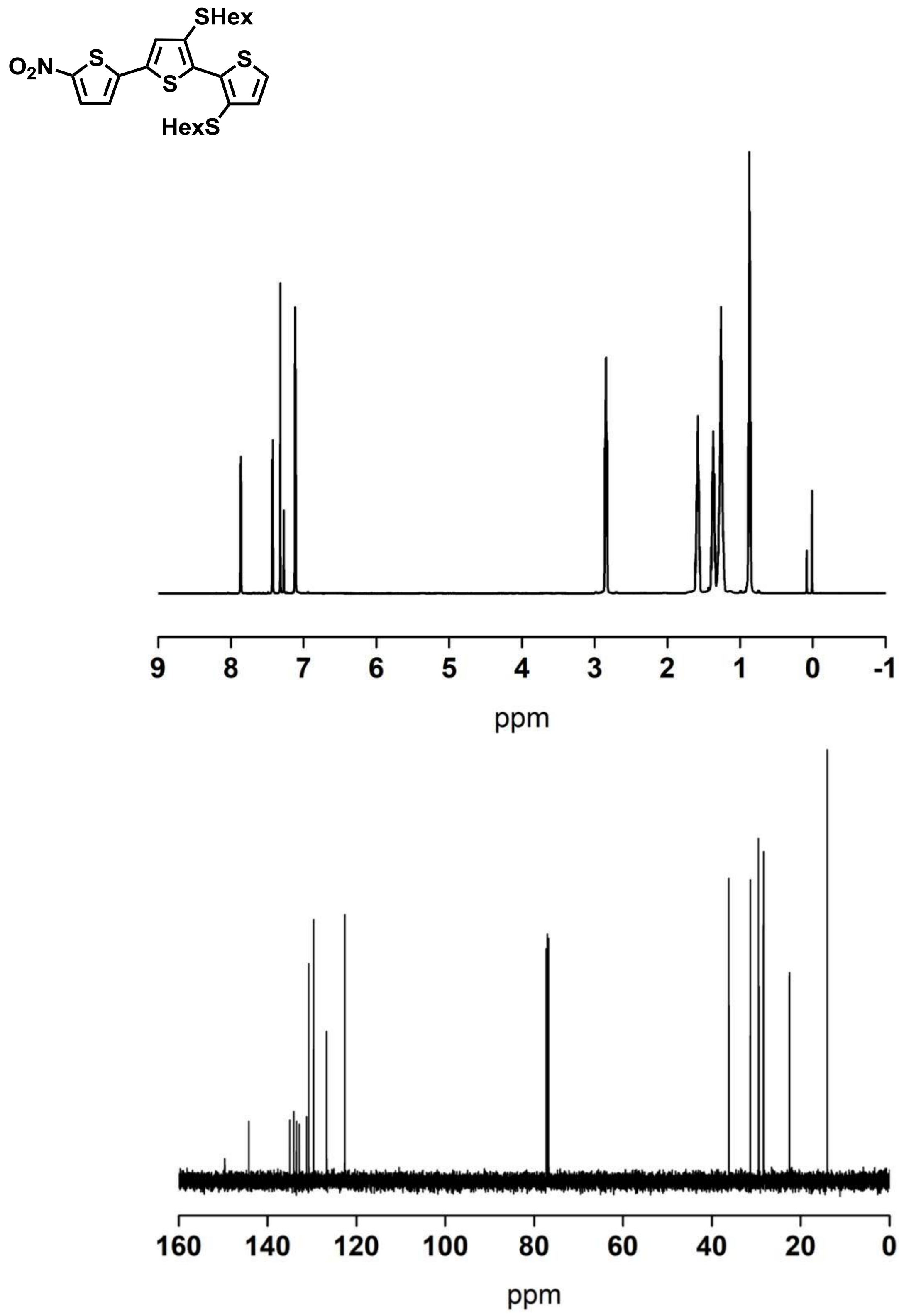


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **1e**.

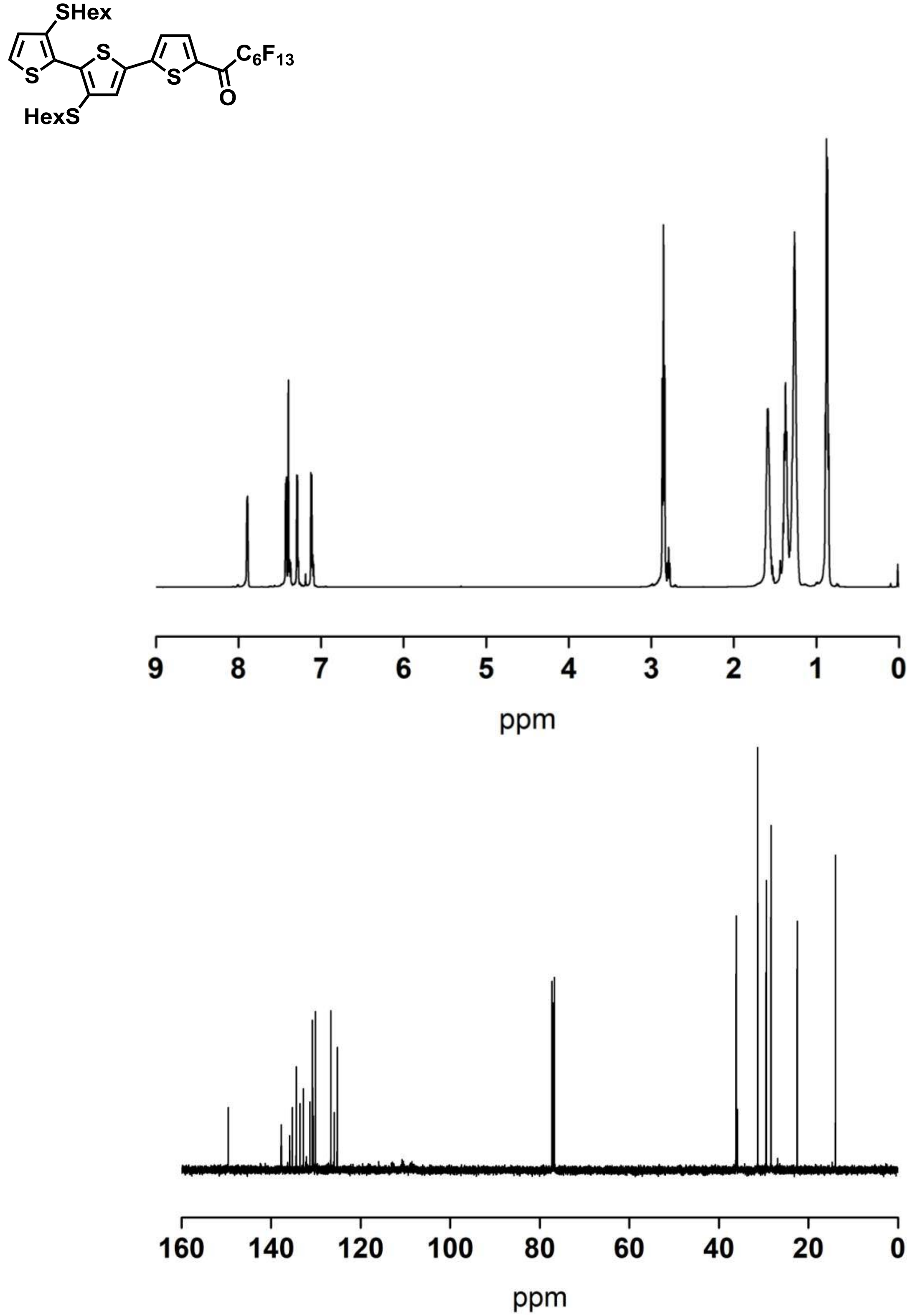


Figure S7. ^{1}H and ^{13}C NMR spectra of compound **1f**.

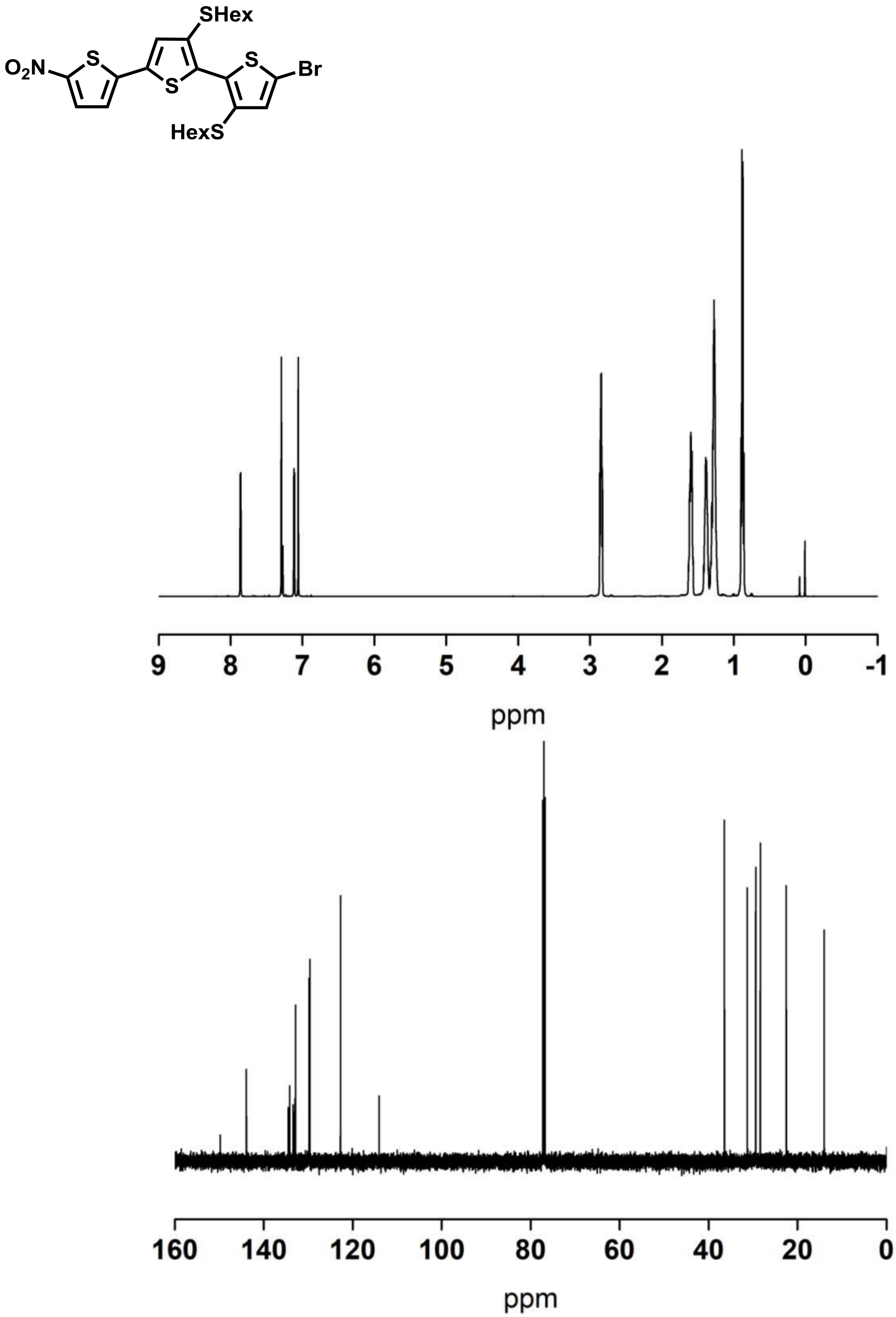


Figure S8. ^{1}H and ^{13}C NMR spectra of compound **1g**.

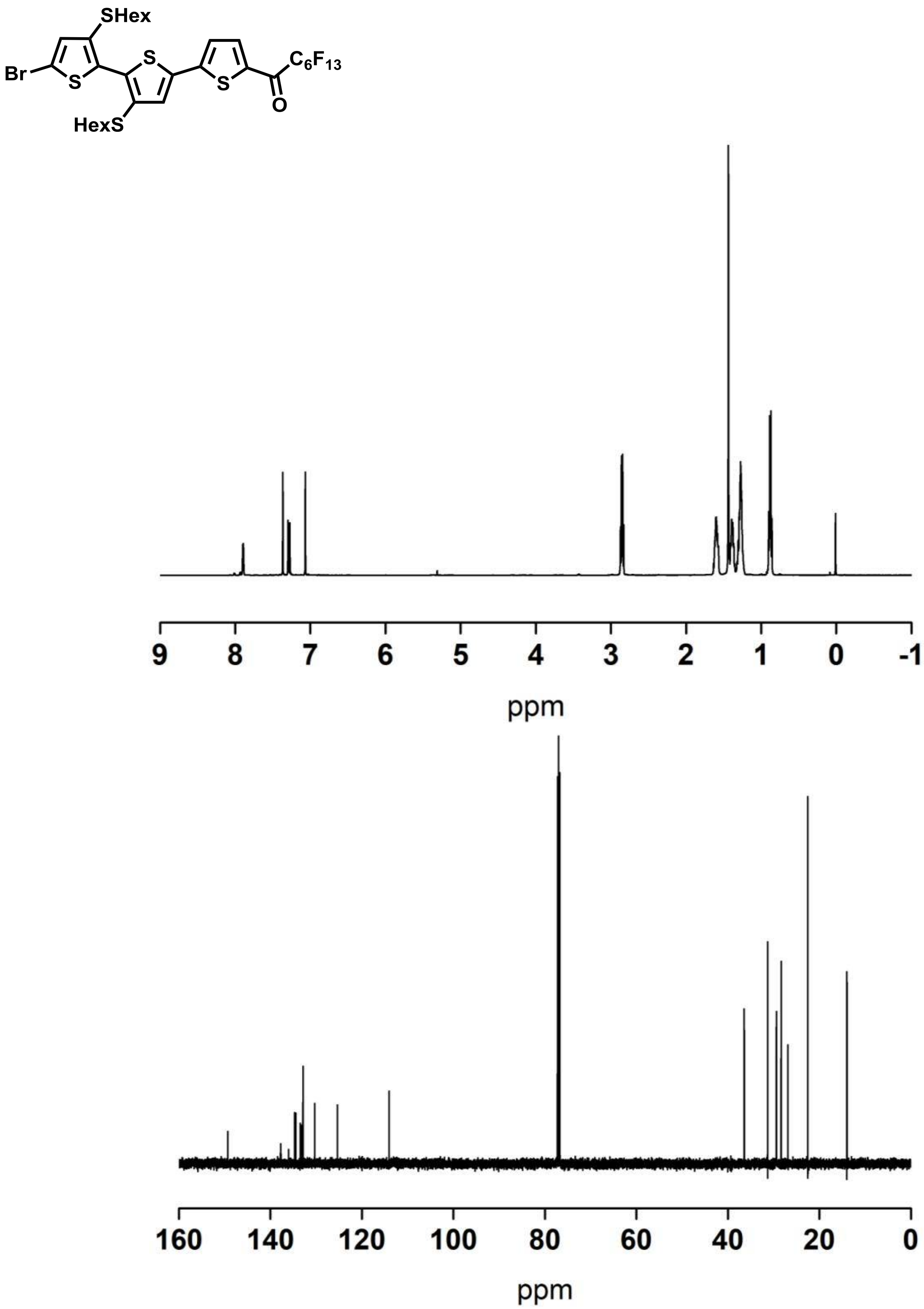


Figure S9. ^{1}H and ^{13}C NMR spectra of compound **1h**.

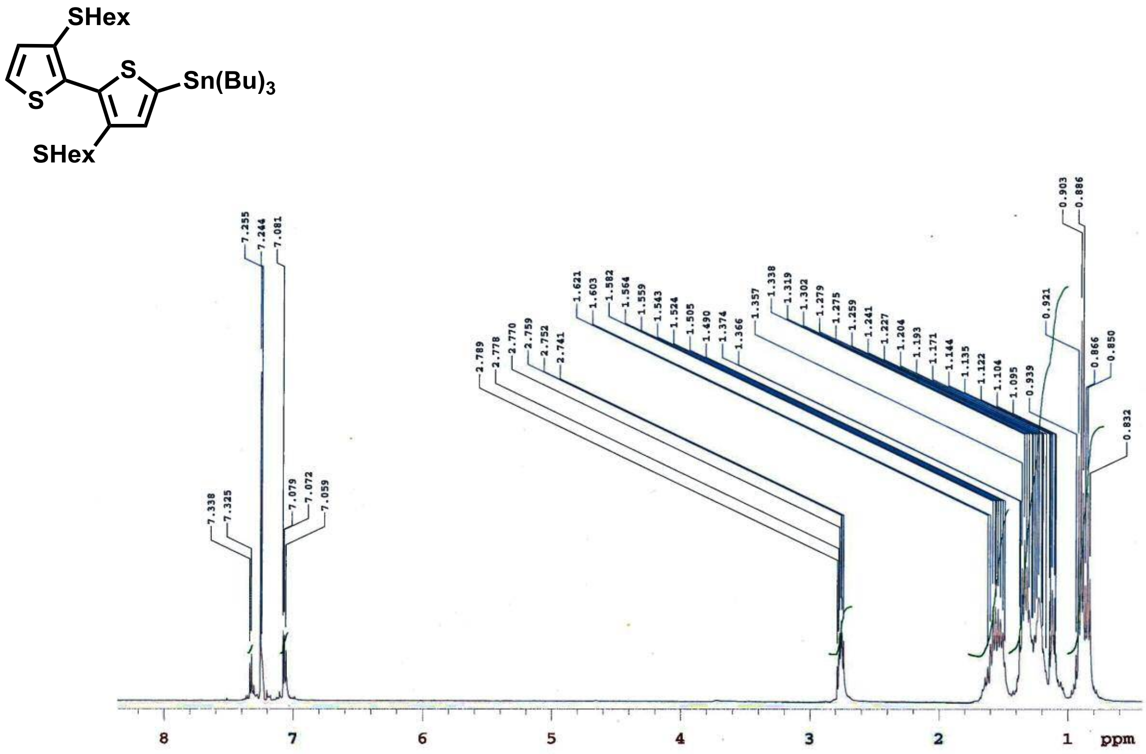


Figure S10. ^{1}H NMR spectrum of compound **1d**.

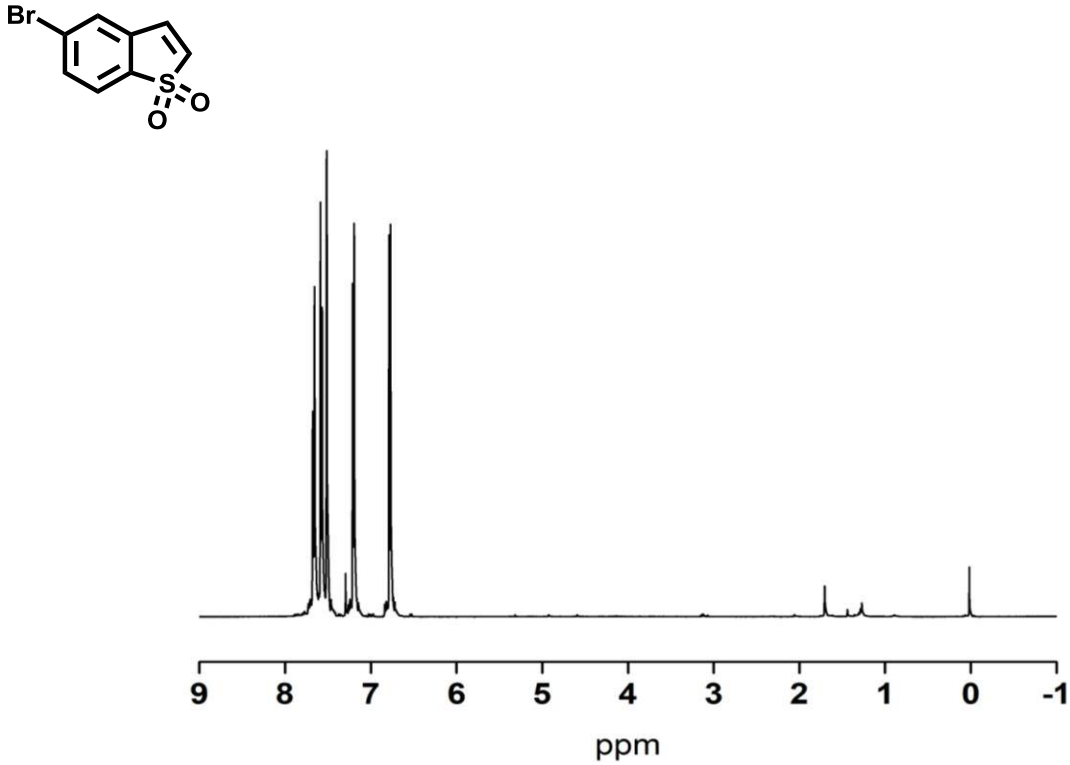


Figure S11. ^{1}H spectrum of compound **2b**.

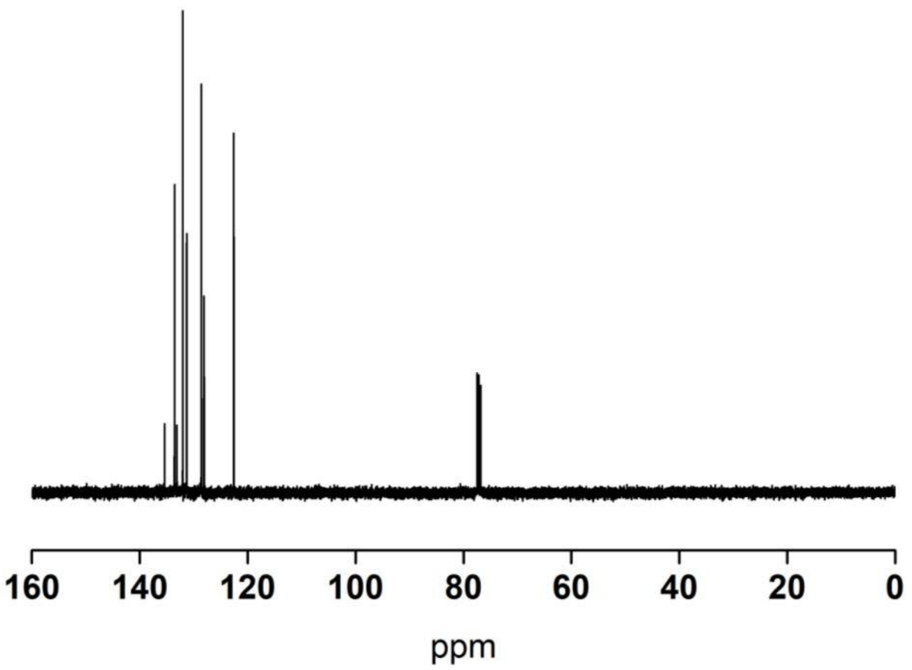


Figure S12. ^{13}C NMR spectrum of compound **2b**.

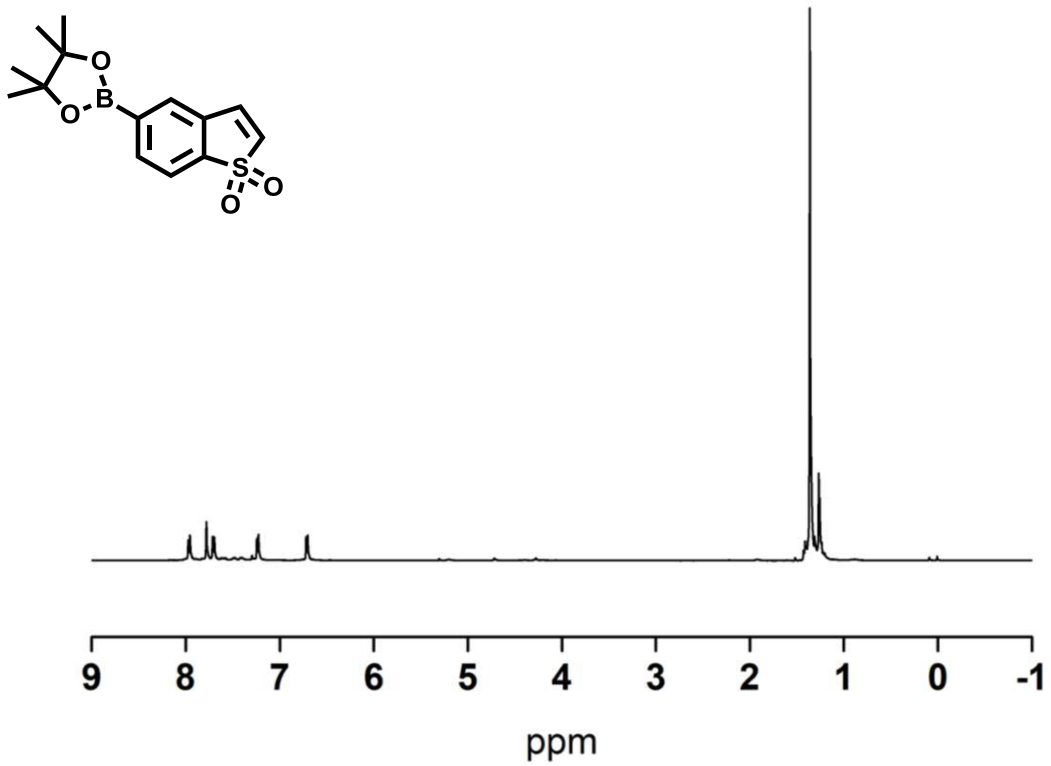


Figure S13. ^{1}H spectrum of compound **2c**.

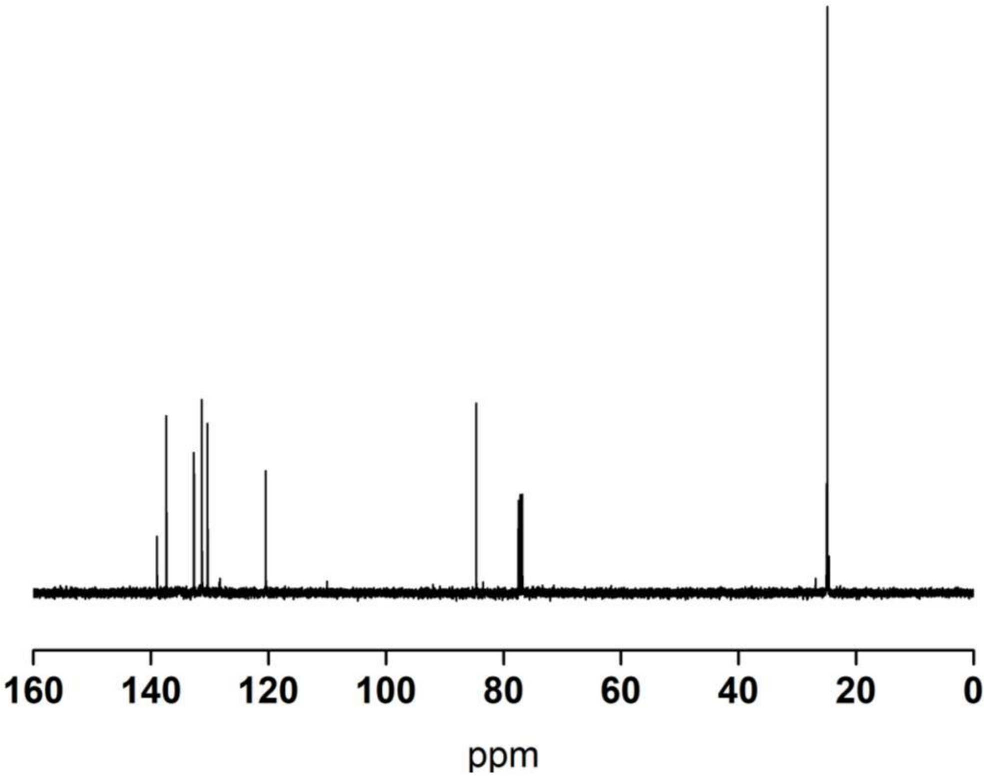


Figure S14. ^{13}C NMR spectrum of compound **2c**.

IV. Optical microscopy

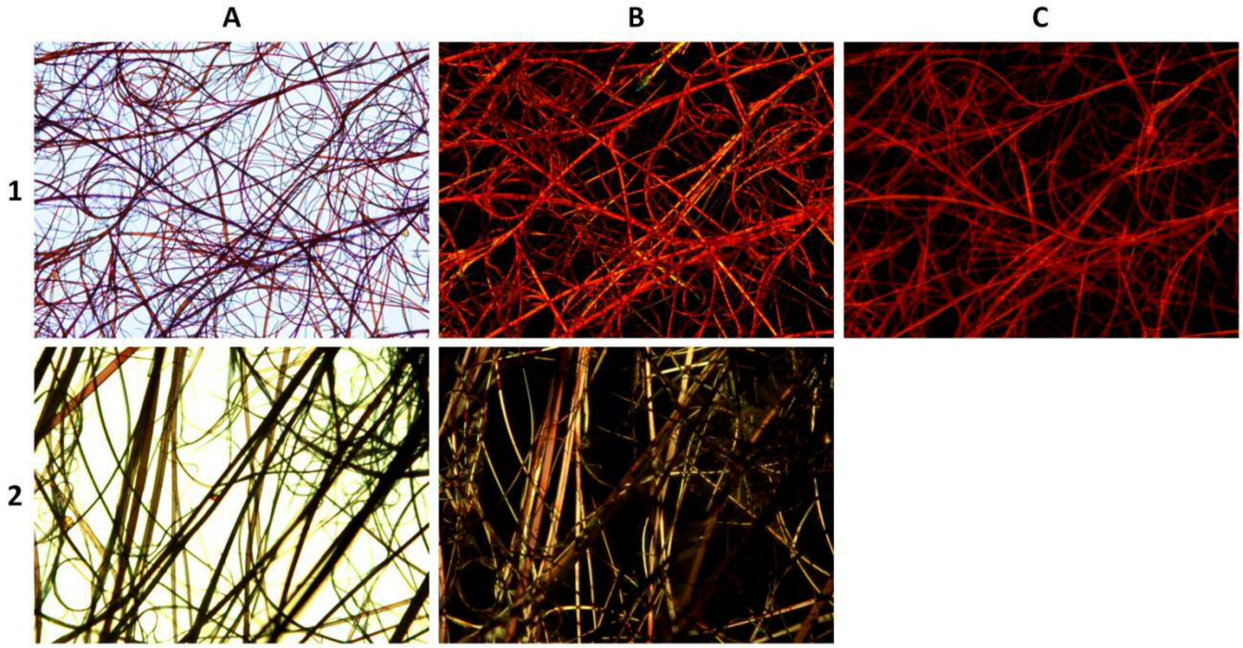


Figure S15. A) Light transmission optical microscopy, B) optical microscopy with cross polars of the fibers of **1,2** and C) fluorescence image of the fibers of **1**. Scale bar = 50nm.

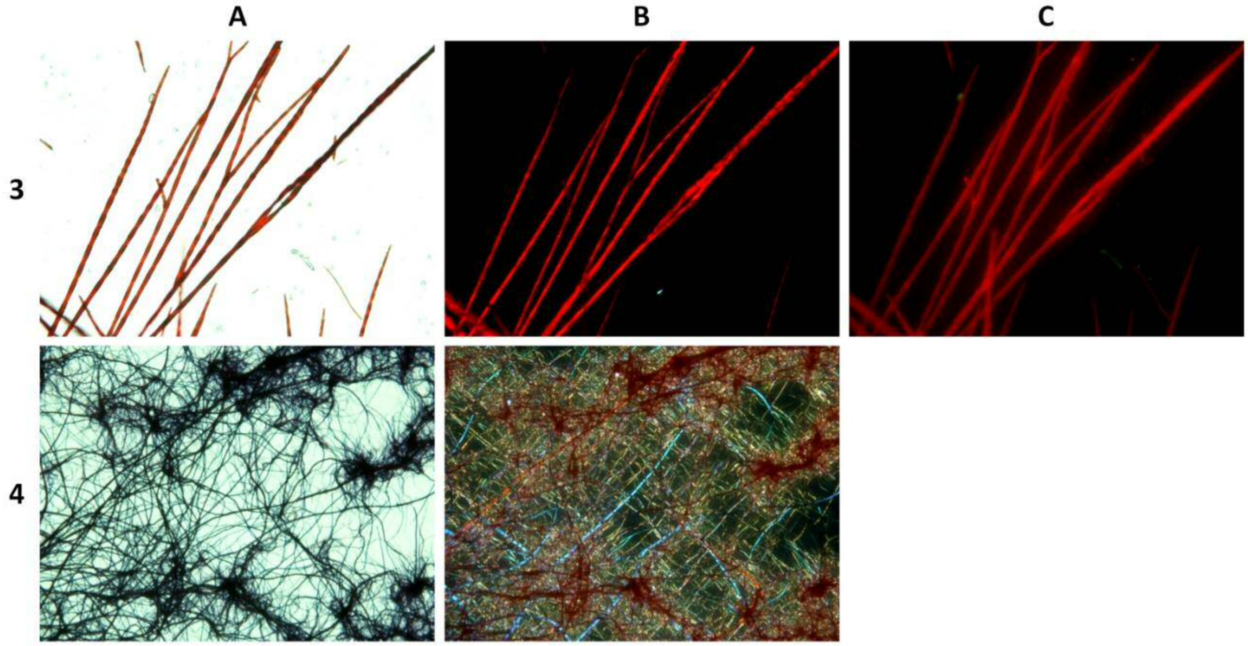


Figure S16. A) Light transmission optical microscopy, B) optical microscopy with cross polars of the fibers of **3,4** and C) fluorescence image of the fibers of **3**. Scale bar = 50nm.

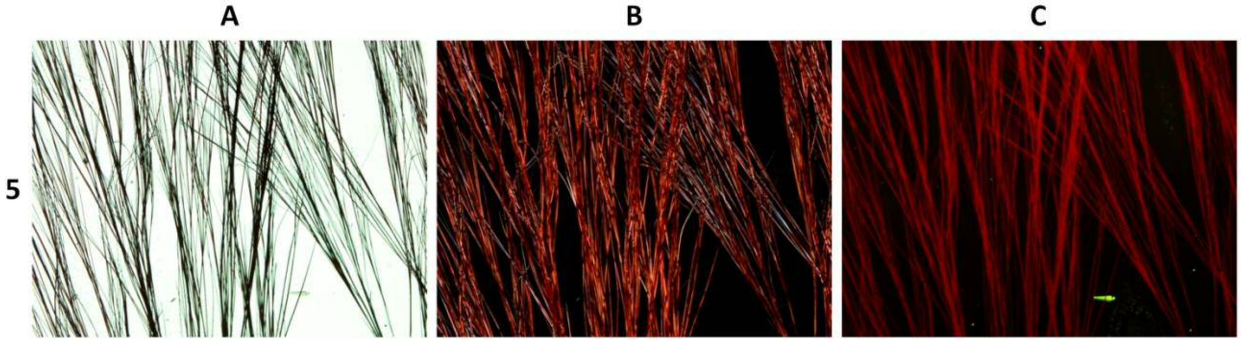


Figure S17. A) Light transmission optical microscopy, B) optical microscopy with cross polars and C) fluorescence image of the fibers of the tape-like polymorph of **5**. Scale bar = 50nm.

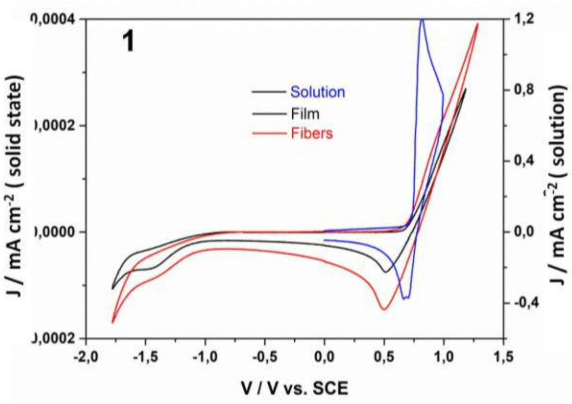
V. Emission Lifetimes

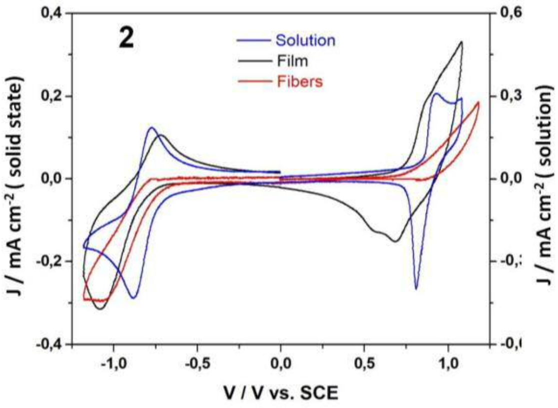
Table S1. Emission lifetimes of **1-5** in CH_2Cl_2 at r.t.[a]

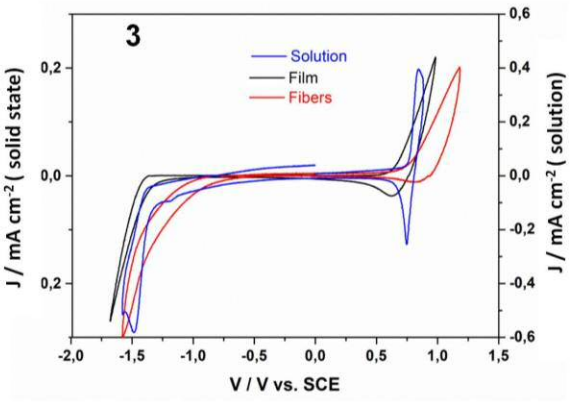
	τ_1 (ns) / %	τ_2 (ns) / %	χ^2
1[b]	0.3, 53%	1.1, 47%	0.853
1[c]	0.1, 53%	2.3, 47%	1.440
1[d]	0.6, 77%	1.0, 23%	0.974
1[e]	0.4, 50%	1.0, 50%	2.138
1[f]	1.1	-	1.166

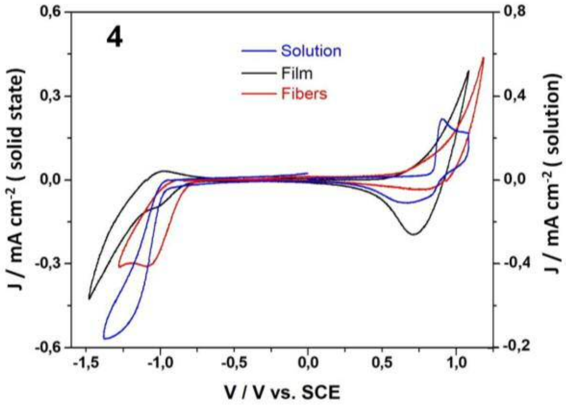
[a] λ_{ex}=405 nm. [b] λ_{em}=540 nm. [c] λ_{em}=660 nm. [d] λ_{em}=575 nm. [e] λ_{em}=670 nm. [f] λ_{em}=670 nm.

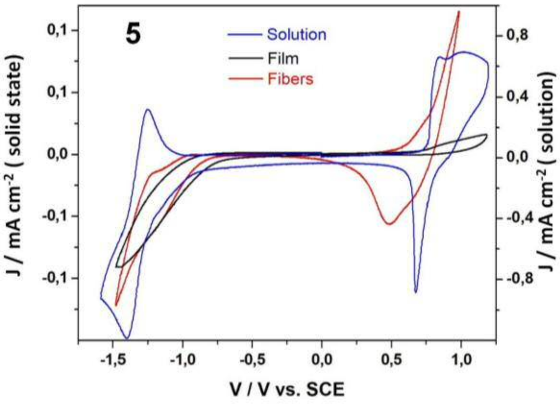
VI. Cyclic Voltammetry

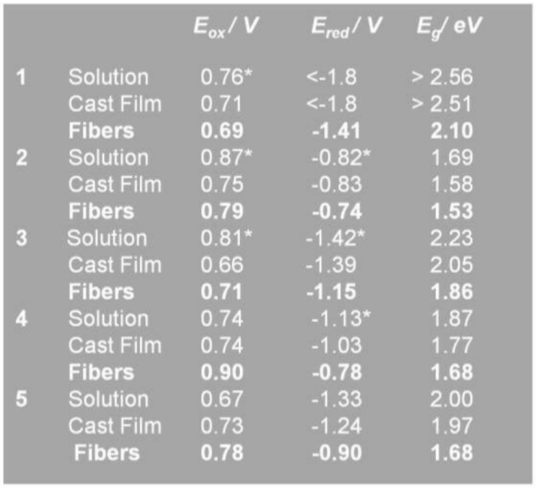












		E_{ox} / V	E_{red} / V	E_g / eV
1	Solution	0.76*	<-1.8	> 2.56
	Cast Film	0.71	<-1.8	> 2.51
	Fibers	**0.69**	**-1.41**	**2.10**
2	Solution	0.87*	-0.82*	1.69
	Cast Film	0.75	-0.83	1.58
	Fibers	**0.79**	**-0.74**	**1.53**
3	Solution	0.81*	-1.42*	2.23
	Cast Film	0.66	-1.39	2.05
	Fibers	**0.71**	**-1.15**	**1.86**
4	Solution	0.74	-1.13*	1.87
	Cast Film	0.74	-1.03	1.77
	Fibers	**0.90**	**-0.78**	**1.68**
5	Solution	0.67	-1.33	2.00
	Cast Film	0.73	-1.24	1.97
	Fibers	**0.78**	**-0.90**	**1.68**

Figure S18. Cyclic voltammograms at 0.1 V s^{-1} of compounds **1-5** in CH_2Cl_2 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ solution and of the related fibers and thin film grown on ITO and tested in propylenecarbonate 0.1 mol L^{-1} $(C_2H_5)_4NBF_4$. In the table the corresponding redox potentials and energy gaps.

Figure S35 shows the CVs of compounds **1-5** in solution, cast films from CH_2Cl_2 and as fibers, together with the corresponding redox potentials and energy gaps. Compound **1** in solution shows a quasi-reversible oxidation wave but the reduction wave is outside the electrochemical window of the electrolyte. The CVs of compounds **2** and **5** in solution show quasi-reversible oxidation waves, with an absorption pre-peak in the case of **5**, characterized by sharp reverse peaks due to the fast reduction of the radical cation absorbed on the surface of the electrode. The reduction waves appear quasi-reversible with a good symmetry of the direct and reverse waves. Compounds **3** and **4** also show reduction waves within the electrochemical windows but they are not reversible. Finally, compound **3** shows an oxidation wave similar to that of compound **2** but 60 mV less positive, whereas compound **4** shows the less positive oxidation wave but also the less symmetric one, due to a broad reverse wave. By comparing the five energy gaps in solution, compound **1** shows the lowest one likely due to the huge shift of the LUMO orbital energy related to the strong effect of the nitro-group in stabilizing radical-anions. In general, the compounds **1-5** show smaller energy gaps when grown in solid state and, in particular, when the order of the solid is driven toward the fibers. This is mainly due to the displacement of the reduction potentials towards less negative values, in the range of 300-500mV compared to the solution, corresponding to a marked increase in electron affinity. So, if the reduction potential of compound **1** is outside the electrochemical window both in solution and in amorphous film, in the fiber-state the reduction standard potential becomes -1.41 V. The energy gaps of the fibers is about 0.2-0.3 eV smaller than that of the cast film, except for compound **2** where it decreases by 0.1 eV. The fibers of compound **2** have also the peculiarity of a satisfactory reversibility of the reduction process.

VII. X-ray Diffraction

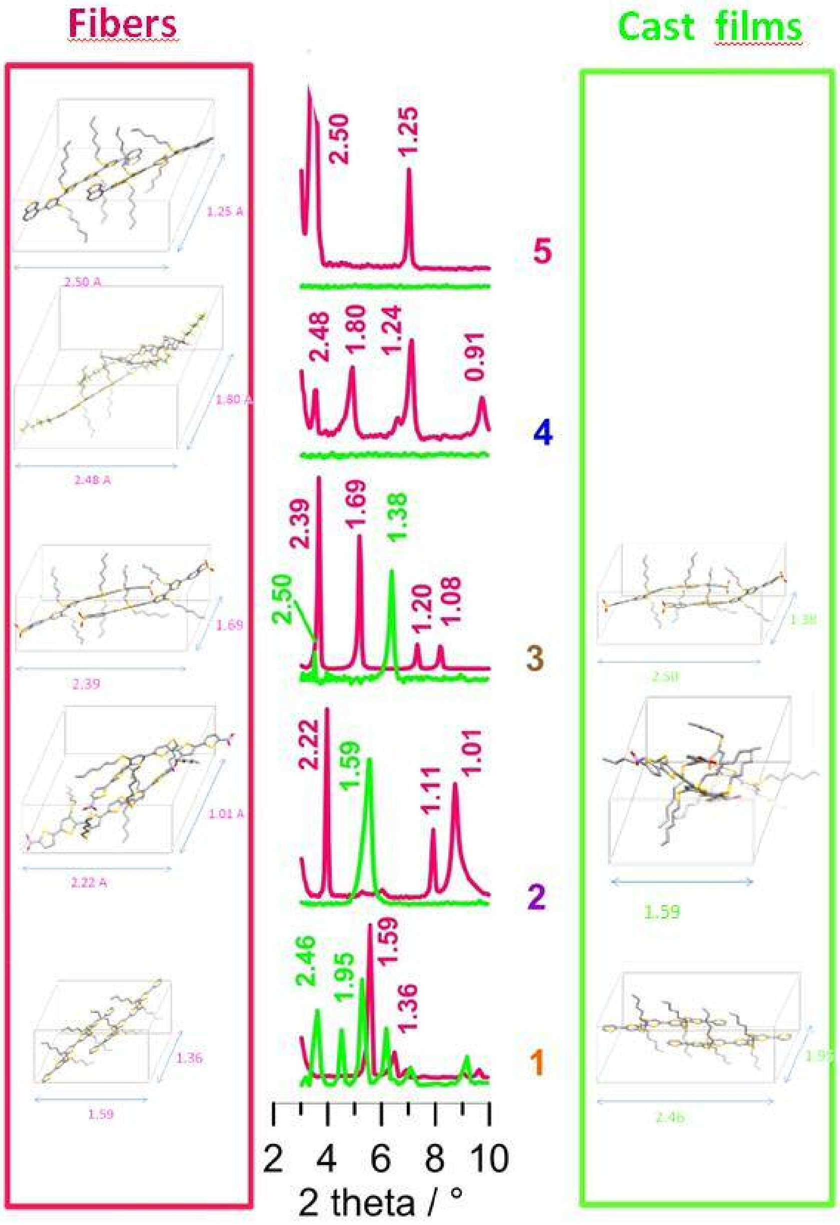


Figure S19. X-ray diffraction of compounds **1-5** in CH_2Cl_2 in cast films and fibers. The crystalline cells are derived with the aid of DFT calculations.

VIII. Photoconductivity

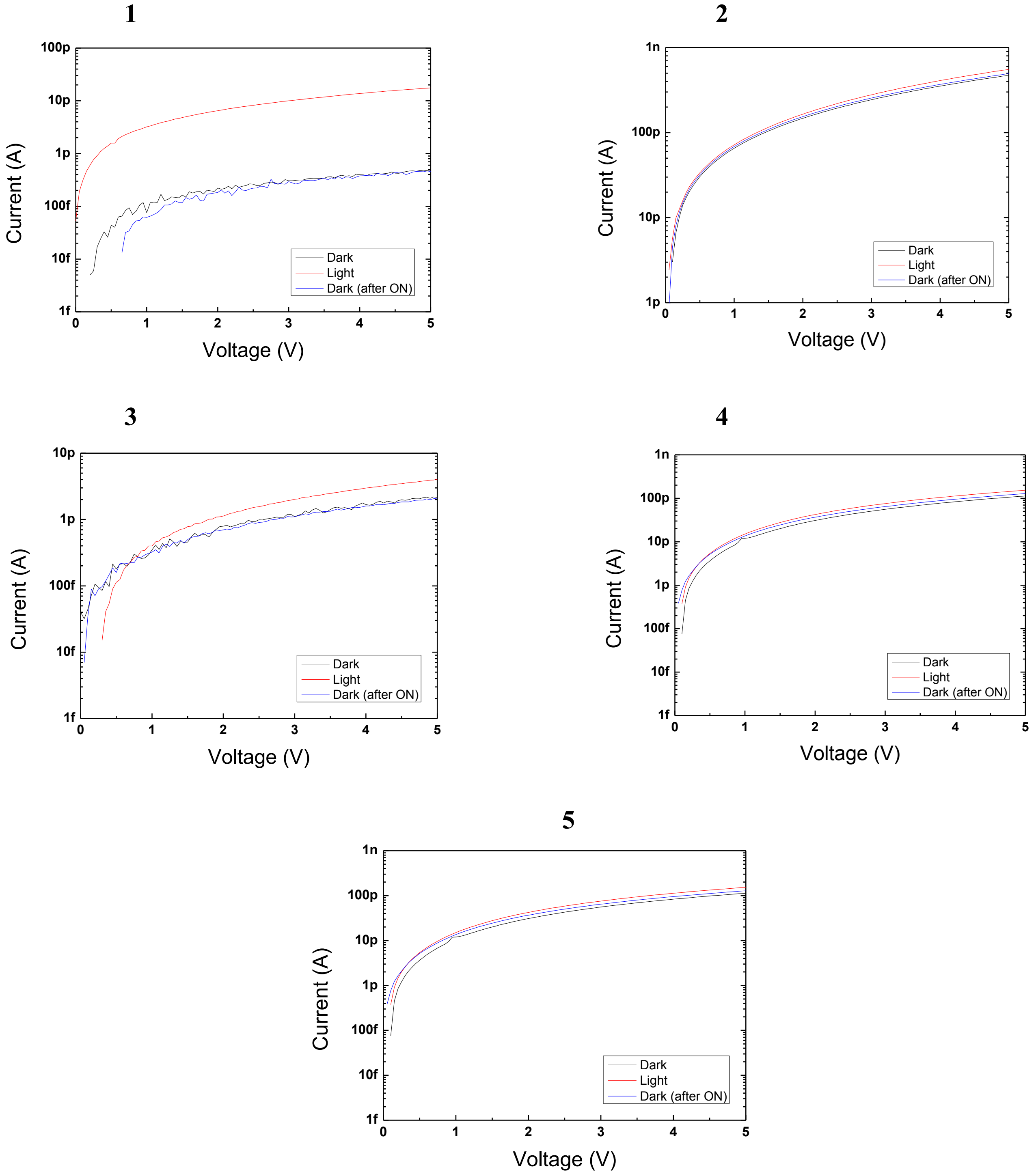


Figure S20