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Influence of Polymer Side Chains on the Photovoltaic Performance of Non-Fullerene Organic Solar Cells

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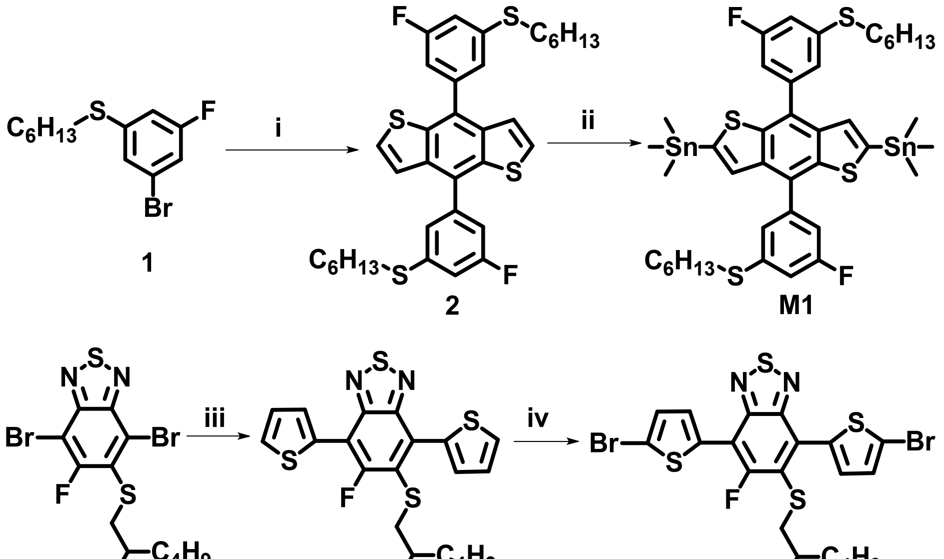
Experimental Part

Materials and Instruments. Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (DCM) were distilled from CaH_2. Chloroform (CF) was distilled before use. ^1H spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 ^oC/min to record TGA and DSC curves. The gel permeation chromatography (GPC) measurements were performed at 80 ^oC on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with chlorobenzene as an eluent. The thickness of the blend films was determined by a Dektak6 M surface profile meter. The powder X-ray diffraction (XRD) patterns were collected using a PANalyticalX'Pert PRO MPD diffractometer with Cu KR radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system.

Chart S1. Synthetic routes of **M1** and **M2**



i. n-butyl lithium, THF, -78 ^{o}C, 1 h, r.t, 8 h, $SnCl_2$•HCl•H_2O; ii. n-butyl lithium, THF, 1 h, $Sn(CH_3)_3Cl$; iv. potassium tert-butoxide, 2-ethylhexane-1-thiol, THF,12 h; iii. 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane, Na_2CO_3, Pd(PPh3)$_4$, THF, H_2O, 48 h; iv. NBS, $CHCl_3$, DMF,12 h.

Material and synthesis

4,8-bis(3-fluoro-5-(hexylthio)phenyl)benzo[1,2-b:4,5-b']dithiophene (**2**)

To a solution of (3-bromo-5-fluorophenyl)(hexyl)sulfane (10 g, 34.3 mmol) in 100 ml dry Tetrahydrofuran (THF) at -78 °C, n-BuLi (14 mL, 34 mmol) was added dropwise under N_2 atmosphere. After being stirred for 1h at -78 °C, the reactant was transferred to benzo[1,2-b:4,5-b']dithiophene-4,8-dione (2.5 g, 11.3 mmol) and stirred at room temperature overnight. $SnCl_2 \bullet H_2O \bullet HCl$ (50mL) was added at 0 °C and the mixture was stirred for 1h. Then, the reactant was poured into water and extracted two times with dichloromethane (DCM). The combined organic phase was dried over anhydrous $MgSO_4$. After removing the solvent under vacuum, the residue was purified by silica gel chromatography using a mixture of petroleum ether (PE) and dichloromethane (10: 1, by volume) as the eluent and then recrystallized from mixed solvent of hexane and ethanol (1:2, by volume) to give a white solid (3.5g, 51%).

(4,8-bis(3-fluoro-5-(hexylthio)phenyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M1**)

To a solution of compound **2** (1 g, 1.6 mmol) in 50 mL dry THF solution at –78 °C, n-BuLi (1.7 mL, 2.4 M in hexane) was added dropwise, and the mixture was kept at -78 °C for 1h. Chlorotrimethylstannane (4 mL, 1 M in hexane) was added slowly and the resulting mixture was stirred overnight at room temperature. Then, it was poured into water and extracted with diethyl ether. After dried over anhydrous $MgSO_4$, the solvent were removed under vacuum and the crude product was recrystallized from hexane. **M1**(1.2g, 80%) was obtained as a white crystal.

5-((2-ethylhexyl)thio)-6-fluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**4**)

Compound **4** was synthesized by the Suzuki coupling method. To a mixture of compound **3** (2 g, 4.4mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (2.8 g, 13.3 mmol), and $NaHCO_3$ (2 g, 23.8 mmol) in 100 mL THF and 15 mL H_2O under N_2 atmosphere, $Pd(PPh_3)_4$(0.1 g, 0.04 mmol) was added and the reactant was refluxed for 3 days. After cooled to room temperature, the mixture was poured into water and extracted with DCB. After removing the solvent, the residue was purified by silica gel chromatography, using a mixture of hexane and dichloromethane (10: 2, by volume) as the eluent to obtain yellow solid (1.7g, 85%).

4,7-bis(5-bromothiophen-2-yl)-5-((2-ethylhexyl)thio)-6-fluorobenzo[c][1,2,5]thiadiazole (**M3**)

Compound **4** (1.5g, 3.2 mmol) was dissolved into 50 ml chloroform (CF), and N-bromosuccinimide (1.2g, 6.7mmol) was added in one portion. The reactant was stirred overnight at ambient temperature in the dark. After removing the solvent, the crude product was purified by silica gel chromatography using hexane as eluent and further purified by recrystallization from hexane. **M3** was obtained as a yellow solid (1.6g, 80%).

General synthetic procedure of **Polymers**

In a 100 mL flask, M1 (0.2 mmol) and M2 (0.2mmol) or M3 (0.2mmol) were dissolved in 10 mL toluene and 2 mL DMF with $Pd(PPh_3)_4$ (5 mg) as catalyst. After 48 h of reflux under N_2 atmosphere, methanol (50mL) was added to the mixture and the crude product was collected by filtering. The two polymers were purified through soxhlet extraction by using acetone, dichloromethane (DCM) and chloroform, then filtered from boiling chlorobenzene (CB) and subsided in methanol. The resulting polymers were collected in the yield of 61.6 % for **POF** and 56.6 % for **PSF**.

Table S1. Elemental analysis

elemental analysis	**Calcd**			**FOUND**		
name	N	C	H	N	C	H
2		66.85	5.94		66.91	5.80
M1		52.68	5.966		51.3	5.6
M2	4.44	42.52	3.465	4.51	42.59	3.41
POF	2.67	63.51	5.207	2.65	63.72	5.44
PSF	2.53	62.00	4.850	2.61	62.77	5.36

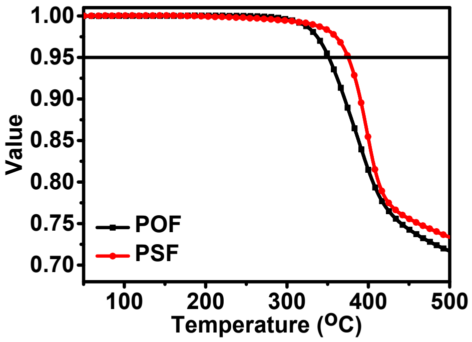


Figure S1. Thermogravimetric Analysis curves of POF and PSF at a heating rate of 10 °C /min under N_2 atmosphere.

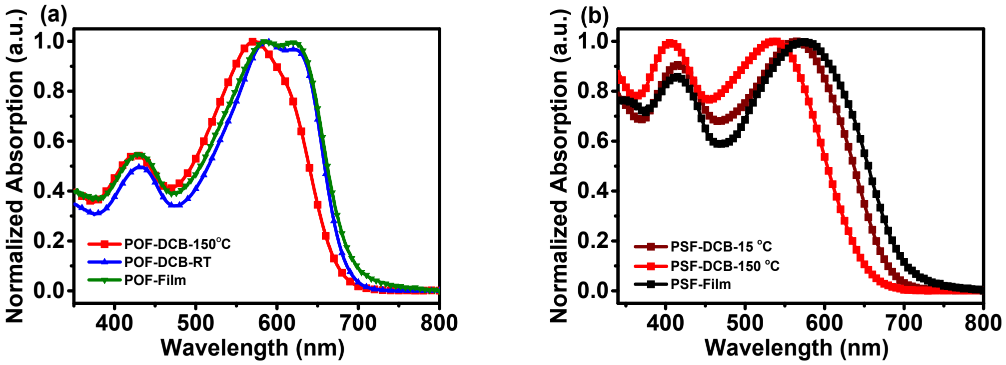


Figure S2. (a) UV absorption spectrum of **POF** in dilute DCB at room temperature, at 150 °C and as film; (b) absorption spectrum of **PSF** in dilute DCB at room temperature, at 150 °C and as film

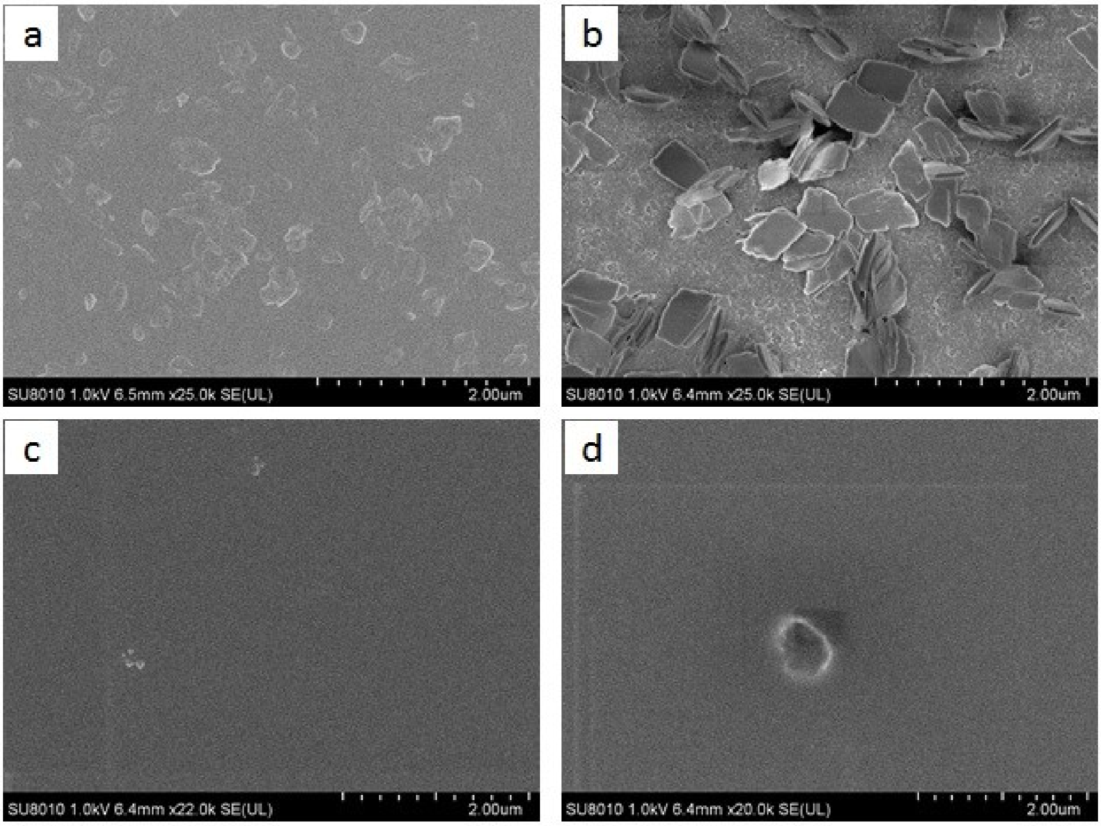


Figure S3. SEM images of a) **POF**:**ITIC** blend films, b) **PSF**:**ITIC** blend film, c) **POF**:**ITIC** blend film washed with acetone, d) **PSF**:**ITIC** blend film washed with acetone under optimized condition. The scale bar is 2 μm.

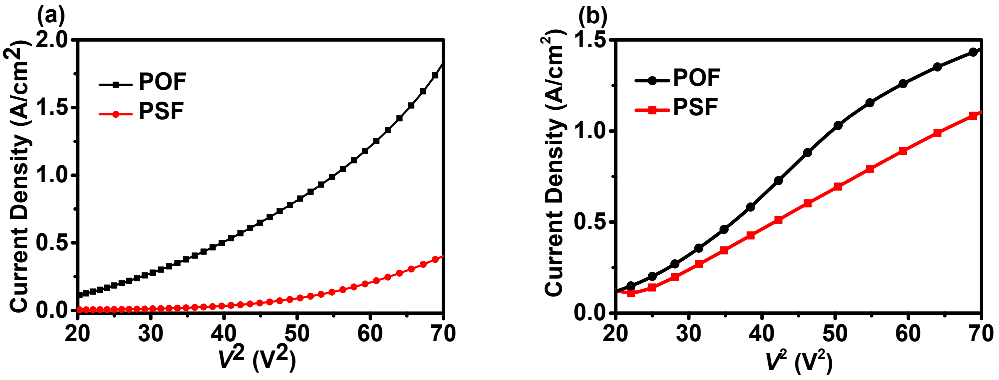
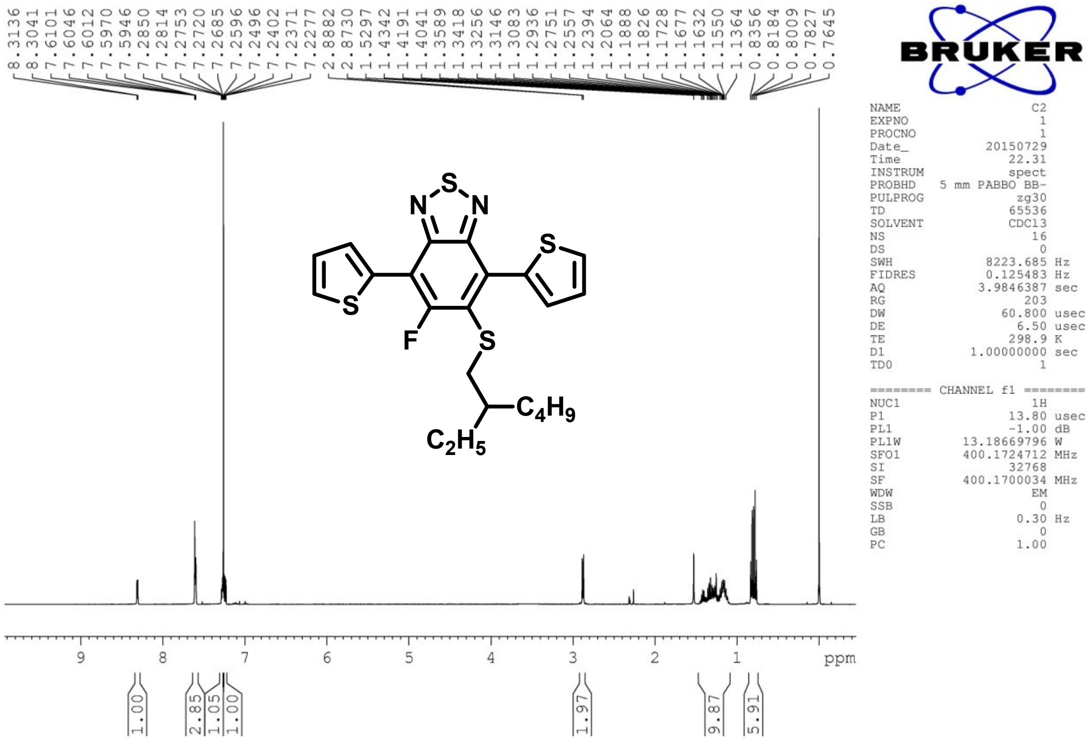
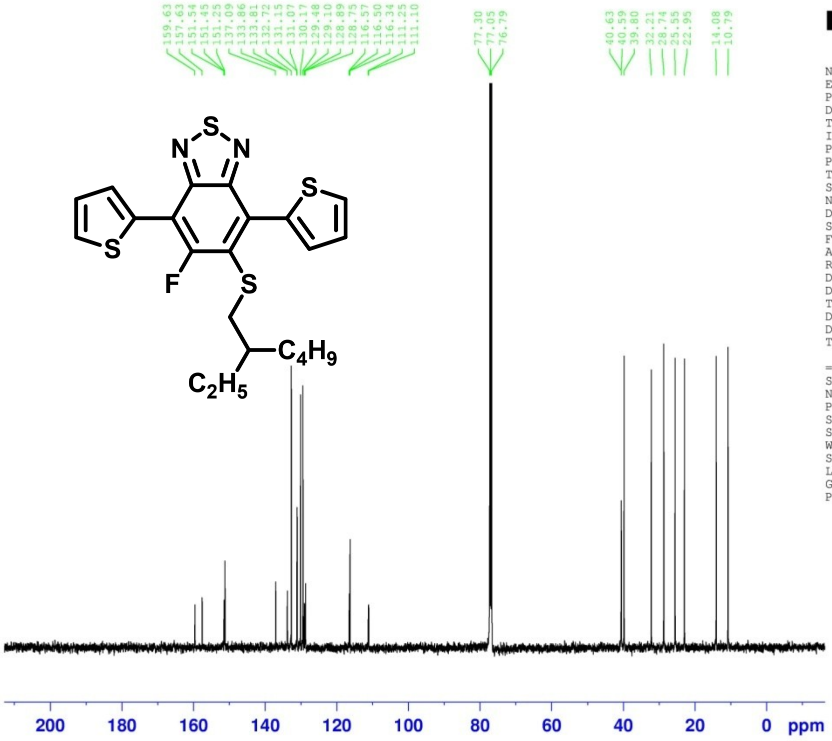


Figure S4. *J*–*V* characteristics in the dark for hole-only (a) and electron-only (b) devices based on **POF**:**ITIC** and **PSF**:**ITIC** blend layers under optimized conditions.





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SOLVENT            CDCl3
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FIDRES          0.454131 Hz
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RG                191.41
DW                16.800 usec
DE                  6.50 usec
TE                 298.0 K
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TD0                    1

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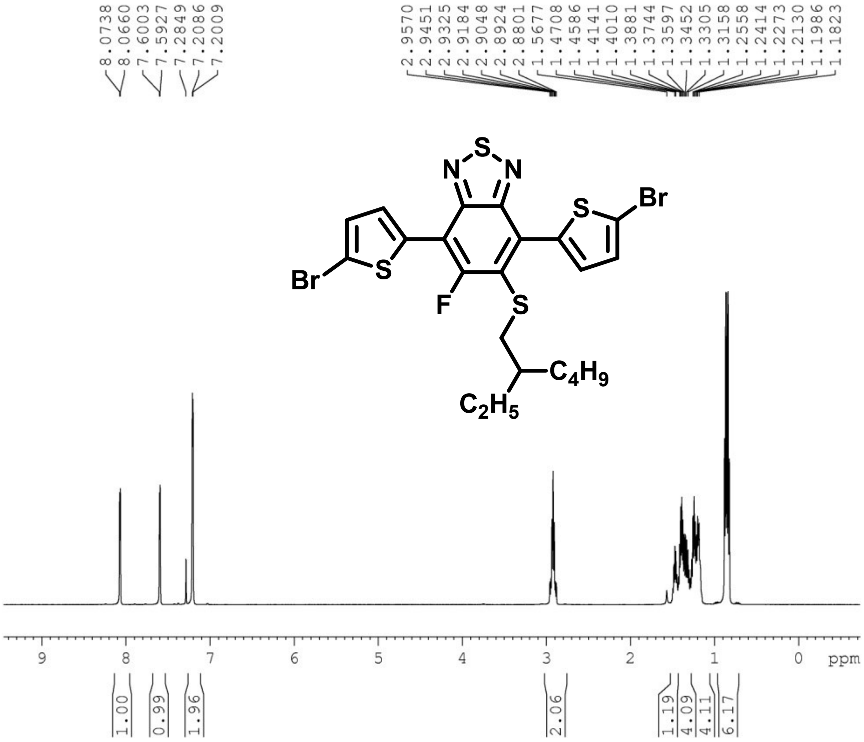

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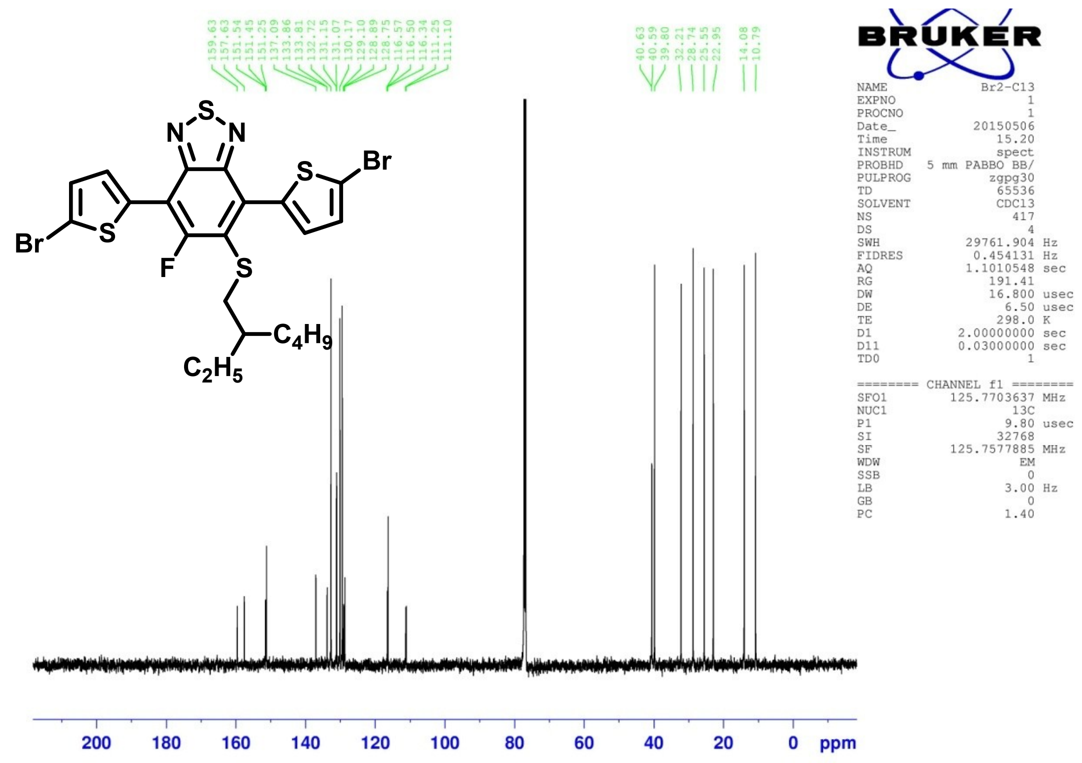

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NS                    417
DS                      4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010548 sec
RG                 191.41
DW                 16.800 usec
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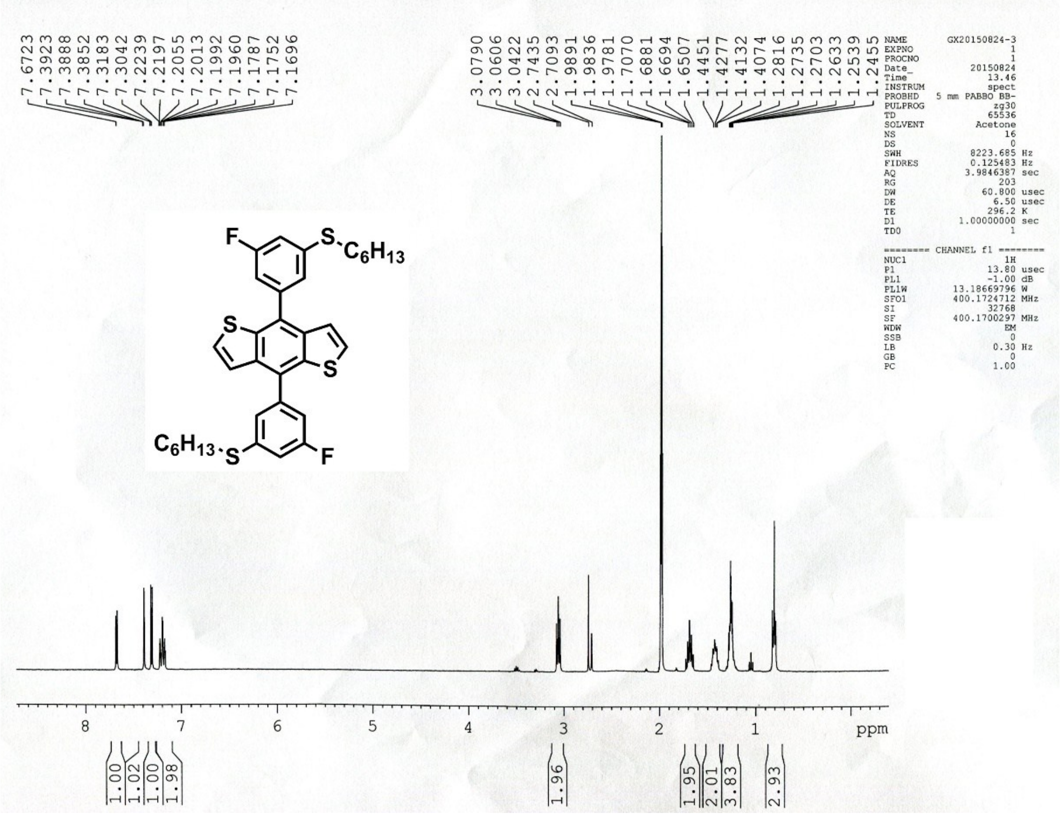

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RG                   203
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DE                  6.50 usec
TE                 296.2 K
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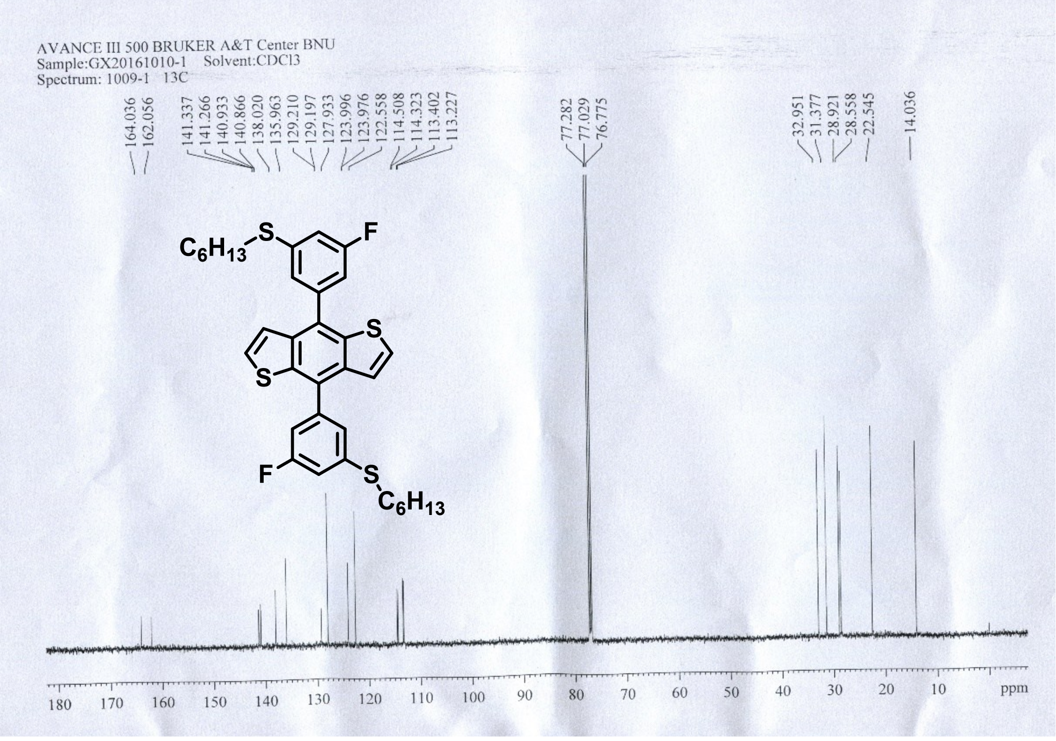
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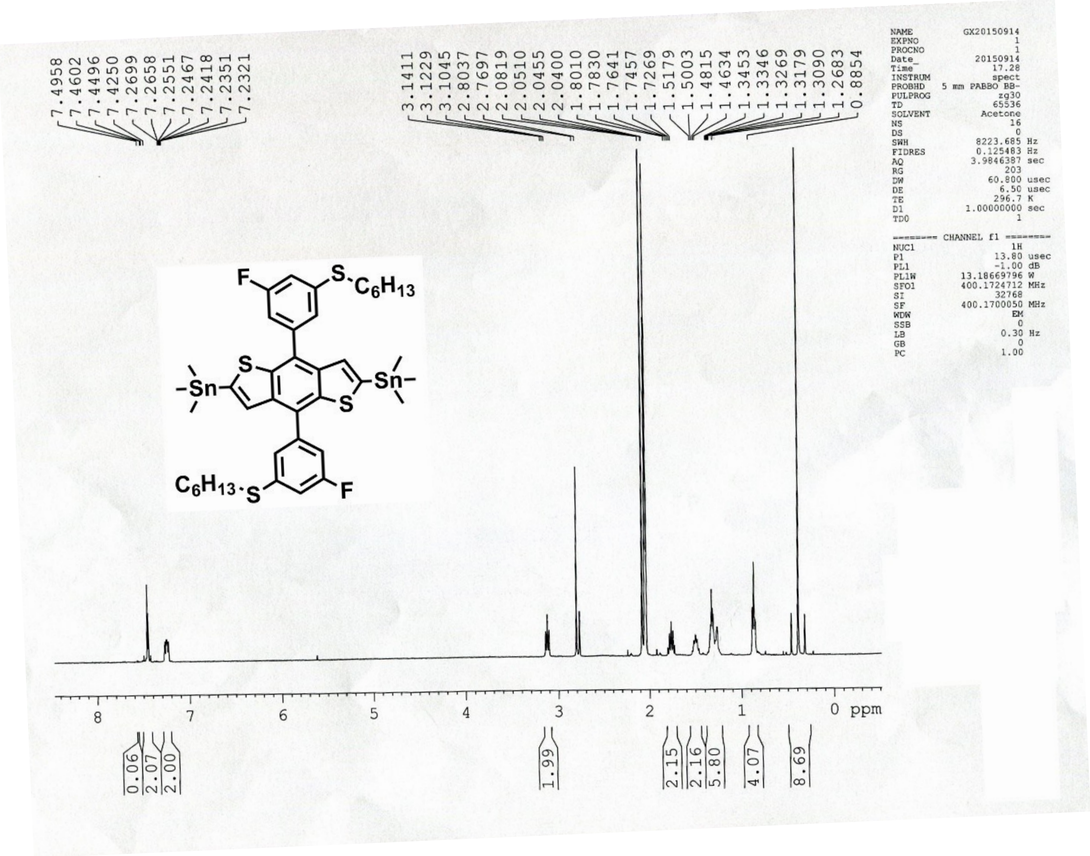
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RG                   203
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DE                  6.50 usec
TE                 296.7 K
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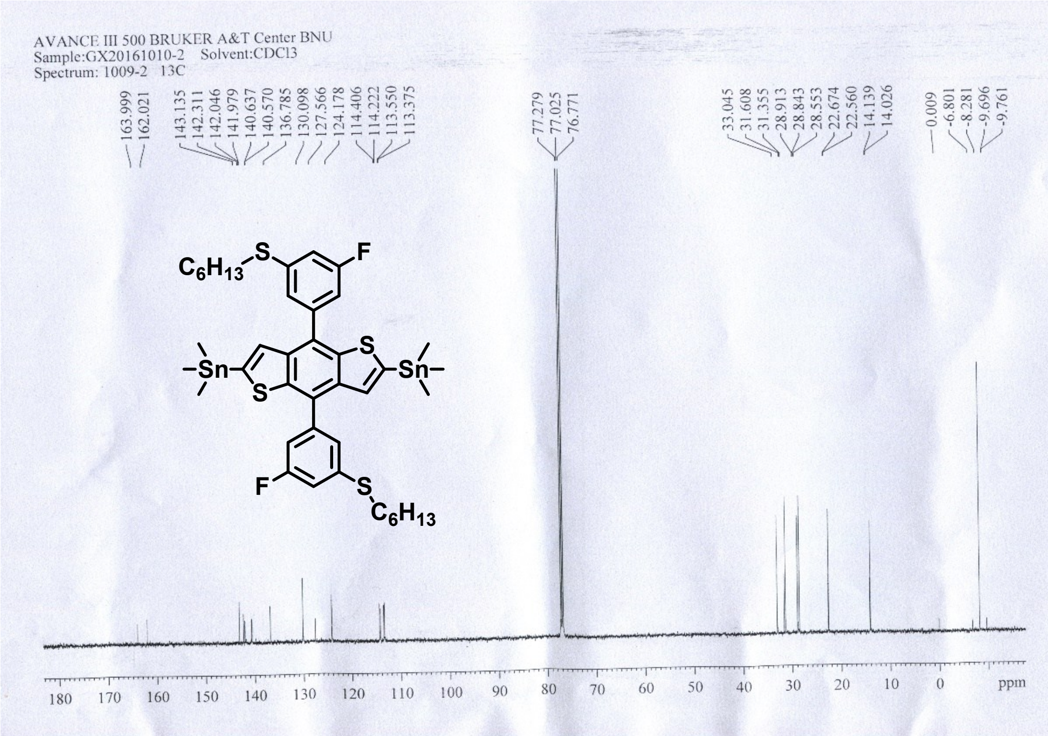
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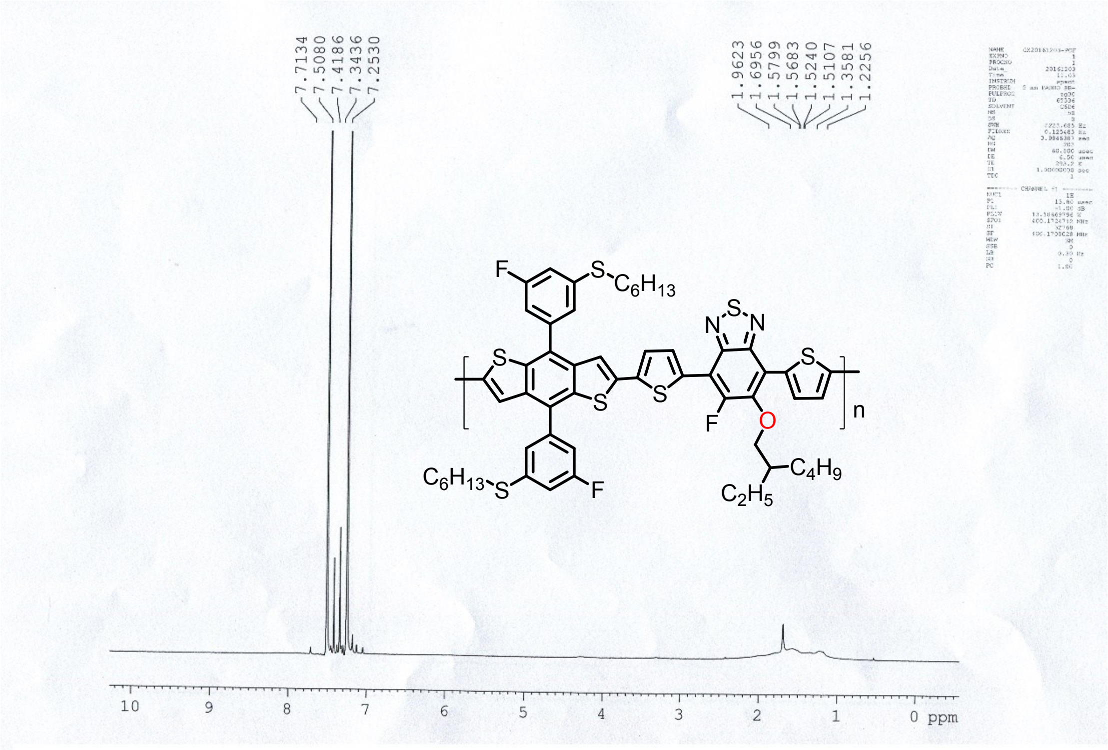
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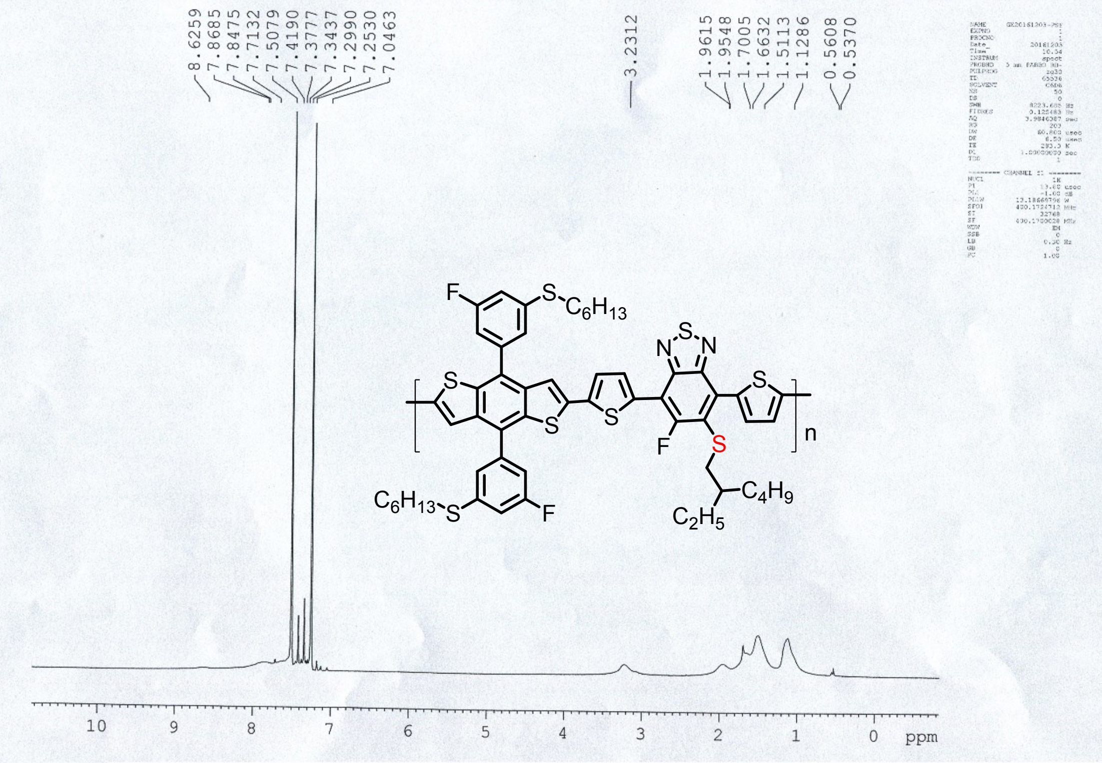 8.6259
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