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Impact of fluorination on optoelectronic properties of thiophene-benzothiadiazole-based hole-transport polymers for perovskite solar cells

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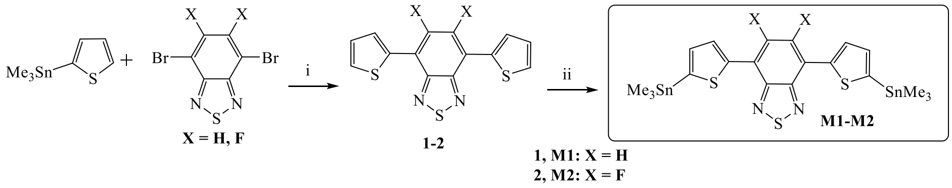
General

All solvents and reagents were purchased from commercial suppliers (Acros Organics, Sigma-Aldrich) and were either used as received or purified following 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. The ^{1}H, ^{13}C and ^{19}F NMR spectra in $CDCl_3$ solution were obtained using Bruker AVANCE III 500 instrument. 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 Elins P-30SM potentiostat at room temperature with a potential sweep rate of 50 mVs^{-1}. The CV 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 1,2-dichlorobenzene. 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 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. PL spectra were measured using QE Pro High-Performance Spectrometer Ocean Insight fiber spectrometer and 405 nm diode laser (10 mW) as excitation source.

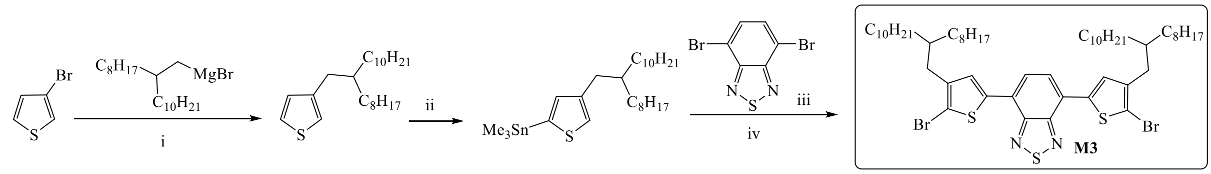
Perovskite solar cells. The perovskite solar cells were assembled in the ITO/SnO_2/PCBA/perovskite/HTM/VO_y/Ag n-i-p configuration following the procedure reported previously.[S1]

Infrared scanning near-field microscopy (IR s-SNOM) measurements. The infrared scanning near-field microscopy (IR s-SNOM, neaSNOM, Neaspec) measurements 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, $Pd(PPh_3)_4$, o-xylene; ii, *n*-BuLi, THF, $SnMe_3Cl$.



Reagents and conditions: i, $Ni(dppp)Cl_2$, THF; ii, *n*-BuLi, THF, $SnMe_3Cl$; iii, $Pd(PPh_3)_4$, o-xylene; iv, NBS, 1,2-dichlorobenzene.

Scheme S1 Synthesis of **M1-M3**

Monomers **M1-M2** were prepared according to the literature methods.[S2] The synthesis of monomer **M3** is described in the literature.[S3-S5]

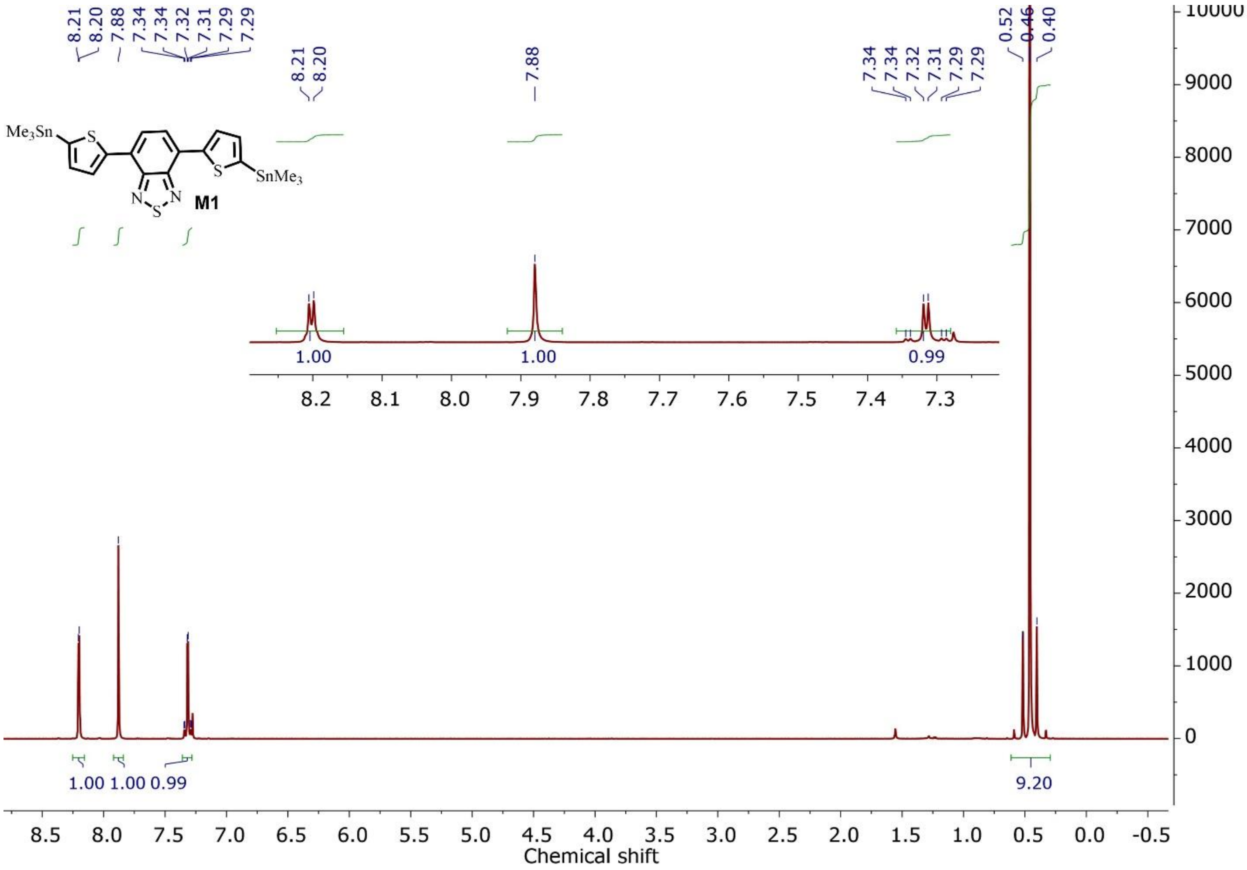
*4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole **M1***: ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 3.4 Hz, 2H), 7.88 (s, 2H), 7.31 (td, J = 3.45 Hz, 2H), 0.40-0.52 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.69, 145.08, 140.25, 136.12, 128.41, 125.85, -8.13.

*5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole **M2**:* ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 3.55 Hz, 2H), 7.36 (td, J = 3.36 Hz, 2H), 0.42-0.53 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.63, 150.47, 149.06, 149.02, 148.99, 148.57, 148.41, 142.65, 142.63, 137.06, 135.54, 135.43, 135.33, 131.59, 131.56, 131.53, 111.67, 111.59, -8.11. ^{19}F NMR ($CDCl_3$, 600 MHz) δ -128.0.

*4,7-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole **M3***: ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 5.5 Hz, 4H), 2.56 (d, J = 7.15 Hz, 4H), 1.73 (s, 2H), 1.22-1.30 (m, 70H), 0.83-0.86 (m, 12H).

Synthesis of polymers P1-P2.

Monomers **M1-M2** (0.15 mmol) and **M3** (0.15 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) (4 mol%) and tri(o-tolyl)phosphine (20 mol%) were added to the monomers in a flow of argon. The flask was immersed in an oil bath and heated at reflux for 5 hours. The molecular weight characteristics of the formed polymer were monitored every 30 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 latter bromobenzene (0.9 mmol; 0.14 g) were added to the mixture and the heating at reflux was continued for 1 h. Then the reaction mixture was cooled down to room temperature and the polymer was precipitated by addition of 20 mL of methanol. The precipitate was filtered and then subjected to Soxhlet extraction with acetone, hexane, dichloromethane, chlorobenzene and finally with 1,2-dichlorobenzene. The polymer fractions extracted with two last solvents were collected, concentrated in *vacuo* to ≈20 ml, treated with 3-mercaptopropionic acid for 3 hours and precipitated again with methanol (≈30 ml). The precipitate was collected by filtration and dried in vacuum. The total yield of the purified polymers **P1-P2** was 65-70%. **P1:** found (%): C, 69.30; H, 7.95; N, 4.97; S, 15.98. Calc. for $C_{68}H_{94}N_4S_6$ (%): C, 70.42; H, 8.17; N, 4.83; S, 16.58. **P2:** found (%): C, 67.41; H, 6.90; N, 4.85; S, 16.99. Calc. for $C_{68}H_{92}F_2N_4S_6$ (%): C, 68.30; H, 7.75; N, 4.69; S, 16.09.



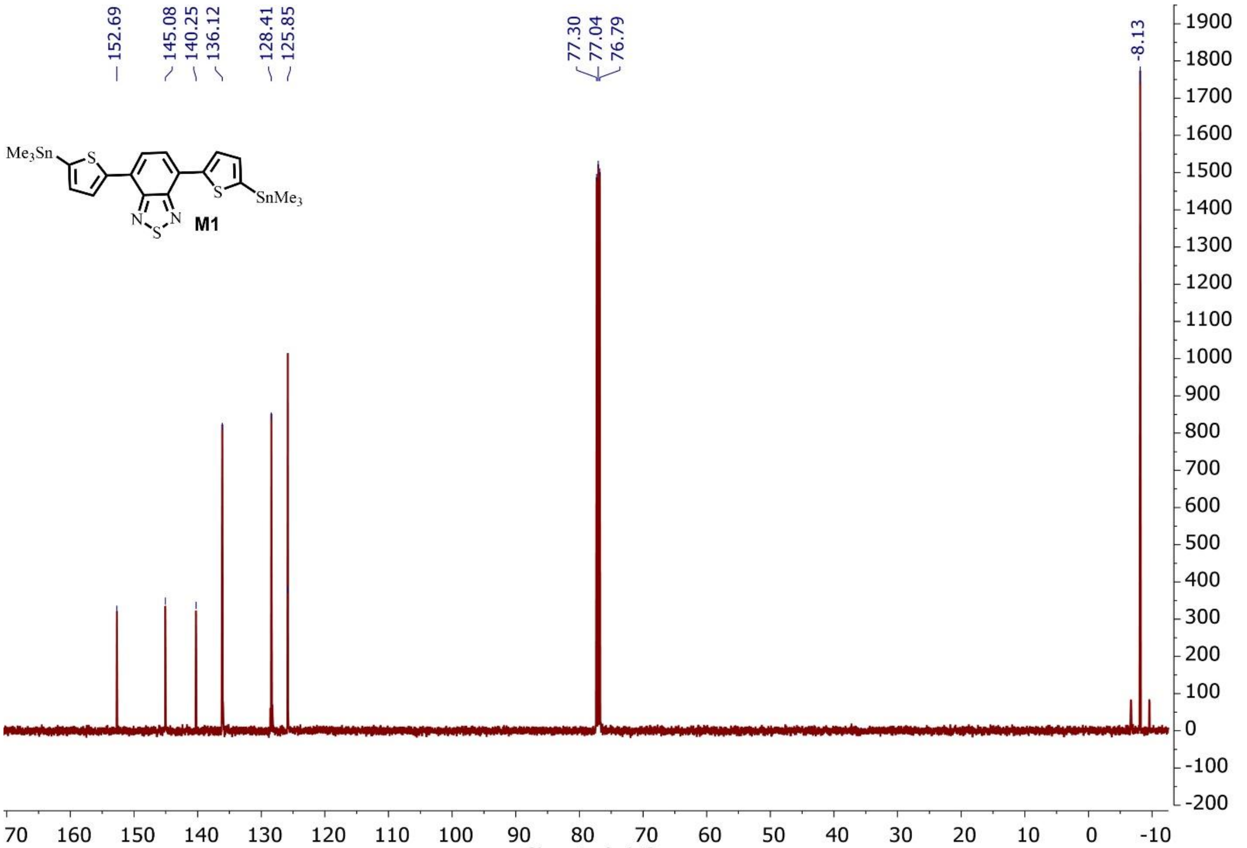


Figure S1 ^{1}H and ^{13}C NMR spectra of **M1**

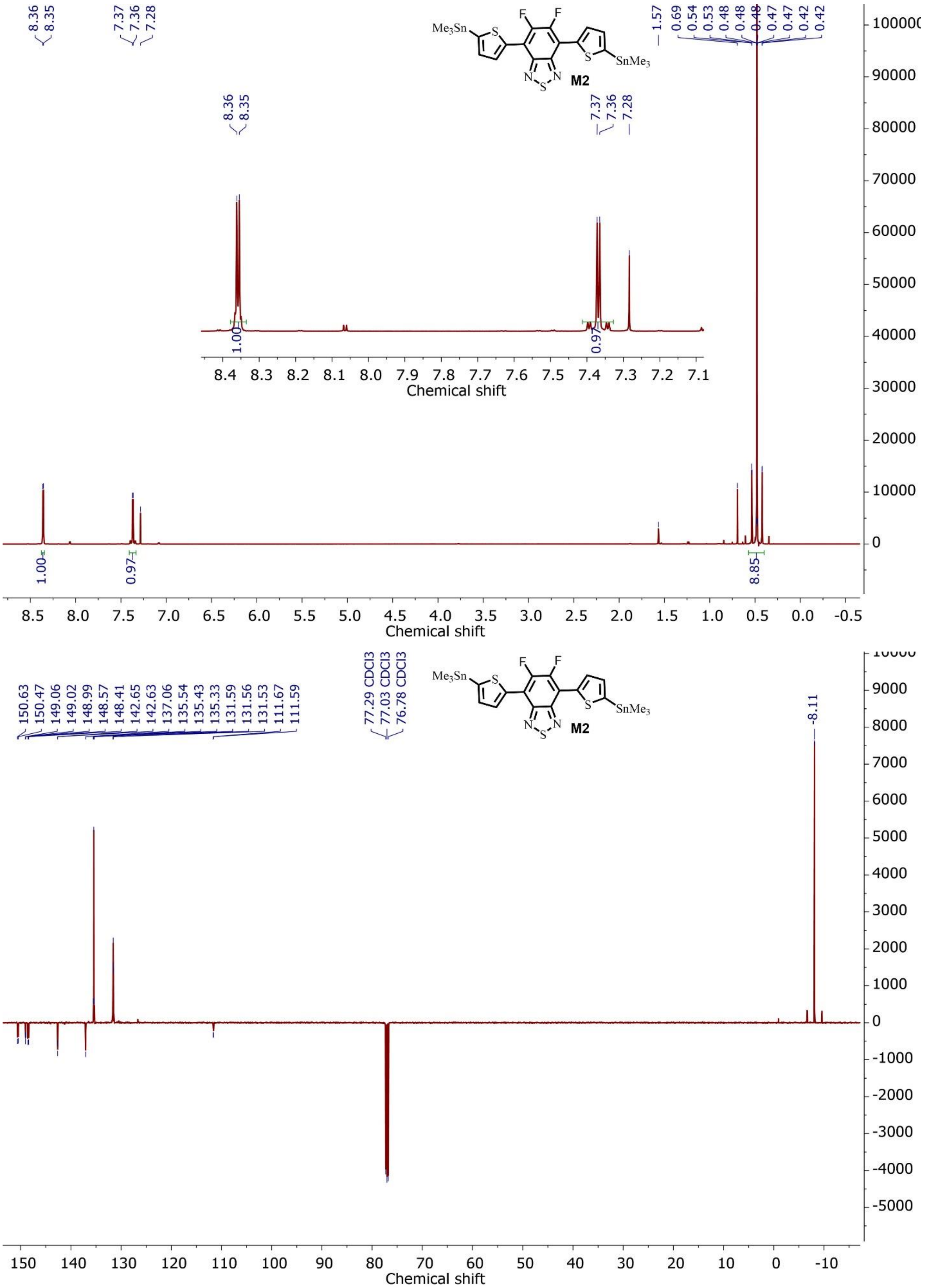


Figure S2 ^{1}H and ^{13}C NMR spectra of **M2**

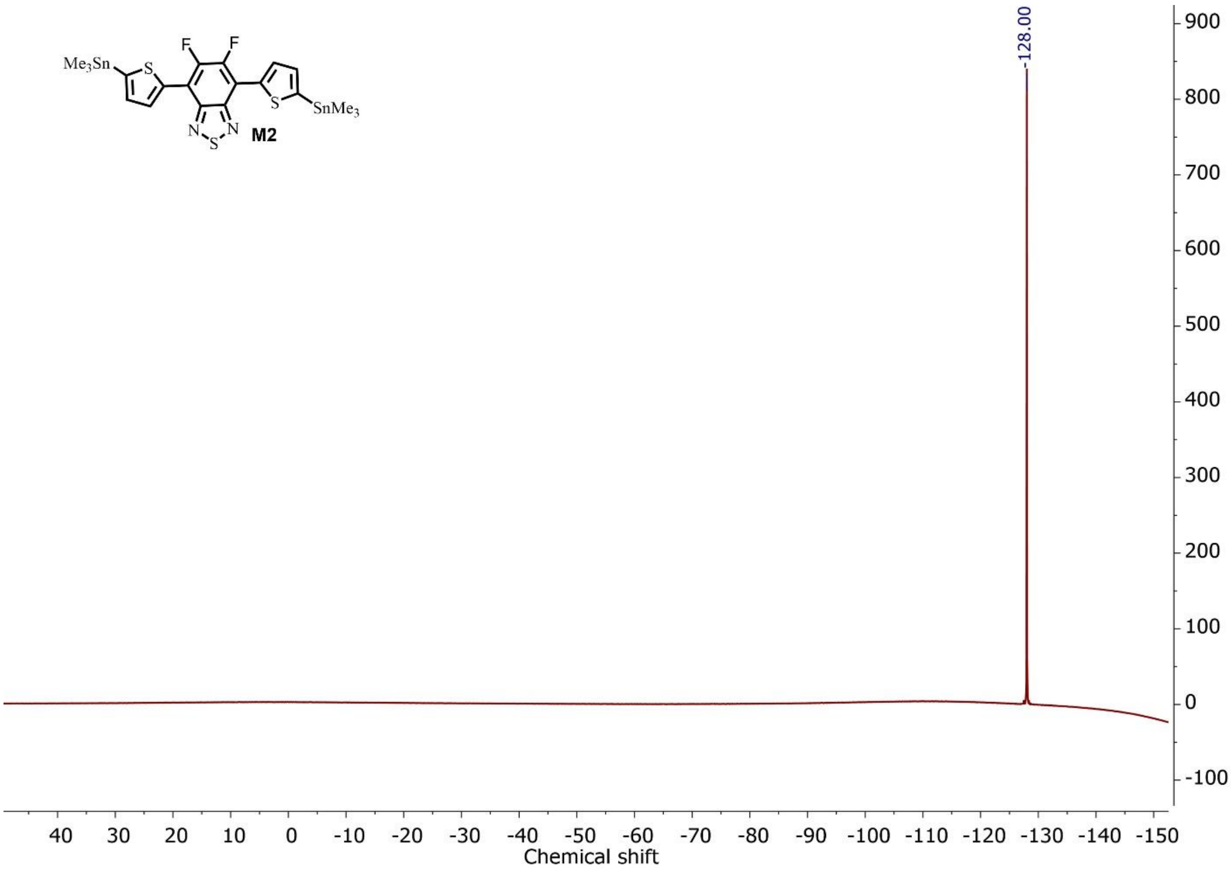


Figure S3 ^{19}F NMR spectrum of **M2**

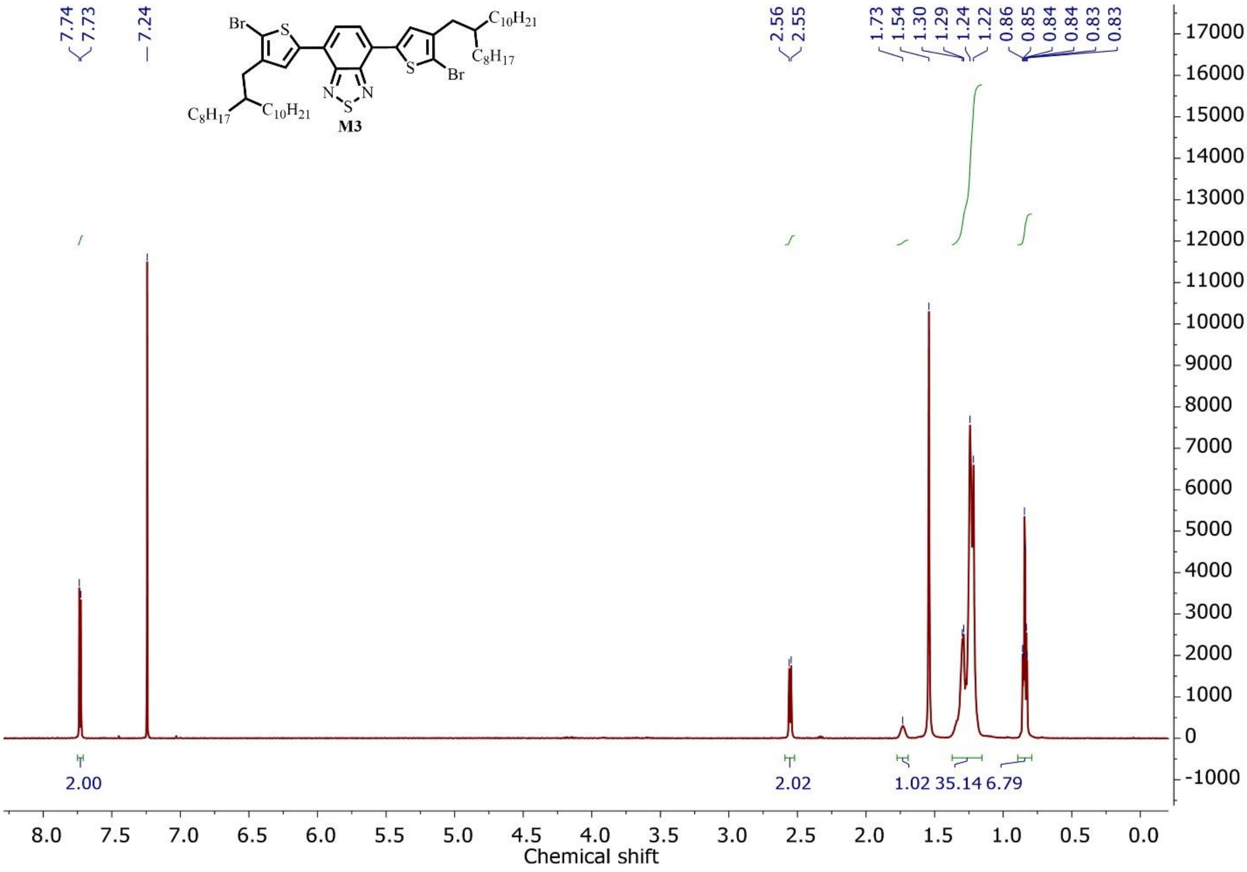


Figure S4 ^{1}H NMR spectrum of **M3**

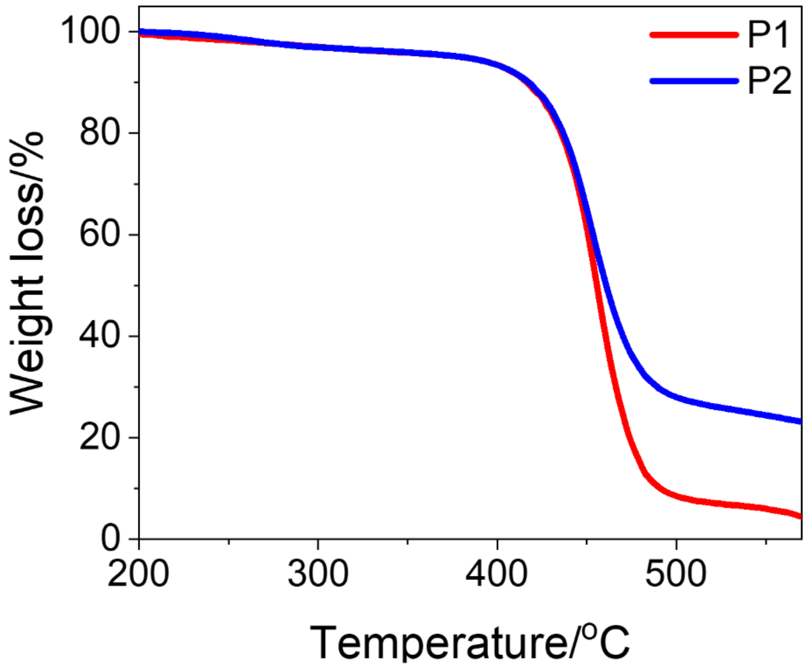


Figure S5 TG curves of polymers **P1-P2**

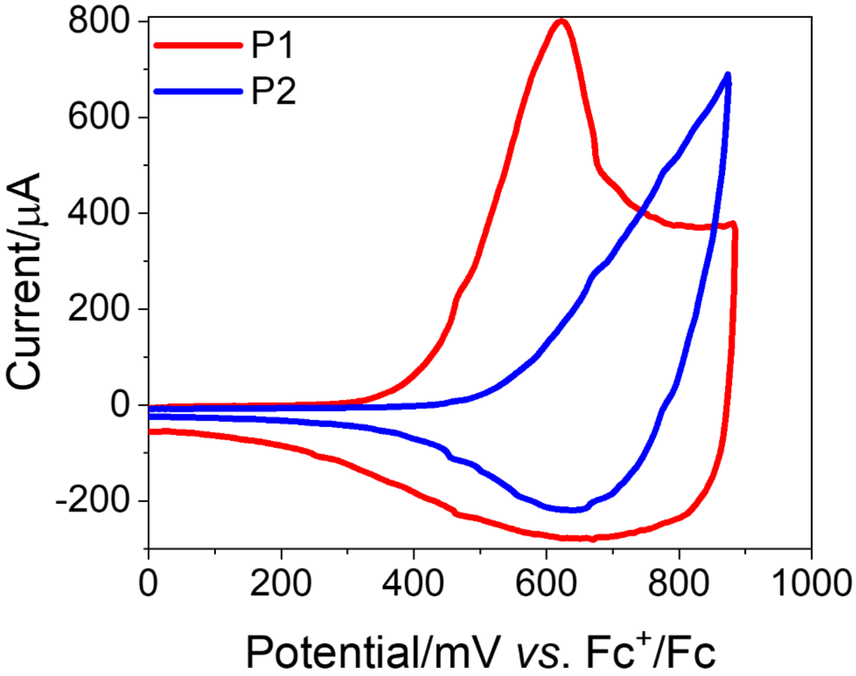


Figure S6 Cyclic voltammograms of polymers **P1-P2**

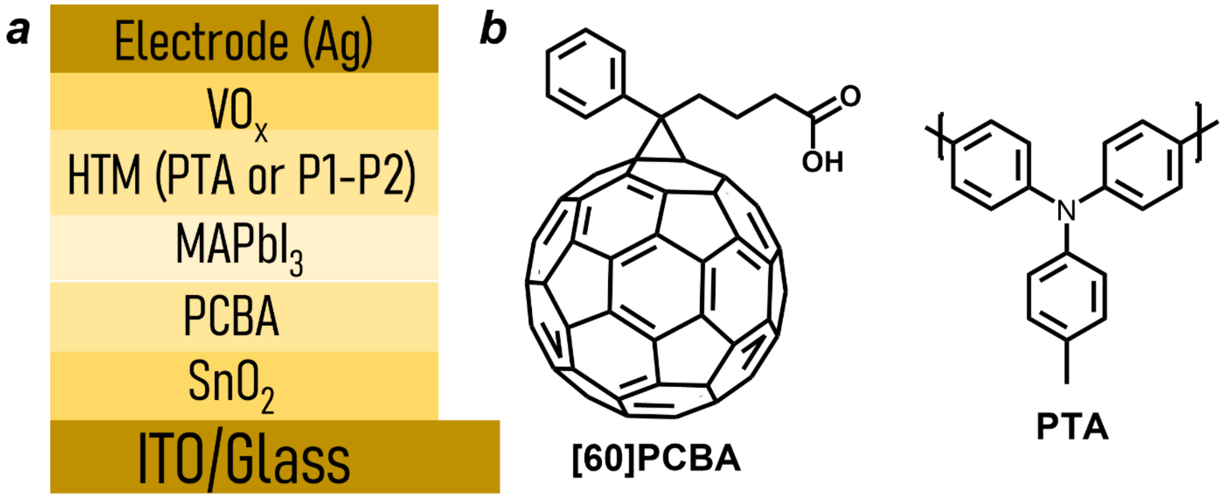


Figure S7 Schematic configuration of PSC (a); the molecular structures of PCBA and PTA (b)

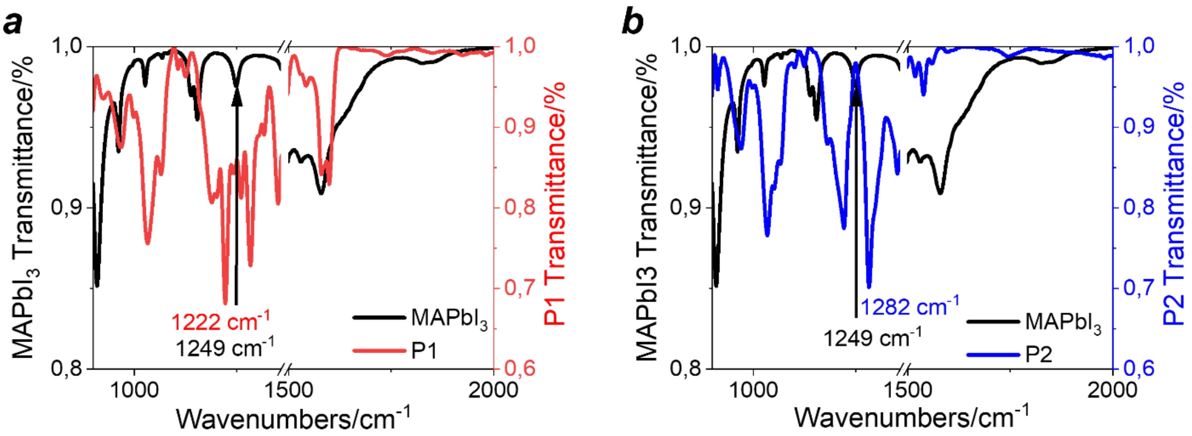


Figure S8 Infrared spectra of **P1-P2** compared to MAPbI$_3$

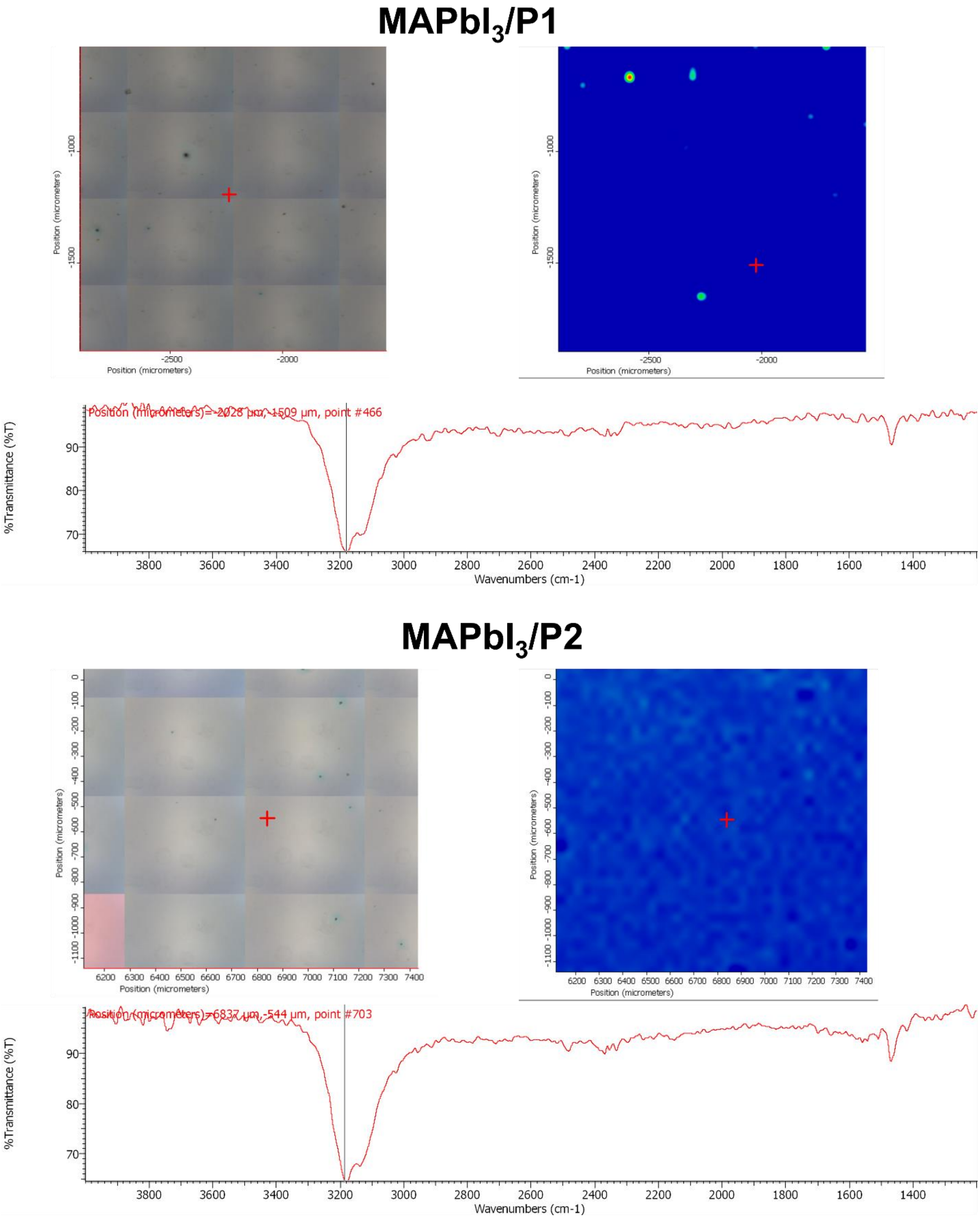


Figure S9 Optical (left) and infrared (right) microscopy data showing point defects in **P1-P2** films deposited atop perovskite absorber layer: big voids in the case of **P1** (red and green spots on the IR map) and some aggregated particles in the case of **P2** (black points on the optical image without any contrast in IR map).

References

S1. A. F. Latypova, N. A. Emelianov, D. O. Balakirev, P. K. Sukhorukova, N. K. Kalinichenko, P. M. Kuznetsov, Y. N. Luponosov, S. M. Aldoshin, S. A. Ponomarenko, P. A. Troshin and L. A. Frolova, *ACS Appl. Energy Mater*., 2022, **5**, 5395.

S2. B. Fu, J. Baltazar, Z. Hu, A.-T. Chien, S. Kumar, C. L. Henderson, D. M. Collard and E. Reichmanis, *Chem. Mater.*, 2012, **24**, 4123.

S3. I. Osaka, M. Shimawaki, H. Mori, I. Doi, E. Miyazaki, T. Koganezawa and K. Takimiya, *J. Am. Chem. Soc*., 2012, **134**, 3498.

S4. A. V. Akkuratov, D. K. Susarova, O. A. Mukhacheva and P. A. Troshin, *Mendeleev Commun*., 2016, **26**, 248.

S5. A V. Akkuratov, D. K. Susarova, Y. L. Moskvin, D. V. Anokhin, A. V. Chernyak, F. A. Prudnov, D. V. Novikov, S. D. Babenko, and P. A. Troshin, *J. Mater. Chem. C,* 2015, **3**, 1497.