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Novel dithieno[3,2-*f*:2′,3′-*h*]quinoxaline-based polymers as hole transport materials for perovskite solar cells

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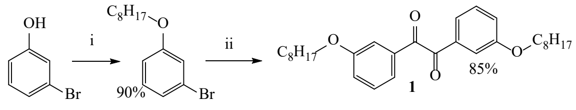
General

All solvents and reagents were purchased from commercial suppliers (Acros Organics, Sigma-Aldrich) and were either used as received or purified using standard methods. All obtained compounds were purified to achieve the purity of at least 99.5% according to HPLC or GC, as well as NMR spectroscopy. Molecular weight characteristics of conjugated polymers were obtained using Shimadzu LC20 instrument equipped with a Phenomenex Luna Phenogel 5u column (0.78×30 cm, 5-500 kDa). Thermal gravimetry analysis was performed using a PerkinElmer Simultaneous Thermal Analyzer STA 8000 with a heating rate of 10ºC min^{-1} and nitrogen flow rate of 20 mL min^{-1}. Cyclic voltammetry (CV) of the polymer films was performed using potentiostat Elins P-30SM at room temperature with a potential sweep rate of 50 mVs^{-1}. The cyclic voltammetry measurements were performed for thin films of polymers deposited on glassy carbon disc electrode (working electrode) by drop casting from a mixture of polymers in chlorobenzene. The measurements were performed in a three-electrode electrochemical cell using 0.1M solution of $TBAPF_6$ in dry acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in a 0.01M solution of $AgNO_3$ in 0.1M TBAP in dry CH_3CN as a reference Ag^+/Ag electrode. Ferrocene was used as an internal standard. The electrolyte solution was purged with argon before the measurements were performed. PL spectra were measured using QE Pro High-Performance Spectrometer Ocean Insight fiber spectrometer and 405 nm diode laser (10 mW) as excitation source.

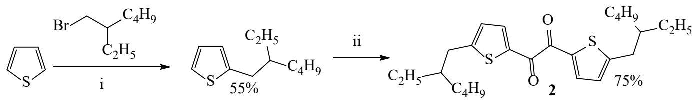
Perovskite solar cells. The perovskite solar cells were assembled in the $ITO/SnO_2/PCBA/perovskite/HTL/VO_y/Ag$ n-i-p configuration following the procedure reported previously.[S1]

Infrared scanning near-field microscopy (IR s-SNOM) measurements. The infrared scanning near-field microscopy (IR s-SNOM) method (neaSNOM, Neaspec) were performed in PsHet mode with a Mid-IR laser MIRcat-2400 (Daylight Solutions) inside an MBraun glove box. ARROW-NCPt (NANOWORLD, Neuchâtel, Switzerland) cantilevers with PtIr coatings with a probe radius of <25 nm, with a typical resonance frequency of 285 kHz and a stiffness of 42 N/m were used. The cantilever oscillation amplitude reached 50–65 nm. The area 5x5 mkm was scanned with resolution 200x200 pixels with speed 1.5 mkm/sec.

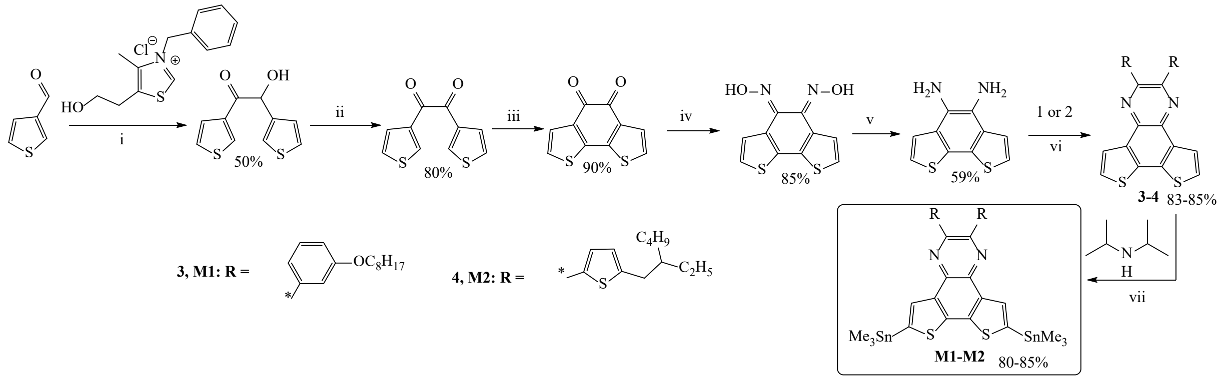
Synthesis



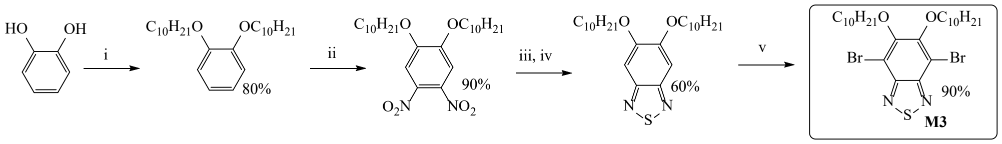
Reagents and conditions: i, $C_8H_{17}Br$, K_2CO_3, DMF; ii, Mg, THF, LiBr, CuBr, $(COCl)_2$



Reagents and conditions: i, BuLi, THF; ii, $(COCl)_2$, $AlCl_3$, DCM/Py



Reagents and conditions: i, Et_3N, EtOH; ii, $CuSO_4$, Py/H_2O; iii, $FeCl_3$, DCM; iv, NH_2OH*HCl, EtOH; v, $SnCl_2$, HCl, EtOH; vi, EtOH; vii, n-BuLi, $SnMe_3Cl$



Reagents and conditions: i, $C_{10}H_{21}Br$, K_2CO_3, acetone; ii, HNO_3, AcOH, DCM; iii, $SnCl_2$*H_2O, HCl, EtOH; iv, $SOCl_2$, Et_3N, DCM; v, Br_2, $CHCl_3$

Scheme S1 Synthesis of **M1-M3**

Monomers **M1-M3** were prepared according to literature methods.[S2-S8]

2,3-Bis(3-(octyloxy)phenyl)dithieno[3,2-f:2',3'-h]quinoxaline **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 5.3 Hz, 2H), 7.54 (d, J = 5.3 Hz, 2H), 7.22-7.26 (m, 4H), 7.17 (d, J = 7.8 Hz, 2H), 6.91 (dd, J = 1.7 Hz, 2H), 3.86 (t, J = 6.5 Hz, 4H), 1. 73 (p, J = 6.6 Hz, 4H), 1.29-1.42 (m, 20H), 0.87-0.90 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 150.83, 140.63, 136.61, 135.22, 134.89, 129.14, 124.60, 124.42, 122.47, 115.81, 115.48, 68.05, 31.83, 29.35, 29.27, 29.16, 26.03, 22.67, 14.11.

2,3-Bis(3-(octyloxy)phenyl)-6,9-bis(trimethylstannyl)dithieno[3,2-f:2',3'-h]quinoxaline **M1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 7.17-7.26 (m, 6H), 6.89 (d, J = 8.2 Hz, 2H), 3.85 (t, J = 6.6 Hz, 4H), 1.69-1.74 (m, 4H), 1.28-1.40 (m, 20H), 0.86-0.88 (m, 6H), 0.41-0.56 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.91, 150.51, 140.82, 140.15, 138.76, 136.50, 135.44, 132.20, 129.14, 122.50, 115.94, 115.31, 68.06, 31.82, 29.32, 29.26, 29.14, 26.01, 22.66, 14.09, -8.06.

2,3-Bis(5-(2-ethylhexyl)thiophen-2-yl)dithieno[3,2-f:2',3'-h]quinoxaline **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 5.3 Hz, 2H), 7.50 (d, J = 5.3 Hz, 2H), 7.24 (d, J = 3.6 Hz, 2H), 6.70 (d, J = 3.6 Hz, 2H), 2.81 (d, J = 6.8 Hz, 4H), 1.64-1.68 (m, 2H), 1.33-1.45 (m, 16H), 0.90-0.95 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.44, 144.31, 139.73, 135.72, 134.99, 134.56, 128.67, 125.74, 124.50, 124.33, 41.45, 34.34, 32.41, 28.87, 25.59, 23.03, 14.16, 10.86.

2,3-Bis(5-(2-ethylhexyl)thiophen-2-yl)-6,9-bis(trimethylstannyl)dithieno[3,2-f:2',3'-h] quinoxaline **M2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.19 (d, J = 3.6 Hz, 2H), 6.70 (d. J = 3.5 Hz, 2H), 2.81 (d, J = 6.6 Hz, 4H), 1.64-1.68 (m, 2H), 1.33-1.44 (m, 16H), 0.91-0.94 (m, 12H), 0.49 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.15, 144.07, 139.99, 139.75, 138.66, 135.69, 135.16, 132.20, 132.06, 131.92, 128.63, 126.94, 125.71, 41.40, 34.31, 32.38, 29.68, 28.85, 25.59, 23.04, 14.16, 10.85, -8.07.

4,7-Dibromo-5,6-bis(decyloxy)benzo[c][1,2,5]thiadiazole **M3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (t, J = 6.6 Hz, 4H), 1.86 (p, J = 7.6 Hz, 4H), 1.47-1.57 (m, 4H), 1.25-1.35 (m, 24H), 0.84-0.87 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.47, 150.34, 106.24, 75.12, 31.88, 30.24, 29.59, 26.41, 29.32, 25.97, 22.67, 14.10.

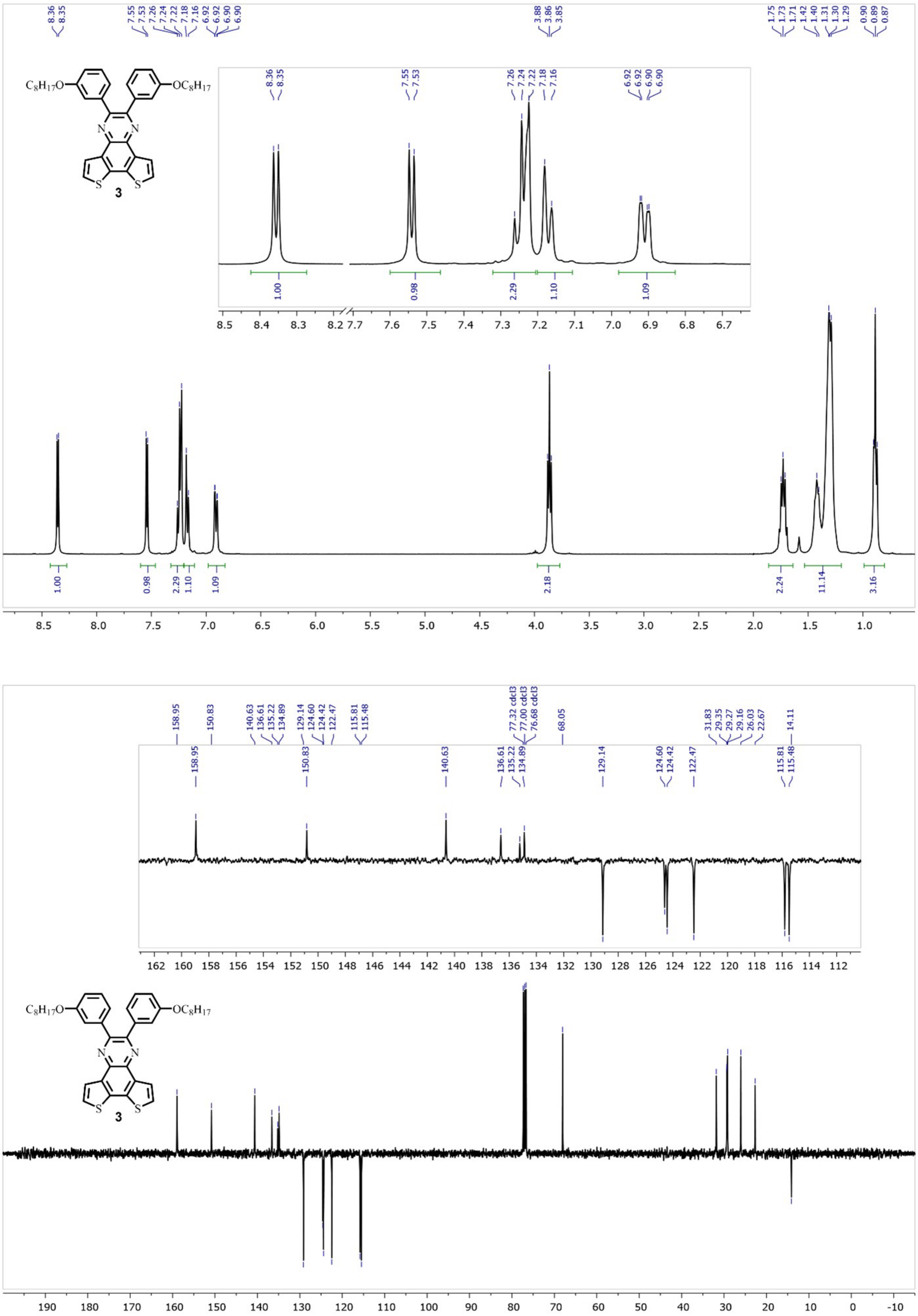


Figure S1 ^{1}H, ^{13}C NMR spectra of the compound **3**

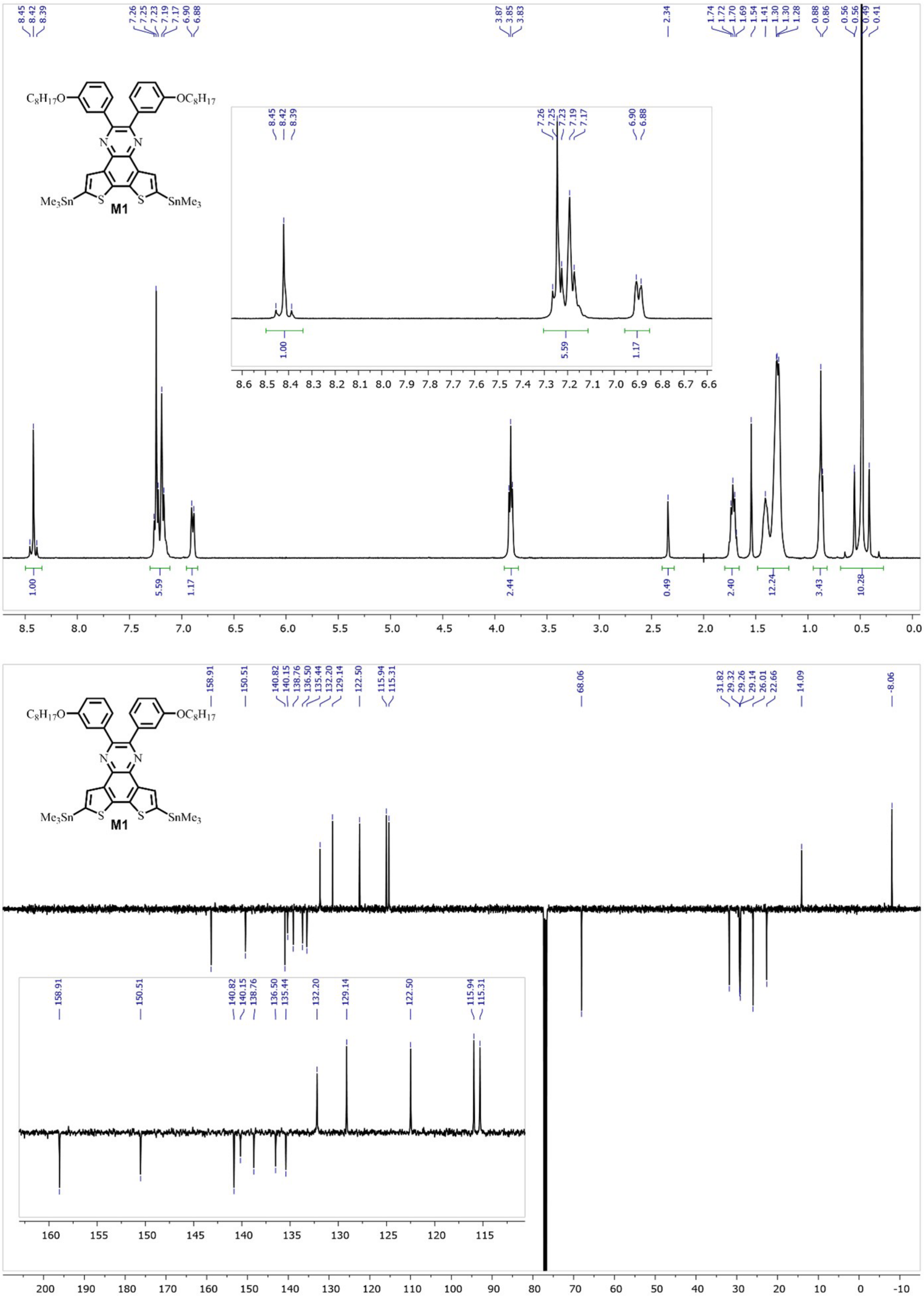


Figure S2 ^{1}H, ^{13}C NMR spectra of the monomer **M1**

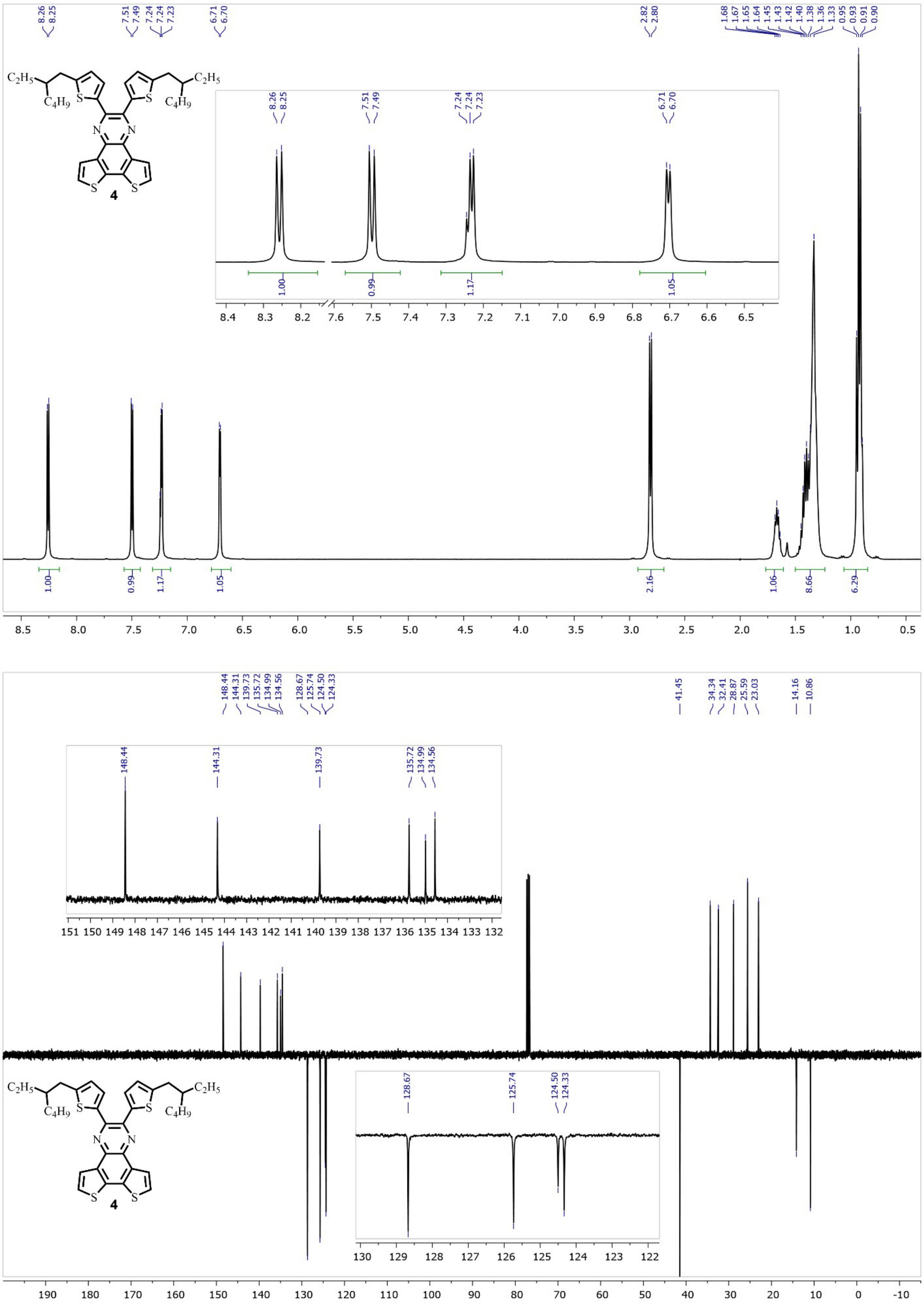


Figure S3 ^{1}H, ^{13}C NMR spectra of the compound **4**

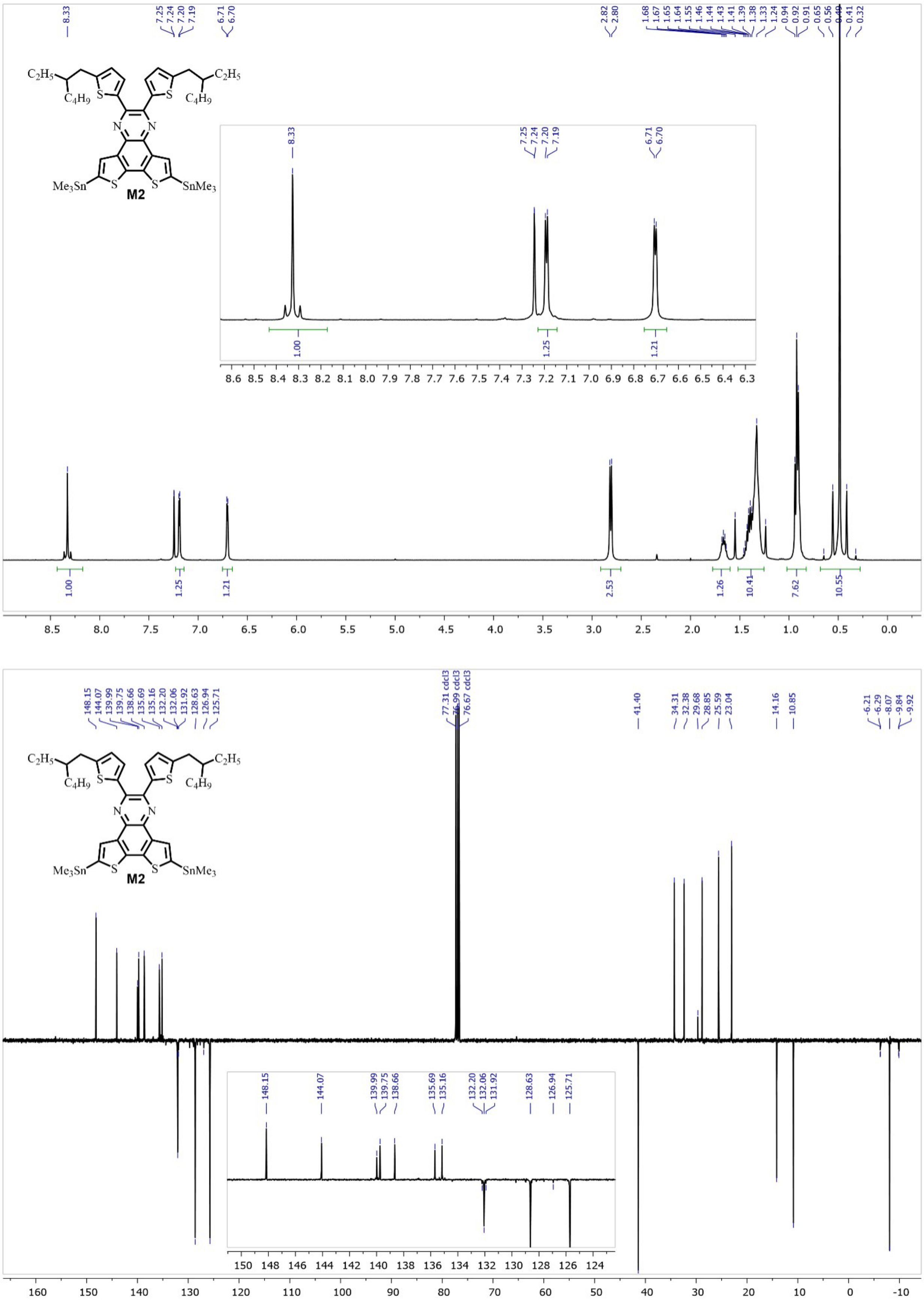


Figure S4 ^1H, ^{13}C NMR spectra of the monomer **M2**

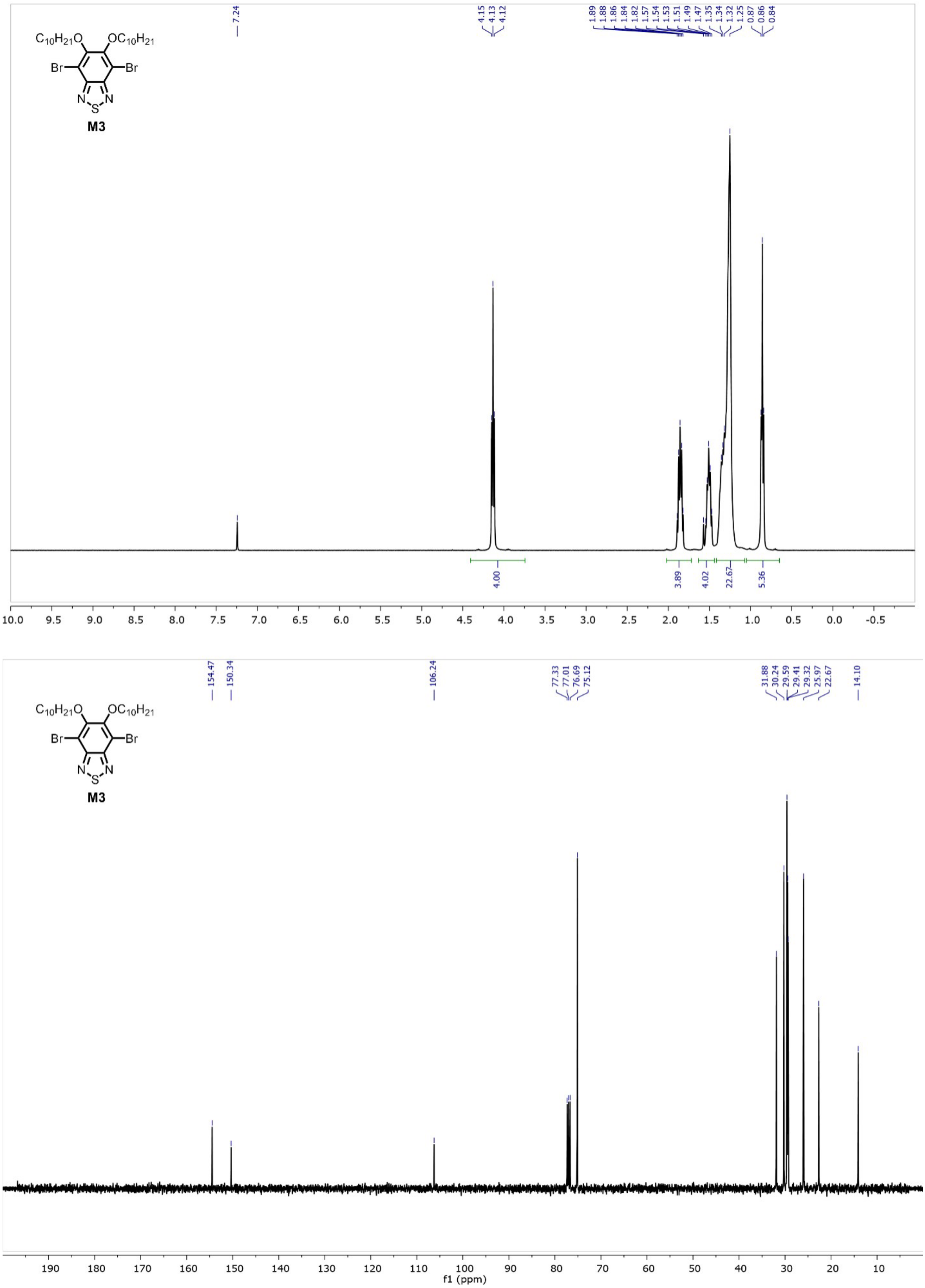


Figure S5 ^{1}H, ^{13}C NMR spectra of the monomer **M3**

Synthesis of polymers P1-P2

Monomers **M1-M2** (0.2048 mmol) and **M3** (0.2048 mmol) were introduced into a degassed and argon-filled round-bottom three-necked 50 ml flask equipped with a reflux condenser and a thermometer. Anhydrous toluene (15 ml), tris(dibenzylidenacetone)dipalladium(0) (5.5 mg) and tri(o-tolyl)phosphine (13 mg) were added to the monomers in a flow of argon. The reaction mass was cooled, degassed again and filled with argon. The flask was then heated to room temperature and immersed in an oil bath and heated at reflux for 5 hours. The molecular weight characteristics of the formed polymer were monitored every 60 min by analytical gel-permeation chromatography (GPC). After the growth of polymer chains was self-terminated or the appropriate molecular weights were reached, 2-(trimethylstannyl)thiophene (0.75 mmol; 0.18 g) and 60 min later bromobenzene (0.9 mmol; 0.14 g) were added to the mixture and the heating at reflux was continued for 2 h. Then the reaction mixture was cooled down to room temperature and the polymer was precipitated by addition of 50 mL of acetone. The precipitate was filtered and then subjected to Soxhlet extraction with acetone, heptane, dichloromethane and chlorobenzene. Subsequently, the chlorobenzene fractions were concentrated to ≈20 ml, treated with 3-mercaptopropionic acid for 3 hours and precipitated again with acetone (≈30 ml). The precipitate was collected by filtration and dried in vacuum. The total yield of the purified polymers **P1-P2** was 80-85%. **P1:** found (%): C, 71.54; H, 7.89; N, 5.02; S, 9.46. Calc. for $C_{66}H_{88}N_4O_4S_3$ (%): C, 72.22; H, 8.08; N, 5.10; S, 8.76. **P2:** found (%): C, 68.41; H, 7.68; N, 5.17; S, 15.54. Calc. for $C_{62}H_{84}N_4O_2S_5$ (%): C, 69.10; H, 7.86; N, 5.20; S, 14.87.

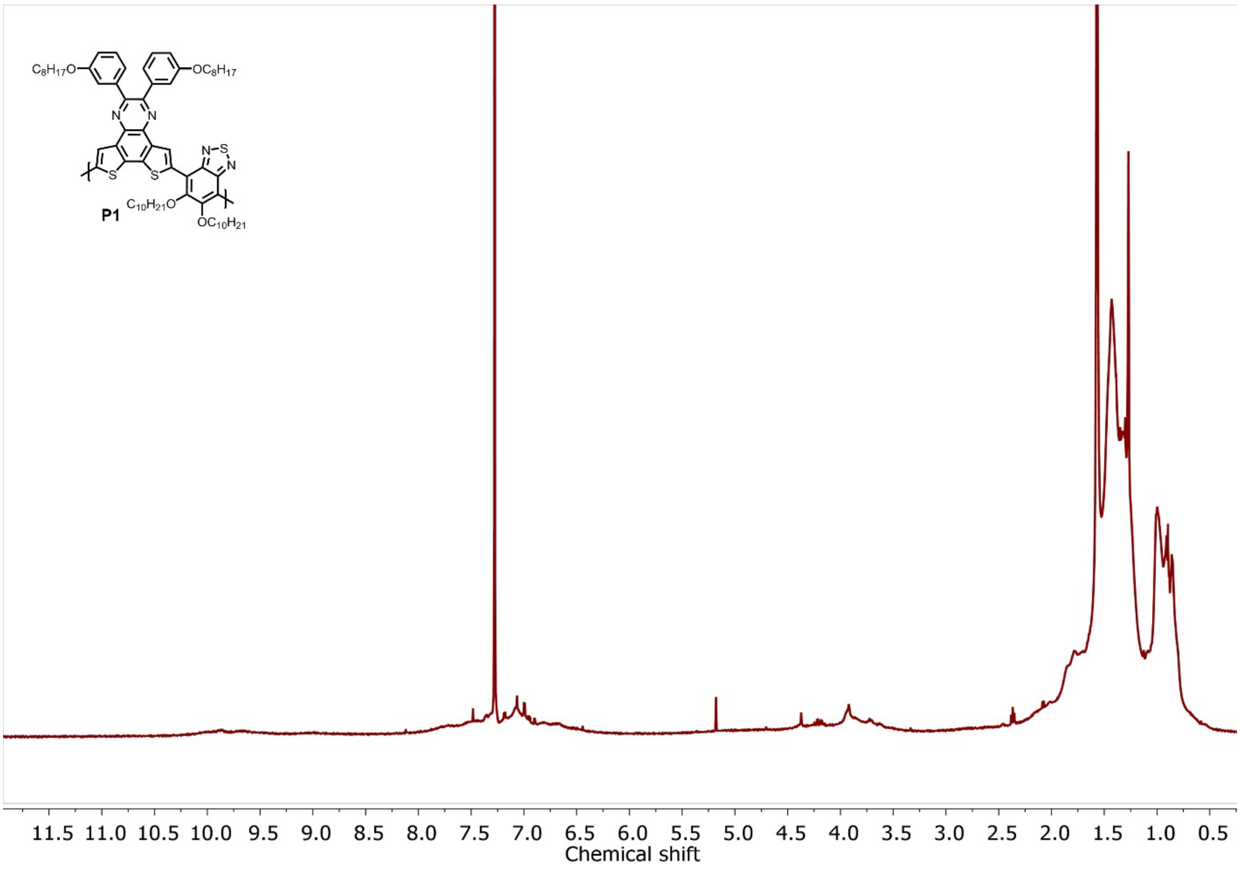


Figure S6 ^{1}H NMR spectra of the **P1**

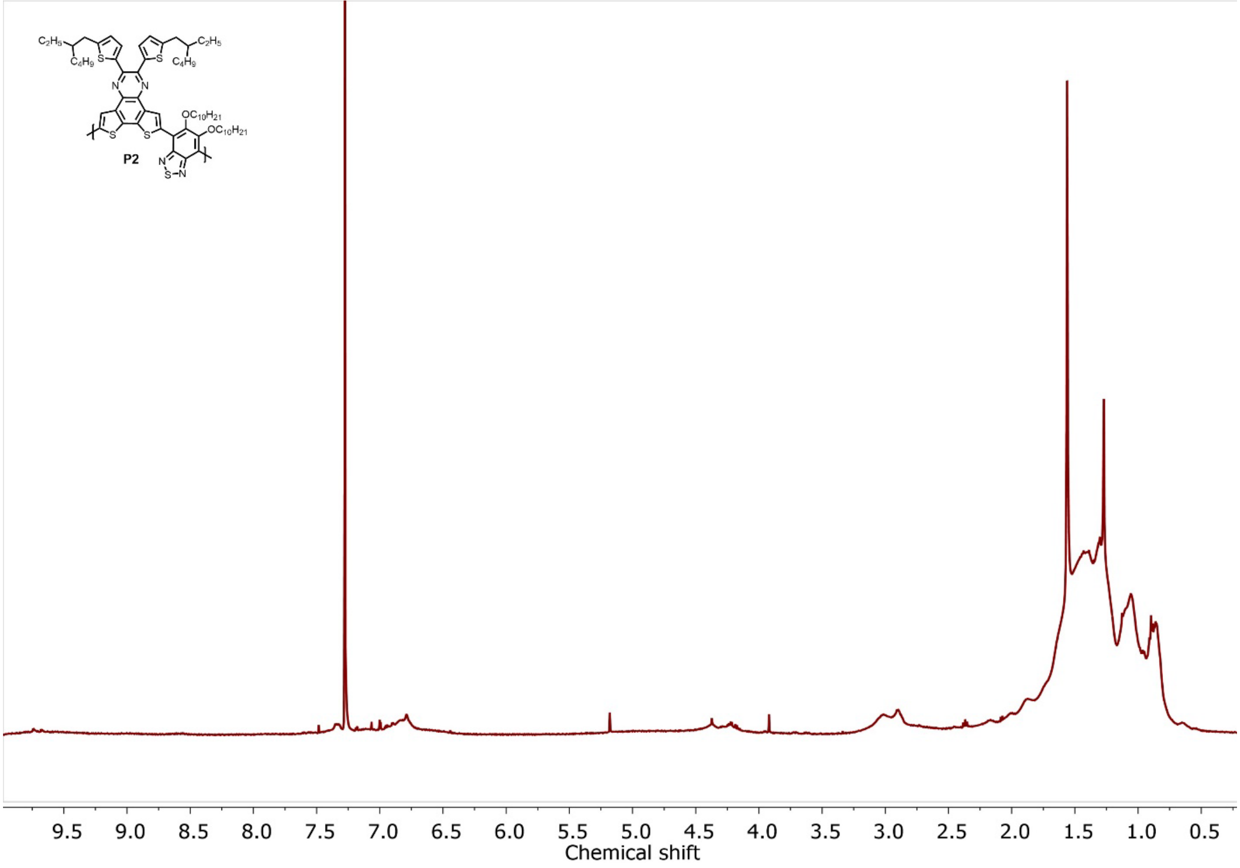


Figure S7 ^{1}H NMR spectra of the **P2**

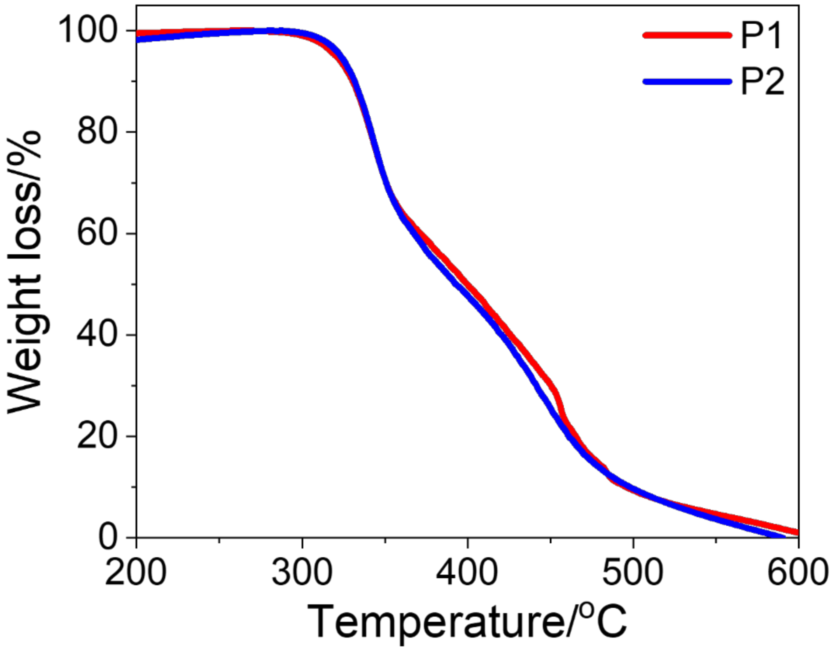


Figure S8 TG curves of polymers **P1-P2**

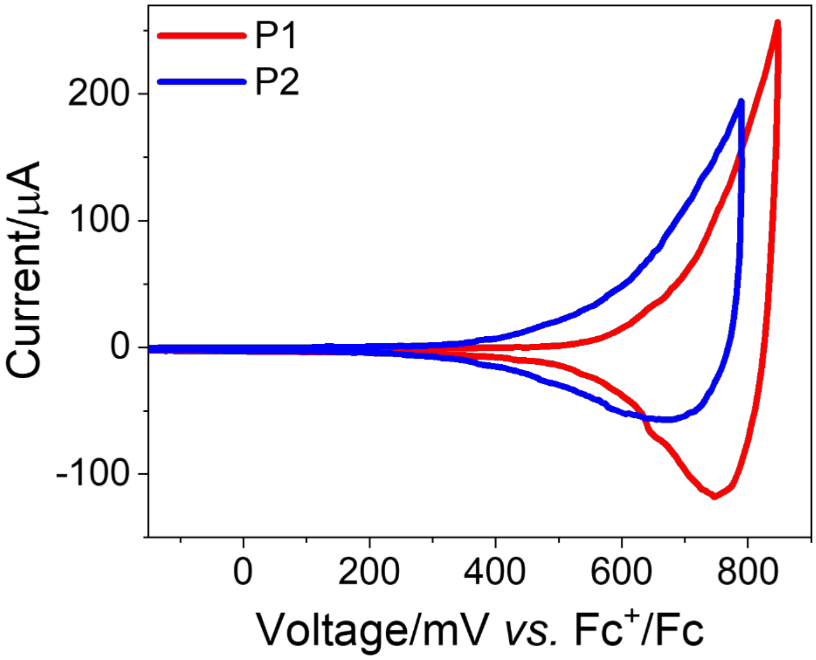


Figure S9 Cyclic voltammograms of polymers **P1-P2**

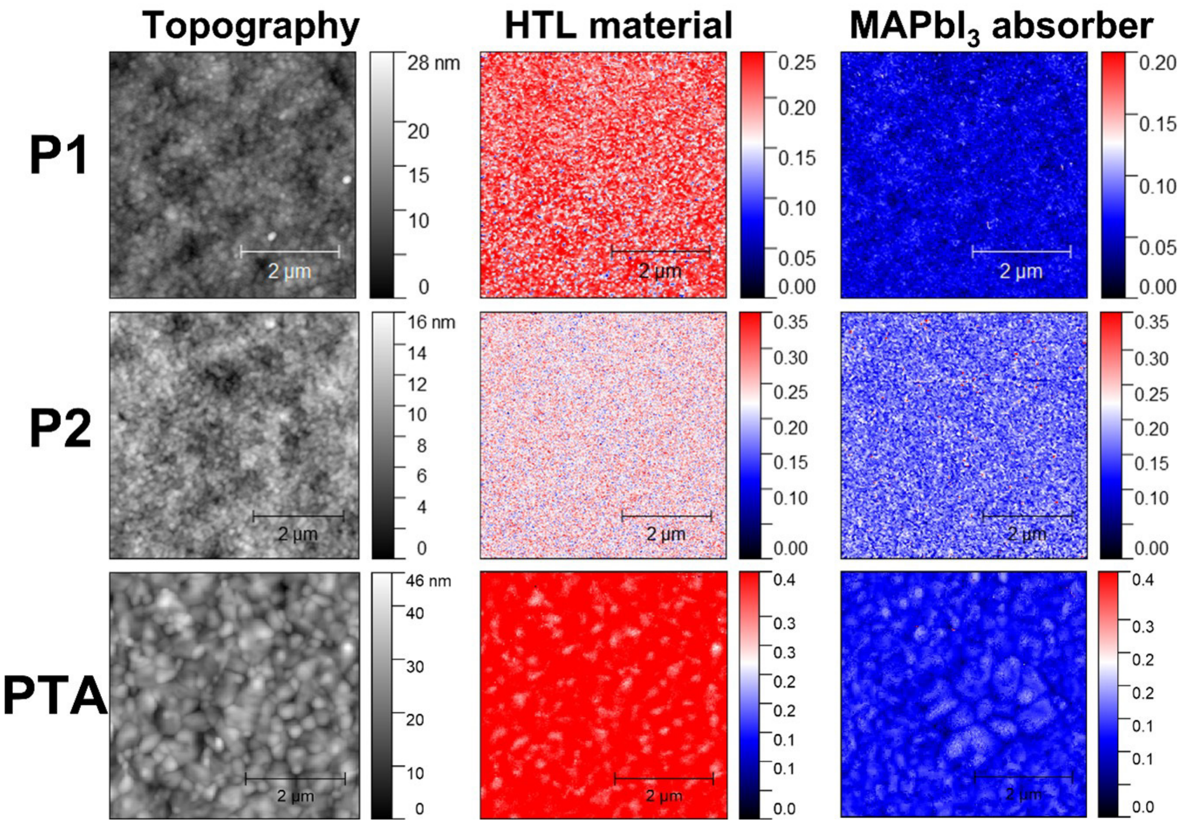


Figure S10 Topographic images of **P1-P2** and **PTA** films deposited over a photoactive perovskite layer (left), as well as the results of IR s-SNOM mapping on the characteristic bands in the IR spectra of the conjugated polymer (center) and MAPbI$_3$ perovskite (right).

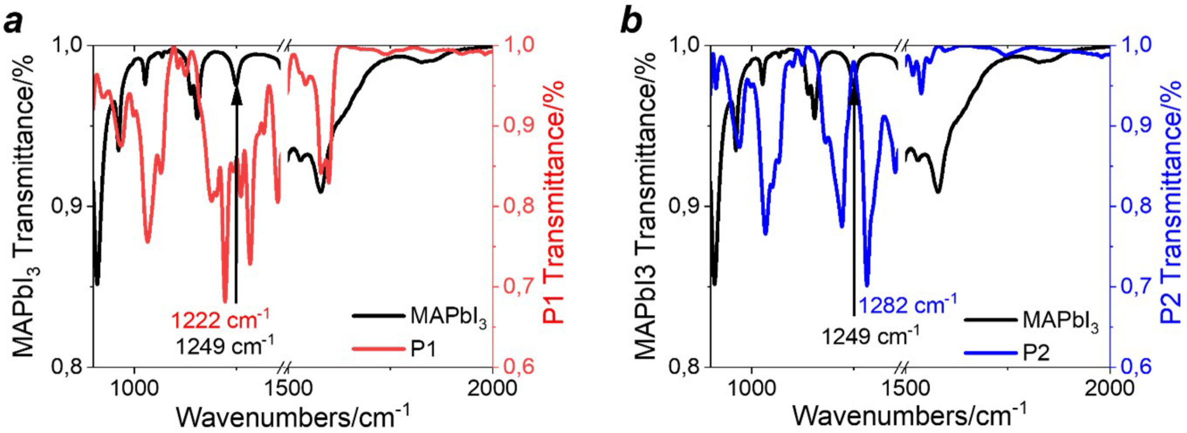


Figure S11 Infrared spectra of the individual films of MAPbI$_3$ and **P1-P2**

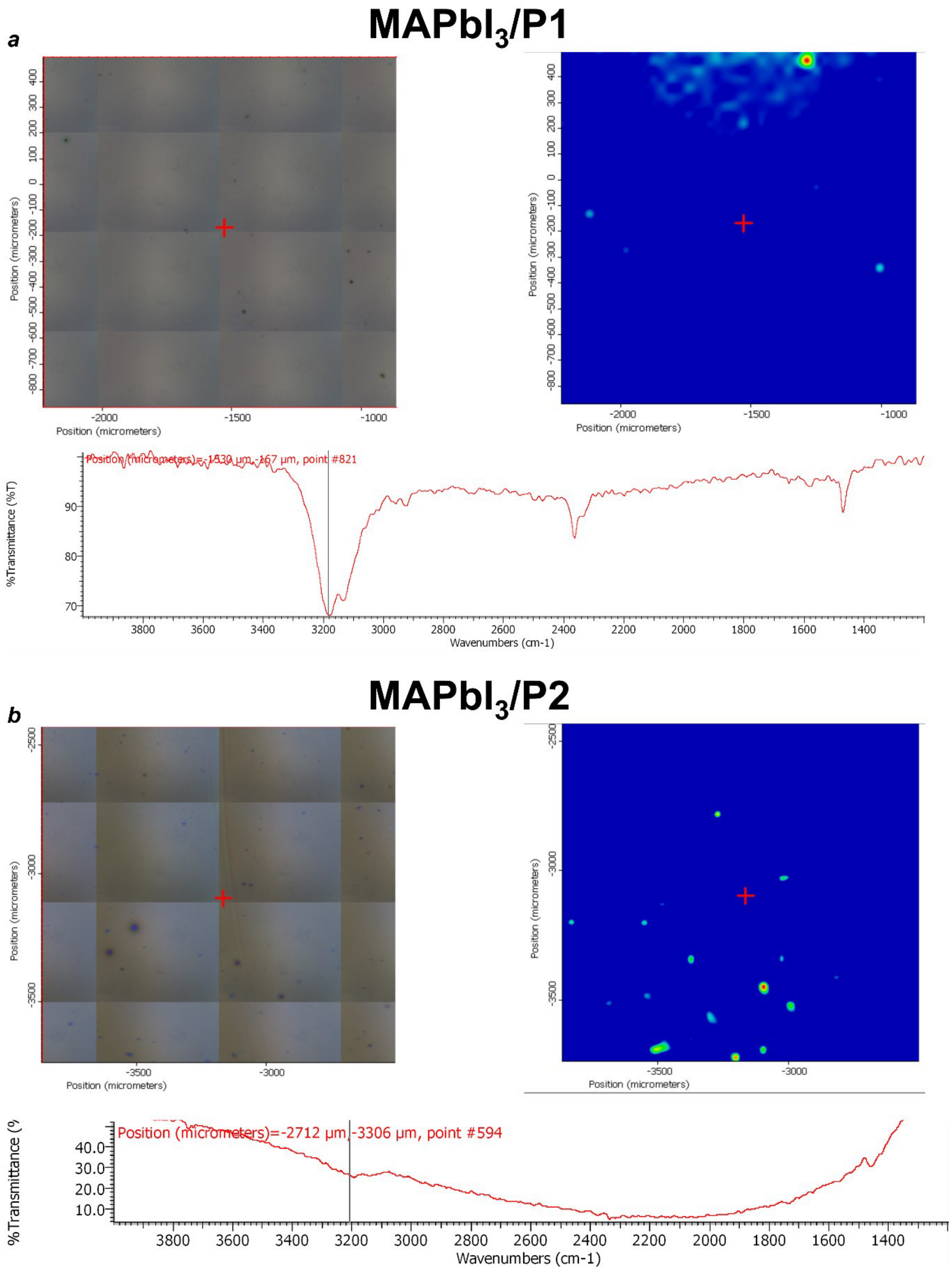


Figure S12 Infrared spectra of **P1-P2** films deposited over a photoactive perovskite layer

Reference

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