

Supporting Information

Side chain effect on difluoro-substituted dibenzo[a,c]phenazine based conjugated polymers as donor materials for high efficiency polymer 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(PPh₃)₄ was prepared according to the literature³⁹ and stored in a Schlenk tube under nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (DCM) were distilled from CaH₂. Chloroform (CF) was distilled before use. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh). ¹H and ¹³C NMR 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 °C/min to record TGA and DSC curves. Gel permeation chromatography (GPC) measurements were performed at 150 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with 1,2,4-trichlorobenzene (TCB) as an

eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The powdery X-ray diffraction (XRD) patterns were collected using a PANalytical X'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 and assumption that the energy level of F_c is 4.8 eV below vacuum.

Fabrication and Characterization of Organic Field-Effect Transistors (OFETs)

Bottom-contact devices were fabricated based on Si/SiO_2 substrates (the back low resistance Si as gate, SiO_2 (500 nm) as gate insulator). Polymer thin films were spin-coated on the OTS-modified Si/SiO_2 substrate from 1,2-dichlorobenzene (DCB) solutions. Electrodes of Au (25 nm) were vacuum deposited on polymer thin films.

Polymer Solar Cell Fabrication and Characterization. PSCs were fabricated with the device configuration of $\text{ITO}/\text{ZnO}/\text{polymer}:\text{PC}_{71}\text{BM}/\text{MoO}_3/\text{Ag}$.¹ The conductivity of ITO was $20 \Omega/\square$. The blend of polymers and PC_{71}BM was dissolved in 1,2-dichlorobenzene (DCB) and heated at 100 °C overnight to ensure sufficient dissolution, and then spin-coated onto ZnO layer. The top electrode was thermally evaporated, with a 7 nm MoO_3 layer, then followed by 100 nm of Ag at a pressure of 10^{-4} Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm^2 . The measurement of devices was conducted in air without encapsulation. Current-voltage characteristics were recorded using an Agilent B2902A Source Meter under an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mWcm^{-2} as the white light source and the intensity was calibrated with a standard single-crystal Si photovoltaic cell. The

temperature while measuring the J - V curves was approximately 25 °C.

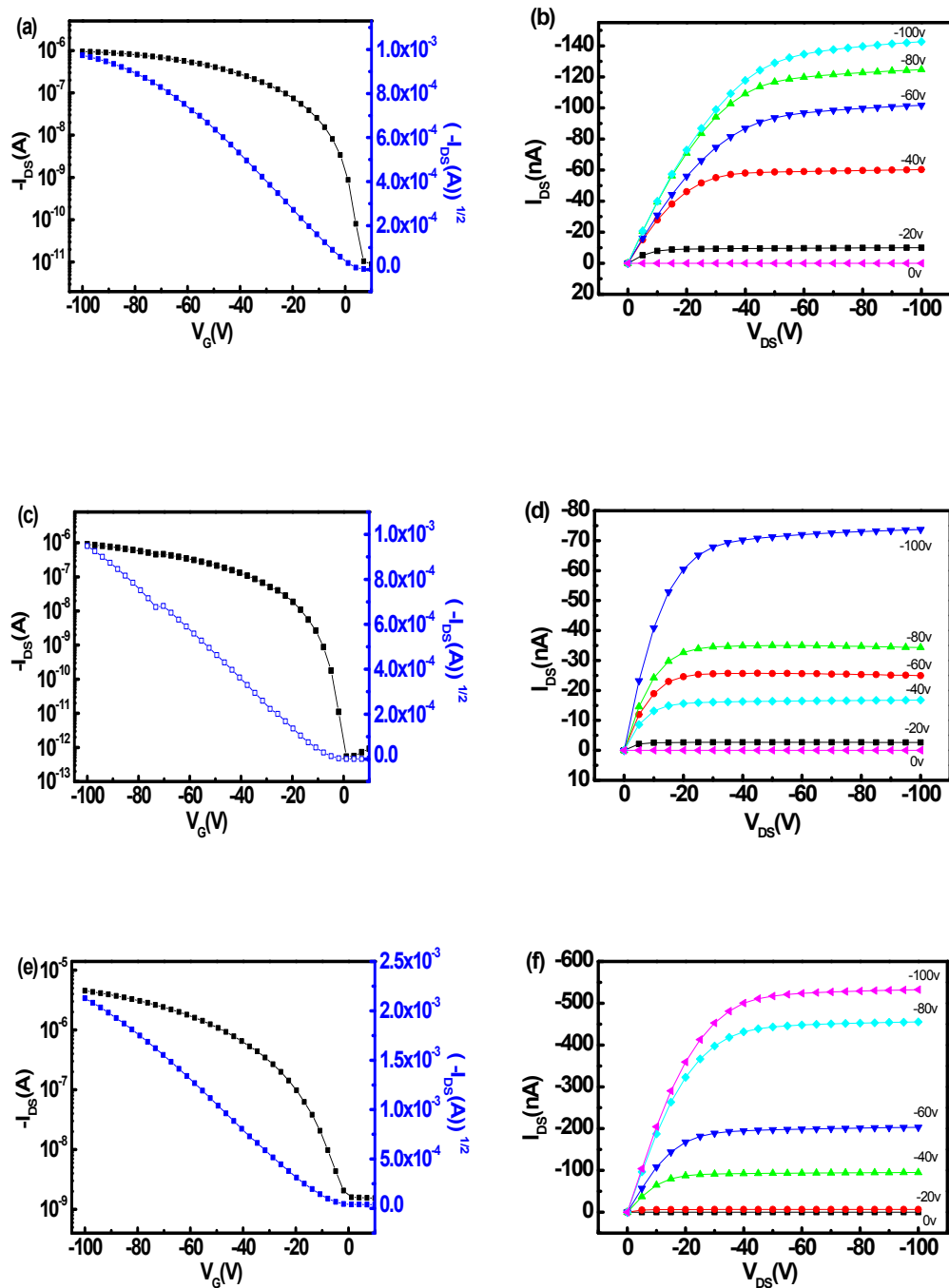


Figure S1. Transfer characteristic and output characteristic of the OFET for **P1** (a, b), **P2-L** (c, d), **P2-H** (e, f)

Table S1. Detailed OFET results of polymers **P1**, **P2-L**, and **P2-H**.

Polymer	Annealing temperature	Device number	μ (cm ² /Vs)	V _T (V)	on/off
P1	No annealing	1	2.14E-03	-2.56E+00	9.2E+4
		2	1.72E-03	-8.25E-01	5.5E+4
		3	1.77E-03	1.17E+00	7.9E+4
		4	1.55E-03	4.82E+00	5.0E+4
		5	1.53E-03	4.64E+00	4.7E+4
	Average value		1.74E-03		
P1	50 °C	1	4.24E-03	1.70E+00	1.1E+5
		2	3.82E-03	1.16E+00	1.2E+5
		3	3.62E-03	1.20E+00	1.1E+5
		4	3.61E-03	2.64E+00	4.7E+4
	Average value		3.82E-03		
P1	100 °C	1	2.45E-03	1.55E+00	8.3E+4
		2	2.38E-03	1.38E+00	8.0E+4
		3	2.49E-03	1.82E+00	7.6E+4
		4	2.55E-03	1.43E+00	7.8E+4
	Average value		2.47E-03		
P1	150 °C	1	2.66E-03	-7.05E-01	9.0E+4
		2	2.68E-03	-4.49E-01	8.8E+4
		3	2.72E-03	-4.68E-01	1.0E+4
		4	2.85E-03	-4.49E-01	1.1E+4
		5	2.67E-03	1.14E+00	7.3E+4
		6	2.88E-03	1.32E+00	8.8E+4
	Average value		2.74E-03		
P1	200 °C	1	2.69E-03	8.20E-01	1.0E+5
		2	3.02E-03	1.03E+00	1.1E+5
		3	2.81E-03	8.98E-01	1.1E+5

		4	3.00E-03	1.05E+00	9.5E+4
		5	4.43E-03	2.18E+00	1.2E+5
		6	3.94E-03	1.95E+00	1.1E+5
		7	3.75E-03	2.10E+00	8.9E+4
		8	3.91E-03	2.07E+00	1.0E+5
	Average value		2.74E-03		
P1	250 °C	1	1.76E-03	4.24E+00	6.0E+4
		2	2.07E-03	1.61E+00	7.0E+4
		3	2.32E-03	2.22E+00	8.2E+4
		4	2.47E-03	2.00E+00	4.4E+4
		5	2.54E-03	8.70E-01	9.1E+4
		6	2.37E-03	1.53E+00	8.5E+4
	Average value		2.25E-03		
P2-L	No annealing	1	1.10E-03	-9.69E+00	3.4E+5
		2	1.00E-03	-7.41E+00	4.3E+5
		3	1.14E-03	-8.98E+00	9.4E+4
		4	1.09E-03	-8.58E+00	1.1E+5
	Average value		1.08E-03		
P2-L	80 °C	1	1.14E-03	-7.12E+00	4.0E+5
		2	1.11E-03	-6.24E+00	4.4E+5
		3	1.12E-03	-5.98E+00	4.8E+5
		4	1.17E-03	-5.90E+00	5.1E+5
	Average value		1.13E-03		
P2-L	140 °C	1	1.83E-03	-5.36E+00	6.1E+5
		2	1.85E-03	-5.70E+00	7.9E+5
		3	1.84E-03	-5.88E+00	8.0E+5
		4	1.91E-03	-5.62E+00	8.2E+5
	Average value		1.86E-03		
P2-L	200 °C	1	4.19E-03	-2.37E+01	1.3E+6
		2	4.34E-03	-2.33E+01	1.5E+6
		3	4.39E-03	-2.19E+01	1.6E+6
		4	4.43E-03	-2.24E+01	1.7E+6
	Average value		4.34E-03		
P2-H	No annealing	1	2.96E-03	-3.62E+00	167.6955E+3
		2	2.66E-03	-3.60E+00	165.4545E+3

		3	2.45E-03	-3.48E+00	176.6535E+3
		4	2.33E-03	-3.73E+00	168.0563E+3
		5	2.32E-03	-1.22E+00	134.1907E+3
	Average value		1.89E-03		
P2-H	50 °C	1	3.86E-03	-2.12E+00	1.7E+5
		2	3.69E-03	-3.70E+00	1.6E+5
		3	3.40E-03	-3.59E+00	1.6E+5
		4	3.71E-03	-3.85E+00	1.7E+5
		5	4.26E-03	-2.98E+00	3.9E+4
		6	4.17E-03	-2.84E+00	2.2E+4
	Average value		3.85E-03		
P2-H	100 °C	1	4.96E-03	-2.53E+00	2.3E+5
		2	5.03E-03	-2.08E+00	2.5E+3
		3	4.62E-03	-2.66E+00	2.3E+5
		4	4.64E-03	-2.50E+00	2.3E+5
		5	4.75E-03	-2.44E+00	2.6E+5
		6	4.42E-03	-3.05E+00	2.6E+5
	Average value		4.74E-03		
P2-H	150 °C	1	4.68E-03	-2.01E+00	2.2E+5
		2	4.82E-03	-1.92E+00	2.8E+5
		3	5.59E-03	-2.58E+00	2.7E+5
		4	5.59E-03	-3.74E+00	3.5E+5
		5	4.52E-03	-1.17E+00	2.8E+5
	Average value		5.04E-03		
P2-H	200 °C	1	7.44E-03	-2.53E+00	4.5E+5
		2	6.39E-03	-2.22E+00	4.2E+5
		3	6.93E-03	-1.03E+01	3.9E+5
		4	5.70E-03	-2.15E+00	3.8E+5
		5	7.29E-03	-2.14E+00	3.5E+5
		6	1.36E-02	-7.57E+00	8.6E+5

	Average value		7.90E-03		
P2-H	250 °C	1	1.38E-02	-7.47E+00	8.7E+5
		2	1.54E-02	-9.26E+00	1.0E+6
		3	1.35E-02	-8.70E+00	9.9E+5
		4	1.37E-02	-9.84E+00	9.2E+5
		5	1.37E-02	-7.72E+00	8.6E+5
	Average value		1.43E-02		

Table S2. Detailed device results of polymers

Polymer:PC₇₁BM	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
P1: PC₇₁BM	0.74	11.94	0.66	5.8
	0.73	12.48	0.63	5.7
	0.73	11.75	0.63	5.5
	0.73	12.06	0.67	5.9
	0.74	11.91	0.64	5.7
	0.73	11.97	0.63	5.5
	0.72	11.71	0.63	5.3
	0.75	11.84	0.62	5.5
	0.75	12.65	0.60	5.7
	0.74	12.50	0.65	6.0
P2-L:PC₇₁BM	0.93	3.71	0.40	1.4
	0.93	3.39	0.44	1.4
	0.93	3.74	0.41	1.4
	0.94	3.94	0.40	1.5
	0.93	3.26	0.45	1.4
	0.93	4.24	0.39	1.6
	0.93	4.55	0.40	1.7

	0.93	3.79	0.38	1.3
	0.94	4.14	0.39	1.5
	0.93	4.07	0.40	1.5
P2-H:PC₇₁BM	0.94	5.90	0.50	2.8
	0.94	4.92	0.52	2.4
	0.93	5.46	0.53	2.7
	0.94	5.28	0.51	2.5
	0.94	5.67	0.50	2.7
	0.94	5.28	0.48	2.4
	0.94	5.64	0.49	2.6
	0.93	5.52	0.49	2.5
	0.94	5.67	0.46	2.5
	0.94	5.60	0.46	2.4
P3HT:PC₇₁BM^a	0.53	9.2	0.65	3.2

^a Devices structure: ITO/PEDOT:PSS/P3HT:P₇₁CBM/LiF/Al

Synthesis of monomers and polymers

11,12-Difluoro-10,13-bis(4-octyl-thiophene-2-yl)dibenzo[a,c]phenazine (2)

A mixture of 5,6-difluoro-4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (1.0 g, 1.8 mmol) and zinc powder (2.314 g, 35.6 mmol) in 100 mL AcOH was heated to 80 °C under nitrogen atmosphere and stirred at this temperature until the color of solution changed to colorless. The mixture was filtrated under nitrogen atmosphere; phenanthrene-9,10-dione (371 mg, 1.8 mmol) was added to the filtrate; and the resulted mixture was heated to 80 °C under nitrogen atmosphere and stirred overnight. Solvent was then removed under reduced pressure, the residue was chromatographically purified by filtration through a short column eluting with toluene:petroleum ether (PE) (1:1) to afford **1** a brick red solid (765 mg, 61%). ¹H NMR (400 MHz, CDCl₃): δ 9.25-9.40 (m, 2H), 8.35-8.55 (m, 2H), 7.85 (s, 2H), 7.59-7.80 (m, 4H), 7.31 (s, 2H), 2.76 (t, *J* = 7.6 Hz, 4H), 8.99 (d, *J* = 7.6 Hz, 2H), 1.69-1.89 (m, 4H), 1.23-1.60 (m, 20H), 0.91 (t, *J* = 6.4 Hz, 6H). ¹³C NMR (100 MHz,

CDCl₃): δ 149.05, 142.58, 140.90, 136.01, 132.18, 131.98, 130.41, 130.05, 129.79, 127.71, 127.59, 124.86, 122.35, 117.45, 31.95, 30.64, 30.56, 29.56, 29.52, 29.35, 22.70, 14.11. Anal. Calcd for C₄₄H₄₆F₂N₂S₂: C 74.96, H 6.58, N 3.97. Found: C 74.72, H 6.64, N 3.65.

11,12-Difluoro-10,13-bis(5-bromo-4-octyl-thiophene-2-yl)dibenzo[a,c]phenazine

(M1)

To a solution of 11,12-difluoro-10,13-bis-(4-octyl-thiophene-2-yl)-dibenzo[a,c]phenazine (500 mg, 0.71 mmol) in CH₂Cl₂ (100 mL) at 0 °C was added Br₂ (450 mg, 2.8 mmol) in one portion. The mixture was stirred at this temperature for 10 Min, poured into aqueous Na₂SO₃ (100 mL), and extracted with CH₂Cl₂ (100 mL×3). The collected organic phase was dried over anhydrous MgSO₄ and evaporated to dryness. The crude product was purified by filtration through a silica gel column eluting with toluene:PE (1:1) and recrystallization from a solvent mixture of toluene and PE (1:1) to afford **M1** as dark red solid (556 mg, 91%). ¹H NMR (400 MHz, CDCl₃): δ 8.99 (d, J = 7.6 Hz, 2H), 8.28 (d, J = 8.0 Hz, 2H), 7.6-7.7 (m, 2H), 7.45-7.6 (m, 4H), 2.65 (t, J = 7.7 Hz, 4H), 1.6-1.8 (m, 4H), 1.2-1.5 (m, 20H), 0.92 (t, J = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 148.68, 140.66, 139.94, 134.13, 131.22, 130.77, 129.98, 129.61, 128.49, 127.23, 127.04, 121.77, 115.55, 31.98, 29.76, 29.53, 29.52, 29.40, 22.74, 14.15. Anal. Calcd for C₄₄H₄₄F₂Br₂N₂S₂: C 61.25, H 5.14, N 3.25. Found: C 61.23, H 5.69, N 2.84.

Synthesis of P1

A mixture of 11,12-difluoro-10,13-bis(5-bromo-4-octyl-thiophene-2-yl)dibenzo[a,c]phenazine (**M1**) (100 mg, 0.12 mmol), 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyl oxy)benzo[c][1,2,5]thiadiazole (**M3**) (89 mg, 0.12 mmol), toluene (15 mL), and DMF (1.5 mL) was carefully degassed and charged with nitrogen several times before and after Pd(PPh₃)₄ (1.4 mg, 0.001 mmol) was added. The mixture was heated to reflux and stirred for 1 day; trimethyl(thiophen-2-yl)stannane (15 mg, 0.06 mmol) was added and refluxed for further 6 hours; and then 2-bromothiophene (30 mg, 0.18 mmol) was added and reacted for another 6 hours to finish the end-capping. After cooling down to room temperature, the reaction mixture was poured into methanol

(200 mL). The resulted precipitates were collected by filtration and extracted successively with methanol, ethyl acetate, hexanes, and chloroform in a Soxhlet Apparatus. The residue was dissolved in chlorobenzene at elevated temperature, hot filtrated, and concentrated to a small amount of solvent under reduced pressure. The concentrated polymer solution was poured into 100 mL acetone and the formed precipitates was collected and dried under reduced pressure to afford **P1** as a black solid (90 mg, 87%).

Synthesis of **P2**

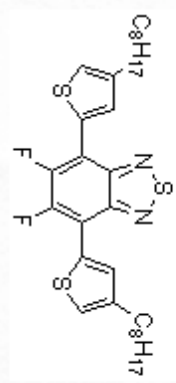
A mixture of 11,12-difluoro-10,13-bis(5-bromo-4-octyl-thiophene-2-yl)dibenzo [a,c]phenazine (**M1**) (139 mg, 0.16 mmol), 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (**M3**) (200 mg, 0.16 mmol), toluene (15 mL), and DMF (1.5 mL) was carefully degassed and charged with nitrogen several times before and after Pd(PPh₃)₄ (2.3 mg, 0.002 mmol) was added. The mixture was heated to reflux and stirred for 2 days, trimethyl(thiophen-2-yl)stannane (15 mg, 0.06 mmol) was added and refluxed for further 6 hours, and then 2-bromothiophene (30 mg, 0.18 mmol) was added and reacted for another 6 hours to finish the end-capping. After cooling down to room temperature, the reaction mixture was poured to 200 mL methanol, the resulted precipitates were collected by filtration and extracted successively with methanol, ethyl acetate, hexanes, and chloroform in a Soxhlet Apparatus; The chloroform extract was collected and evaporated to dryness to afford the low molecular weight fraction **P2-L** (125 mg). The residue was dissolved in chlorobenzene at elevated temperature and filtered. After removal of most solvent, the residue was poured into acetone (200 mL), and the formed precipitates were collected by filtration and dried in high vacuum to give the high molecular weight fraction **P2-H** as a dark green solid (90 mg). ¹H NMR (400 MHz, CDCl₃): δ 9.80-10.20 (br, 2H), 8.60-9.00 (br, 2H), 8.25-8.60 (br, 4H), 8.03-8.25 (br, 2H), 7.91-8.03 (br, 2H), 7.72-7.90 (br, 2H), 2.7-3.7 (br, 12H), 1.29-2.69 (br, 46H), 0.88-1.29 (br, 18H).

Reference:

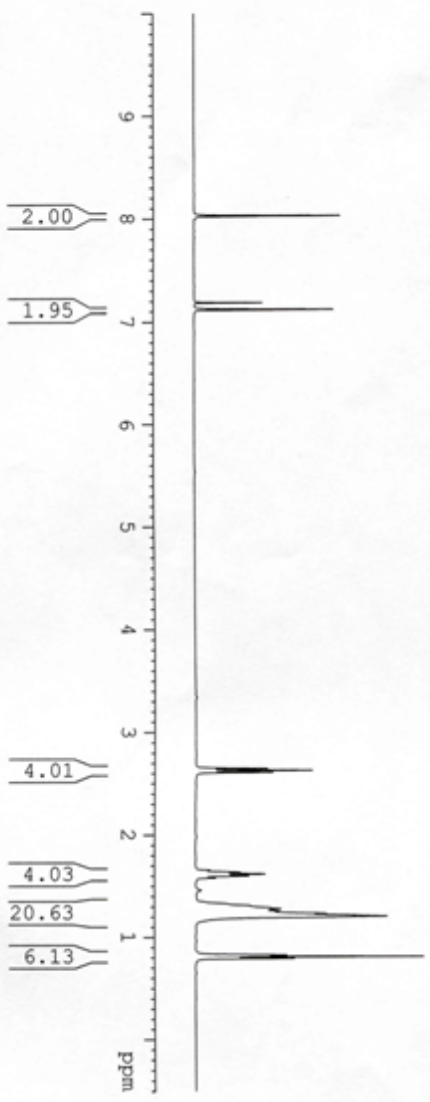
1. Y. Sun, J. H. Seo, C. J. Takacs, J. Seifert and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679-1683.

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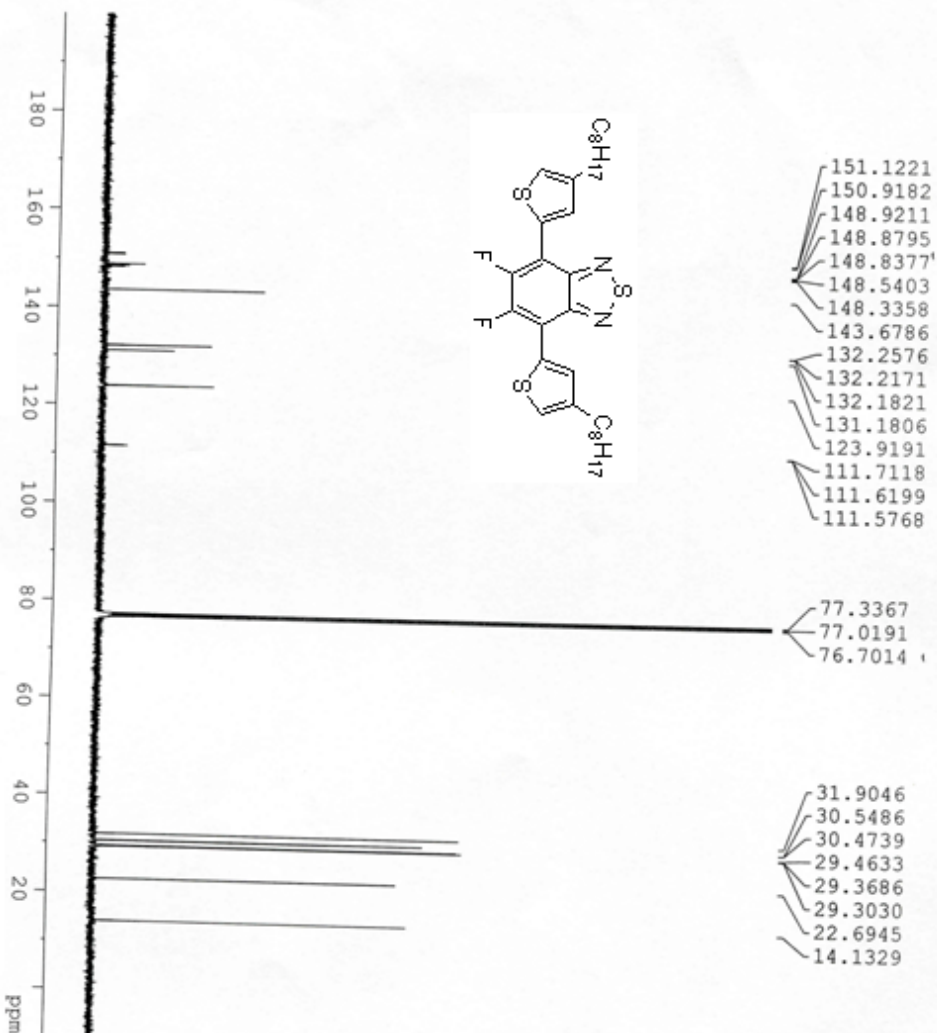


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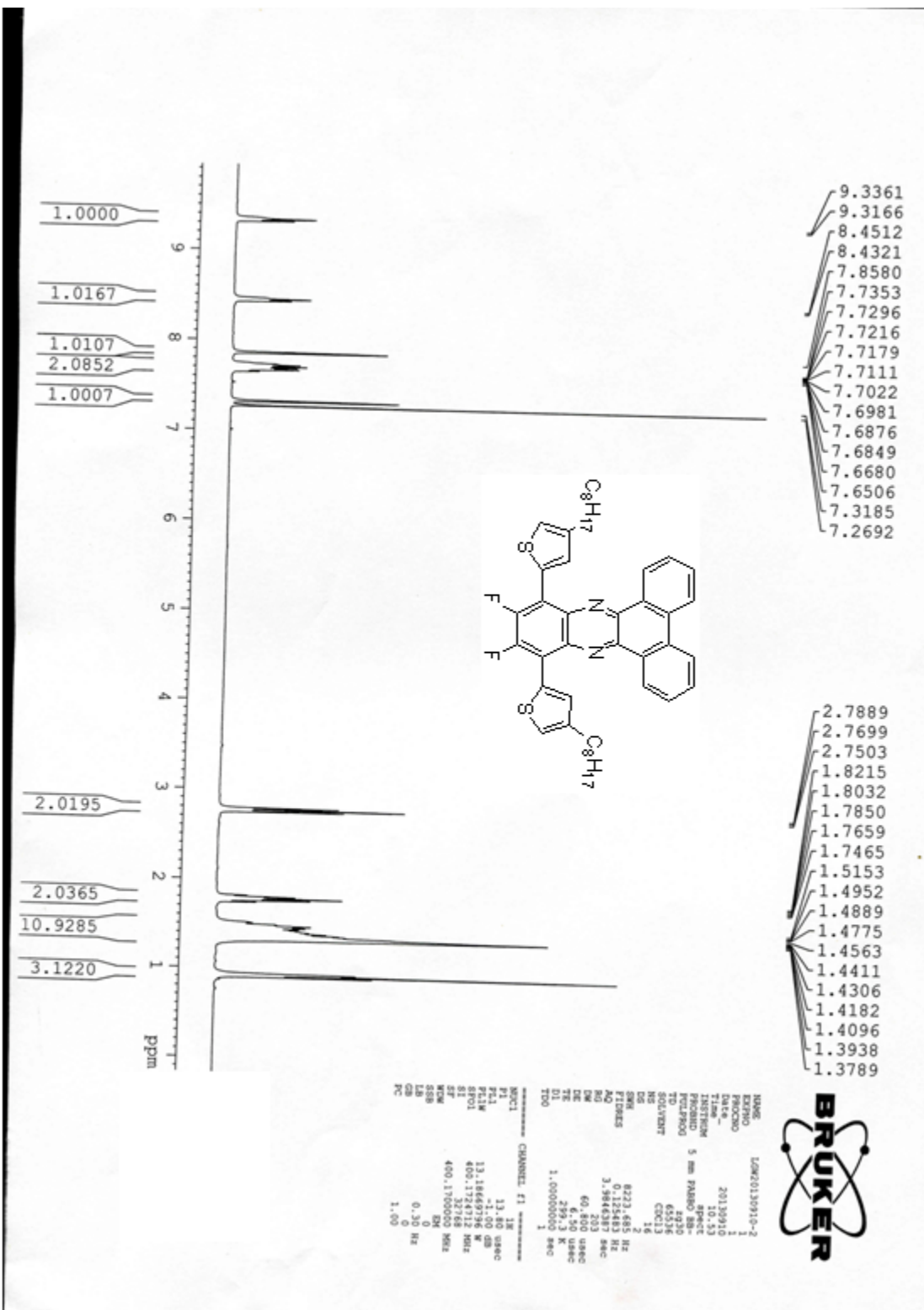
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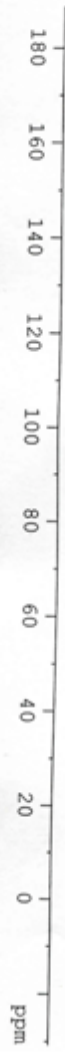


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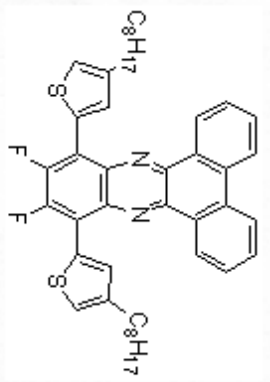
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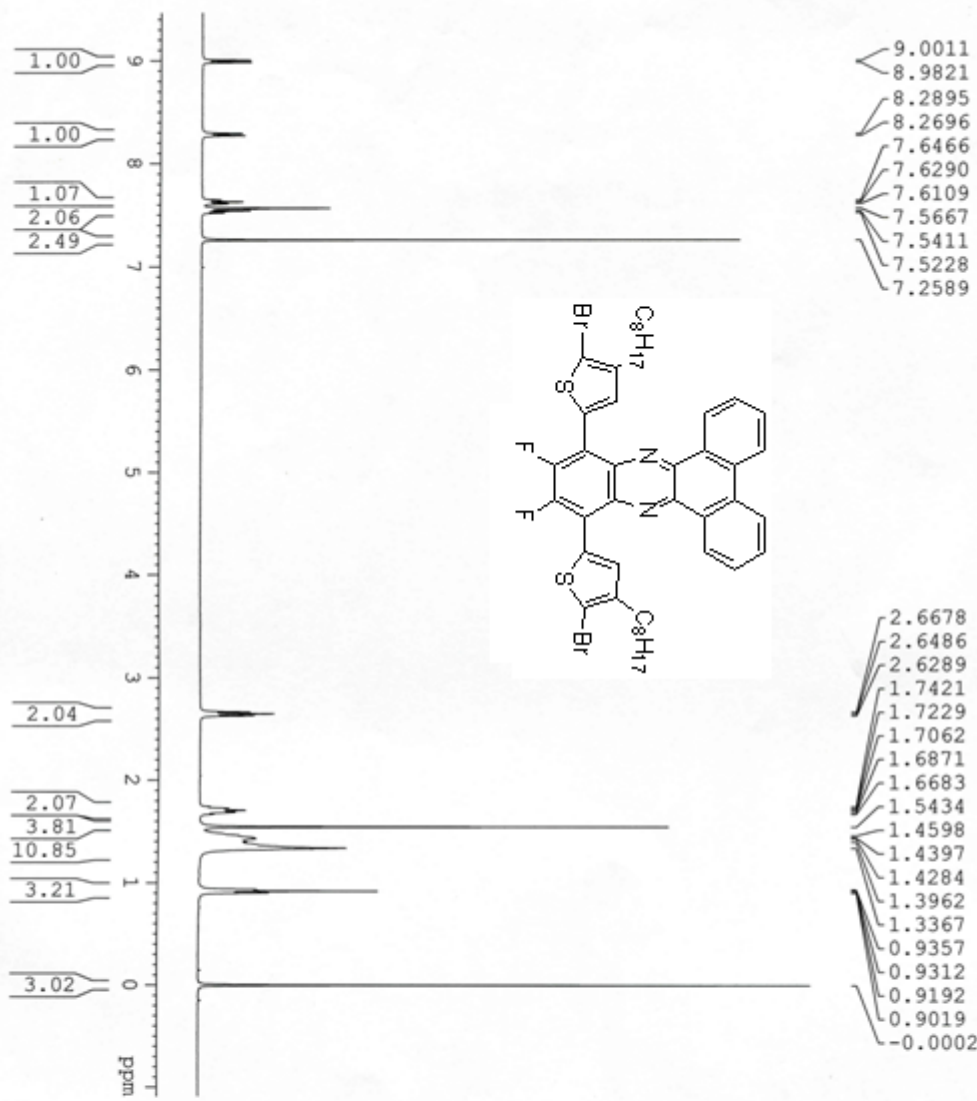


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PL1       -2.00 dB
PL1W      57.32743073 W
SFO1      100.628888 MHz

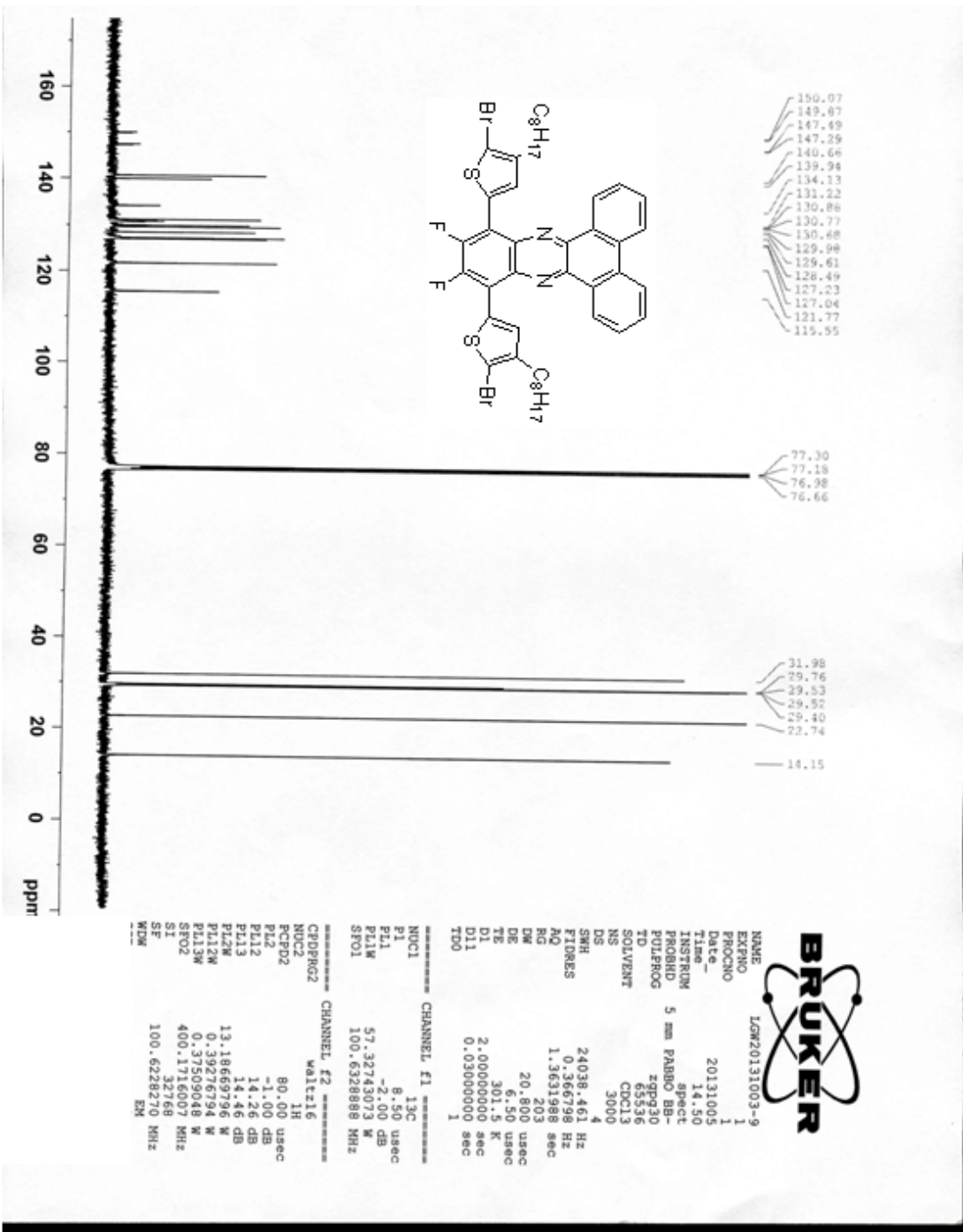
===== CHANNEL f2 =====
CAPPROG2 waltz16
NUC2      1H
PCPD2     90.00 usec
P12       -1.00 dB
PL12      14.26 dB
PL13      14.46 dB
PL2W      13.18669796 W
PL12W     0.39276794 W
PL13W     0.37509048 W
SFO2      400.1716007 MHz
SI        32768
SRW       100.6288870 MHz
SFO2W     400.1716007 MHz
SFB        4
GB         0
PC         1.40
  
```



```

NAME LGW20120502-1
EXPNO 1
PROCNO 1
Date_ 20120502
Time_ 20.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DM 60.800 usec
DE 6.50 usec
TE 298.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700040 MHz
WDW EM
SSB 0
L8 0.30 Hz
GB 0
PC 1.00
  
```



ADVANCE III BRUKER A&T Center BNU
 Sample: IGM-PI Solvent: o-C6D4Cl2
 Spectrum: huaxueyuan-bozhishan 0910-3 1H

