Electronic Supplementary Information

Vinyl Flanked Difluorobenzothiadiazole-dithiophene Conjugated Polymer for High Performance Organic Field-effect Transistors

Xianfeng Liang,[a,b] Wandong Sun,[a] Yanlin Chen,[a] Luxi Tan,*[,a] Zhengxu Cai,[c] Zitong Liu,[c] Lin Wang,*[,b] Jing Li,[d] Wei Chen,[e,f] Lichun Dong*[,a]

a. School of chemistry and chemical engineering, Chongqing University, Chongqing, 401331, China. E-mail: tanluxi@cqu.edu.cn, lcdong72@cqu.edu.cn

b. YMU-HKBU Joint Laboratory of Traditional Natural Medicine, Yunnan Minzu University, Kunming 650500, China. E-mail: myxbwanglin@163.com

c. Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

d. Chongqing Institute of Green and intelligent technology, Chinese Academy of Sciences, Chongqing 400714, China. E-mail: jingli@cigit.ac.cn

e. Materials Science Division, Argonne National Laboratory, 9700 Cass Avenue, Lemont, IL, 60439, United States

f. Institute for Molecular Engineering, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL, 60637, United States.

Contents

1. General information

Chemicals were purchased form Alfa-Aesar, Sigma-Aldrich etc. and used without further purification. Gel permeation chromatography (GPC) analysis was performed on a Waters 1515 chromatograph at 35 °C, polystyrene was used as the calibration standard and THF as eluent. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker DMX-600

NMR Spectrometers using tetramethylsilane as internal standard. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. MALDI-TOF MS were recorded with BEFLEX III spectrometer. Thin films absorption spectra were measured with PE lambda 950 UV-Vis spectrophtometer. TGA-DTA measurements were carried out on a NETZSCH STA 449 F3 Jupiter® instruments under a dry nitrogen flow, heating from room temperature to 550 °C, with a heating rate of 20 °C/min. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using glassy carbon (GC) as working electrodes of 2 mm diameter, a platinum wire as counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI660E instruments at room temperature. X-ray crystallographic data were collected with a Bruker Smart CCD diffractometer through using Cu Kα radiation (λ = 1.54178 Å). The computation was performed with the SHELXL-97 program. Grazing-incident X-ray diffraction (GIXRD) measurements were performed at 8ID-E beam line at the Advanced Photon Source (APS), Argonne National Laboratory using X-ray with a wavelength of λ = 1.6868. The molecular structures of the compounds were optimized using the DFT method at the level of RB3LYP/6-311G. All calculations were performed with the programs Gaussian 09.

2. GPC

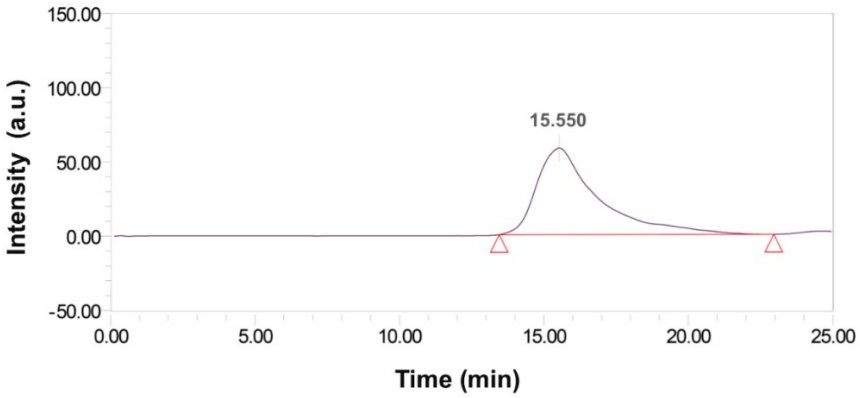

Figure S1. Retention time of **PTFBTV** in Gel permeation chromatography analysis with THF as eluent at 35 ºC.

3. TGA and DSC analysis

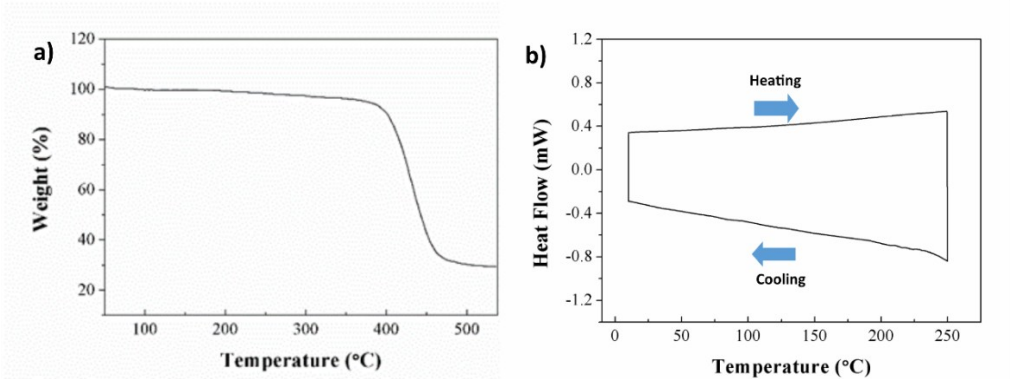

Figure S2. TGA (a) and DSC (b) analysis of **PTFBTV**. (T_d = 398.2 ºC)

4. UV-Vis absorption

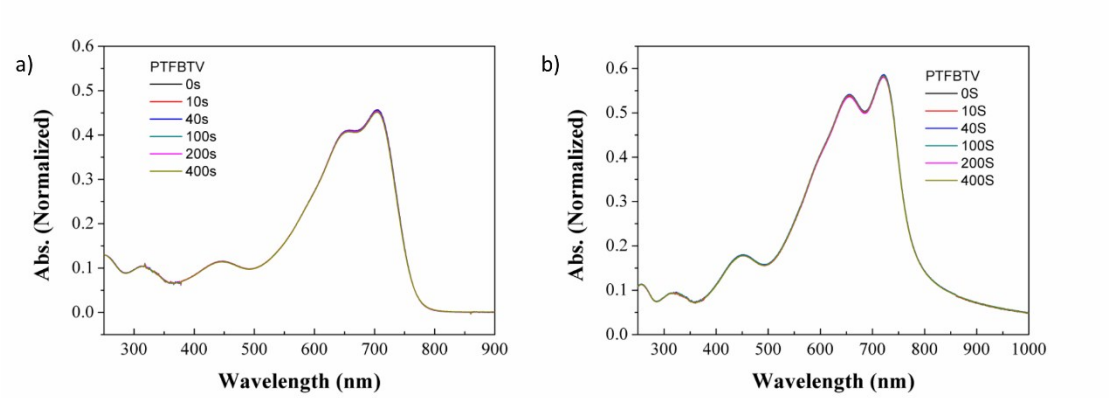

Figure S3. Absorption spectra changes of (a) **PTFBTV** in solution, (b) **PTFBTV** in thin film. The samples were all irradiated under Xe lamp (3.2 mW cm^{-2}).

7. Theoretical calculations

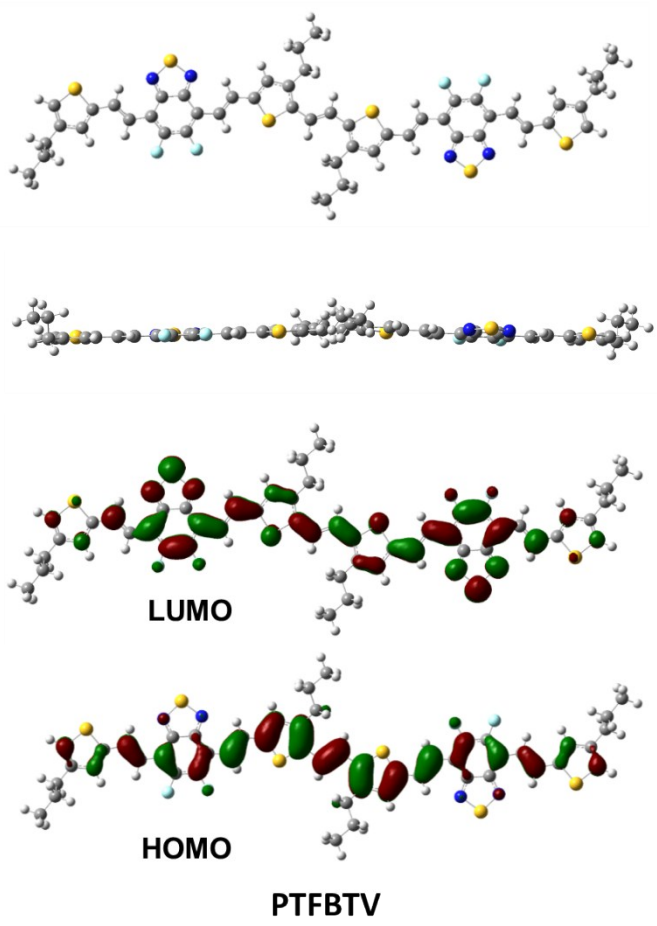

Figure S4. Calculated structure of **PTFBTV** oligomer (n=2) and its LUMO/HOMO orbitals.

Coordinates			
C	-10.9799	-0.00884	-0.21688
C	-10.1193	-1.09092	-0.25537
C	-8.71125	-0.99797	-0.20498
C	-8.00614	0.188827	-0.11051
C	-8.84998	1.359307	-0.06781
C	-10.3044	1.262355	-0.12051
N	-8.41649	2.613911	0.020628
S	-9.73435	3.591297	0.035819
N	-10.9059	2.447993	-0.06961
C	-14.7939	0.442302	-0.28955
C	-4.30032	1.180995	0.082033
C	-3.45141	2.269512	0.191424
C	-2.07302	1.965545	0.225271
C	-1.8408	0.589445	0.135862
S	-3.36222	-0.28817	0.015808
S	-15.9319	1.774499	-0.21403
C	-17.2789	0.69928	-0.32867
C	-16.8945	-0.61545	-0.42093
C	-15.4784	-0.75016	-0.39823
C	10.9799	0.008886	-0.21696
C	10.11919	1.090879	-0.25562
C	8.711156	0.997812	-0.20535
C	8.006141	-0.18904	-0.11084
C	8.850078	-1.35944	-0.06798
C	10.30449	-1.26237	-0.12056
N	8.416694	-2.61408	0.020525
S	9.734638	-3.59135	0.035893
N	10.90614	-2.44795	-0.06953
C	14.79394	-0.44188	-0.28923
C	4.30039	-1.18146	0.081733
C	3.451558	-2.27002	0.191433
C	2.073151	-1.96615	0.225196
C	1.840822	-0.59009	0.135427
S	3.362182	0.287606	0.015123
S	15.93208	-1.77391	-0.21289
C	17.27897	-0.69857	-0.32776
C	16.89444	0.616066	-0.42065
C	15.47833	0.750615	-0.39829
C	-0.64735	-0.21339	0.131692
C	0.647329	0.212667	0.130959

C	-6.56457	0.168691	-0.06336
C	-5.73245	1.236162	0.032943
C	-12.4078	-0.2224	-0.27007
C	-13.3779	0.722161	-0.23666
C	5.732521	-1.23653	0.032699
C	6.564562	-0.16902	-0.06378
C	12.40781	0.222574	-0.26998
C	13.37799	-0.72189	-0.23648
C	0.305737	-5.43478	0.71532
C	1.469174	-4.45165	0.559841
C	0.987369	-3.00956	0.358083
C	-0.30538	5.433875	0.716712
C	-1.46888	4.450852	0.56102
C	-0.98717	3.008895	0.358073
C	18.91077	3.77471	0.691712
C	17.94806	2.589586	0.800325
C	17.85112	1.778086	-0.50545
C	-18.9117	-3.77311	0.692612
C	-17.9489	-2.58802	0.800884
C	-17.8513	-1.77739	-0.50539
H	-3.84302	3.276046	0.250548
H	-18.2837	1.094335	-0.32609
H	-14.9783	-1.70797	-0.46828
H	3.843243	-3.27651	0.250771
H	18.28387	-1.0935	-0.3248
H	14.97807	1.708329	-0.4689
H	-0.83266	-1.27929	0.116159
H	0.832583	1.278559	0.113874
H	-6.13167	-0.82505	-0.11081
H	-6.1546	2.232733	0.080845
H	-12.6972	-1.26459	-0.34132
H	-13.0897	1.763362	-0.16292
H	6.154747	-2.23306	0.080822
H	6.131593	0.824682	-0.11141
H	12.69711	1.264797	-0.34118
H	13.08986	-1.76312	-0.16274
H	0.668137	-6.45601	0.857346
H	-0.31604	-5.18009	1.579025
H	-0.3386	-5.43166	-0.16926
H	2.08879	-4.7555	-0.29071
H	2.109882	-4.5027	1.44683
H	0.336501	-2.73829	1.199061
H	0.347894	-2.97849	-0.53407

H	-0.66772	6.455003	0.859579
H	0.316729	5.178588	1.579999
H	0.338613	5.431354	-0.16812
H	-2.08883	4.755309	-0.28907
H	-2.10925	4.501273	1.448295
H	-0.33576	2.737115	1.198464
H	-0.34825	2.978407	-0.53451
H	18.95921	4.333257	1.630117
H	19.92526	3.441448	0.451407
H	18.59683	4.469958	-0.09313
H	16.95062	2.948354	1.076618
H	18.26588	1.922493	1.608727
H	18.84638	1.409652	-0.77477
H	17.53985	2.445317	-1.31825
H	-18.9606	-4.33106	1.631349
H	-19.9261	-3.4399	0.451669
H	-18.5975	-4.46889	-0.09166
H	-16.9516	-2.94671	1.077853
H	-18.267	-1.92036	1.608707
H	-18.8464	-1.409	-0.77538
H	-17.5398	-2.4452	-1.31761
F	8.045554	2.166474	-0.2542
F	10.6191	2.337562	-0.34561
F	-10.6193	-2.33756	-0.34532
F	-8.04575	-2.1667	-0.25368

Total energy = -4940.01594591 hartree

8. Crystallographic data of DVBT and DVFBT

Synthesis of monomer **DVBT** is via similar process to compound 2 with a proximate yield of 61.5%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, J = 15.9 Hz, 2H), 7.52 (s, 2H), 7.19 (d, J = 16.0 Hz, 2H), 6.91 (s, 2H), 2.56 (t, J = 7.6 Hz, 4H), 1.66–1.55 (m, 4H), 1.39 (q, J = 7.4 Hz, 4H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.61, 142.95, 142.73, 128.77, 128.14, 127.52, 126.38, 124.25, 109.23, 31.74, 29.22, 22.30, 13.86. HR-MS (MALDI): calcd for $C_{26}H_{26}Br_2N_2S_3$ 619.9604; found 619.9600; EA: calcd for $C_{26}H_{26}Br_2N_2S_3$: C, 50.17; H, 4.21; N, 4.50; S, 15.45; found: C, 49.84; H, 4.21; N, 4.52; S, 15.39. (Synthesis of DVFBT is included in the main article.)

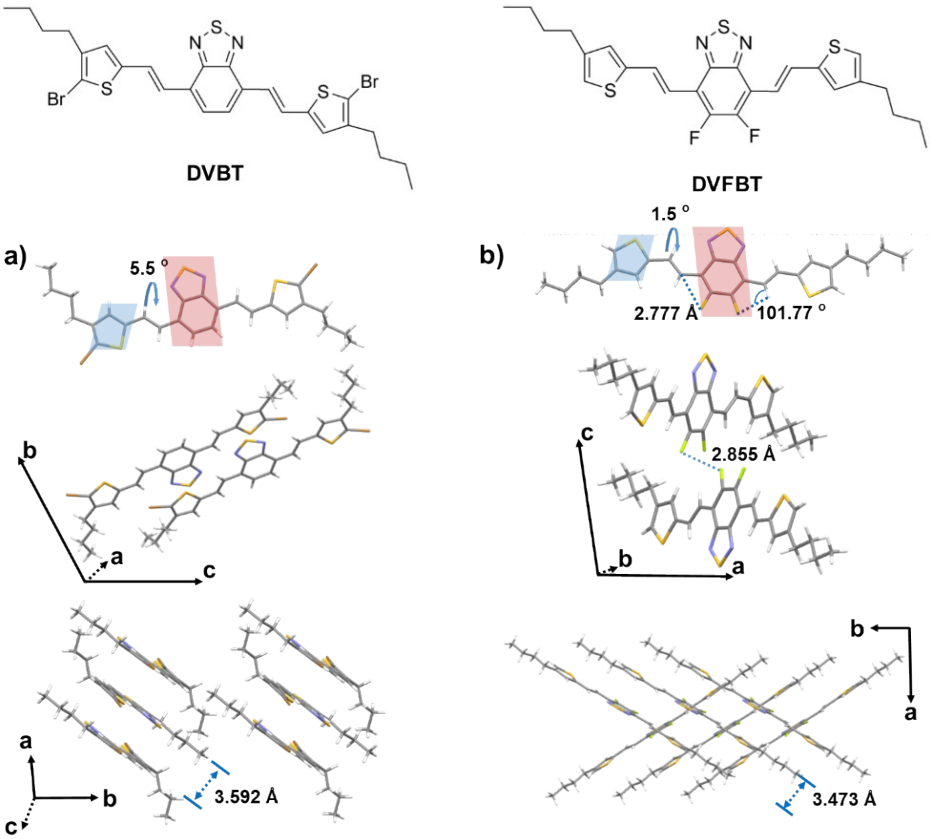

Figure S5. Overview of single crystal structure of **DVBT** (a) and **DVFBT** (b)

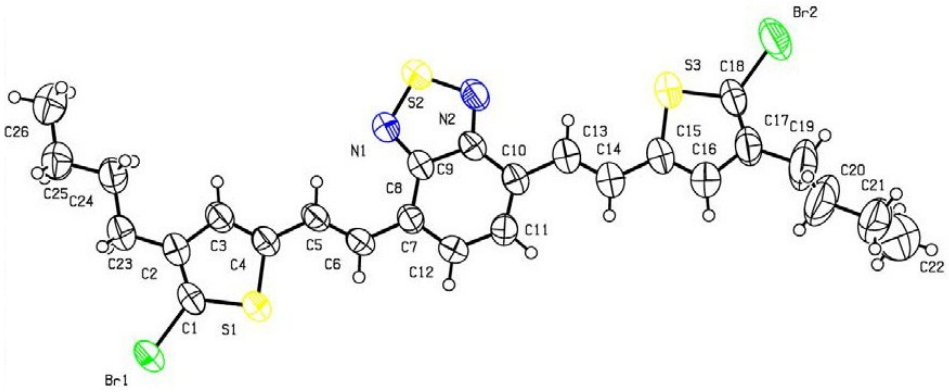

Figure S6. Thermal ellipsoids of **DVBT** in 50% probability at 298K.

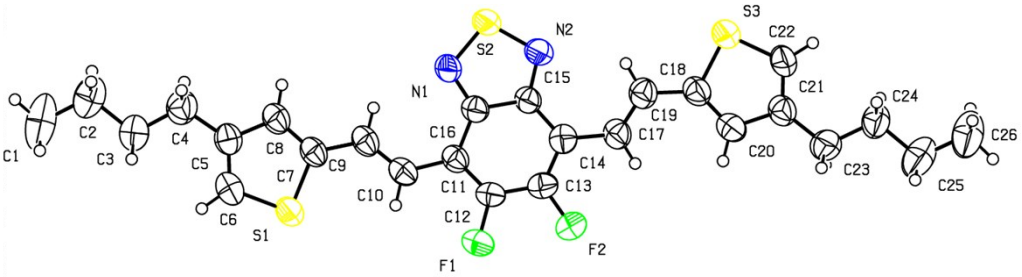

Figure S7. Thermal ellipsoids of **DVFBT** in 50% probability at 290K.

Table S1. Crystallographic data of **DVBT** and **DVFBT**

Name	DVBT(CCDC 1516212)	DVFBT (CCDC 1516172)
Empirical formula	$C_{26}H_{26}Br_2N_2S_3$	$C_{26}H_{26}F_2N_2S_3$
Formular weight	622.47	500.67
***T*/K**	298	290
Crystal system	triclinic	monoclinic
Space group	P-1	P-21
Color	red	red
***a*, Å**	8.7980(15)	13.5975(6)
***b*, Å**	13.210(3)	6.7176(2)
***c*, Å**	13.288(2)	13.7523(6)
***α*, deg**	113.098(14)	90
***β*, deg**	104.841(14)	97.379(4)
***γ*, deg**	97.140(14)	90
Volume, Å	1328.6(5)	1245.77(9)
Z	2	2
R	$R_1 = 0.0670$, $wR_2 = 0.1953$	$R_1 = 0.0853$, $wR_2 = 0.2061$
Goddness-of-fit on F^2	1.085	1.262

9. ^{1}H NMR and ^{13}C NMR

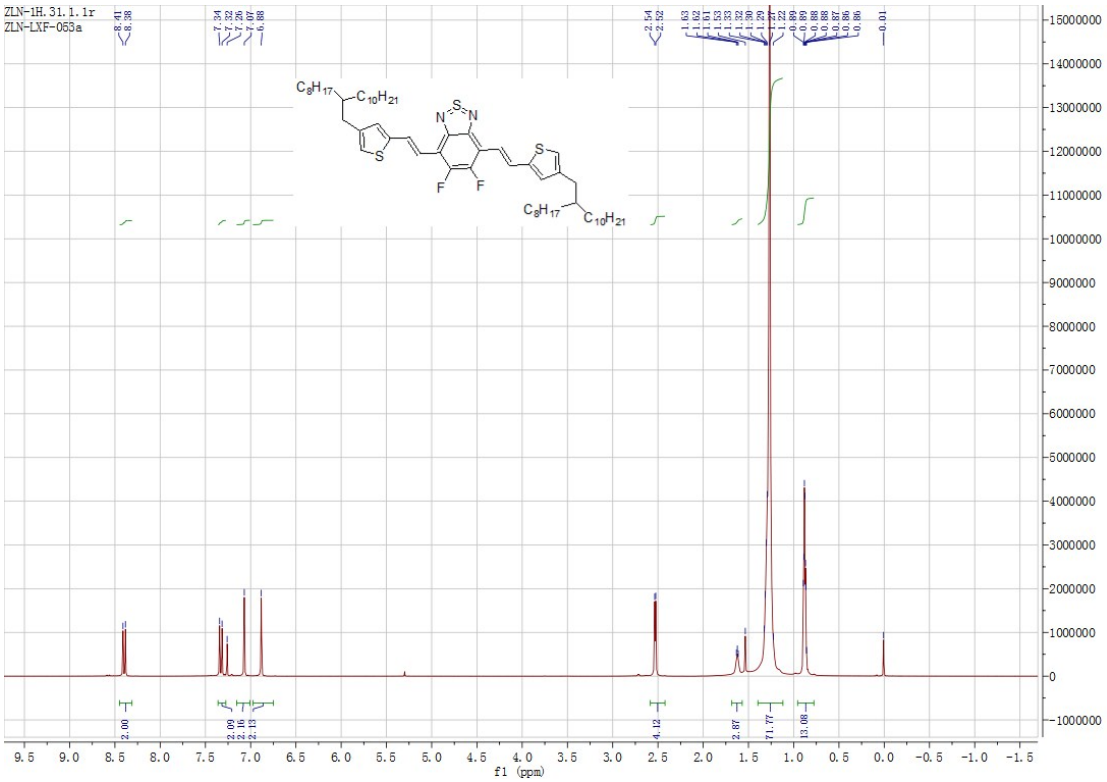

Figure S8. ^{1}H NMR spectra of compound **2** (600 MHz, $CDCl_3$)

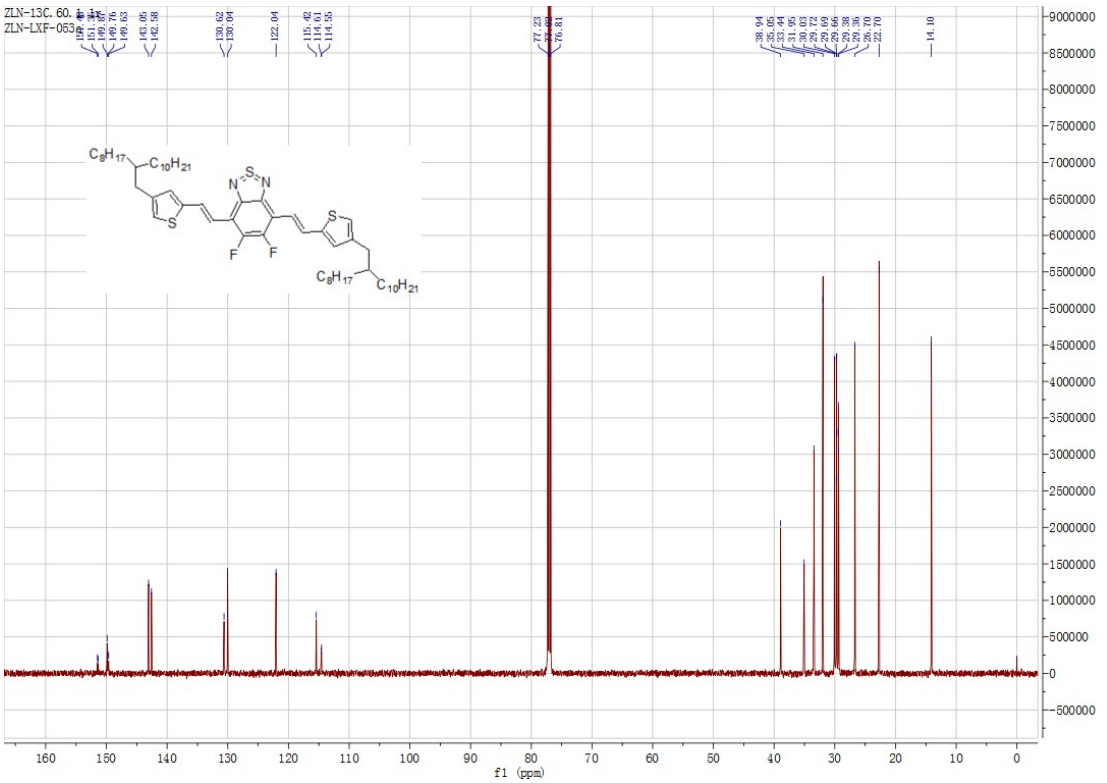

Figure S9. ^{13}C NMR spectra of compound **2** (151 MHz, $CDCl_3$)

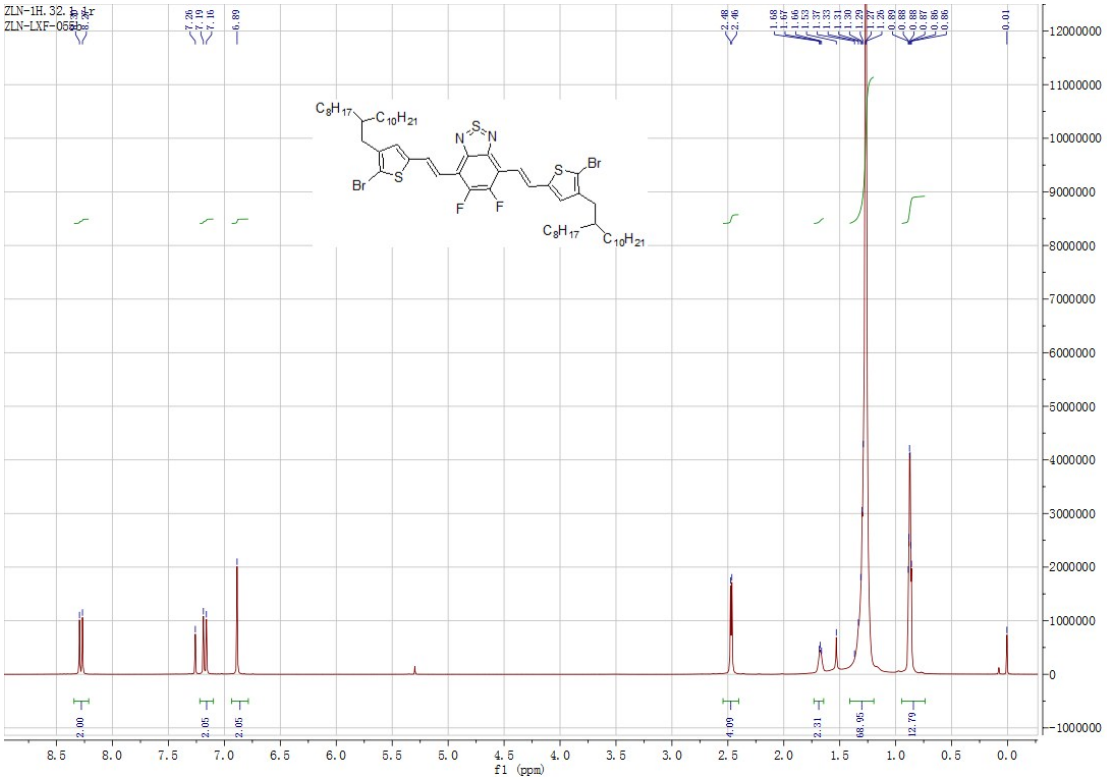

Figure S10. ^{1}H NMR spectra of compound **1** (600 MHz, $CDCl_3$)

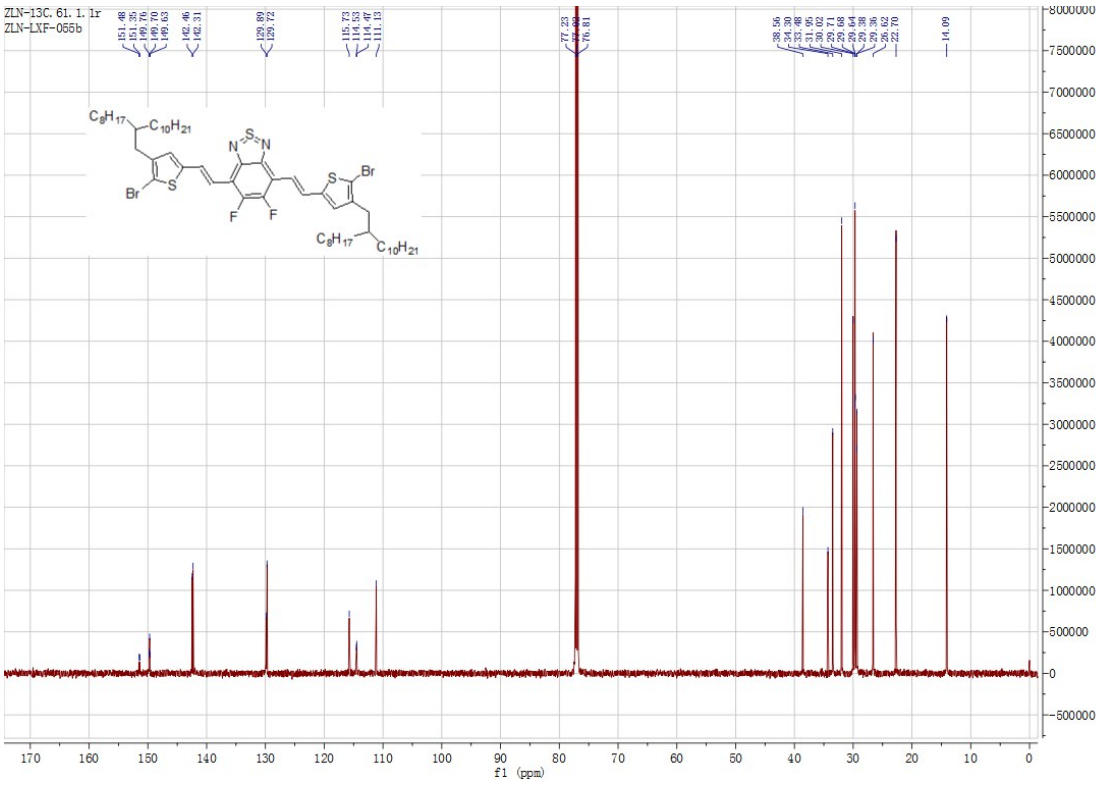

Figure S11. ^{13}C NMR spectra of compound **1** (151 MHz, $CDCl_3$)

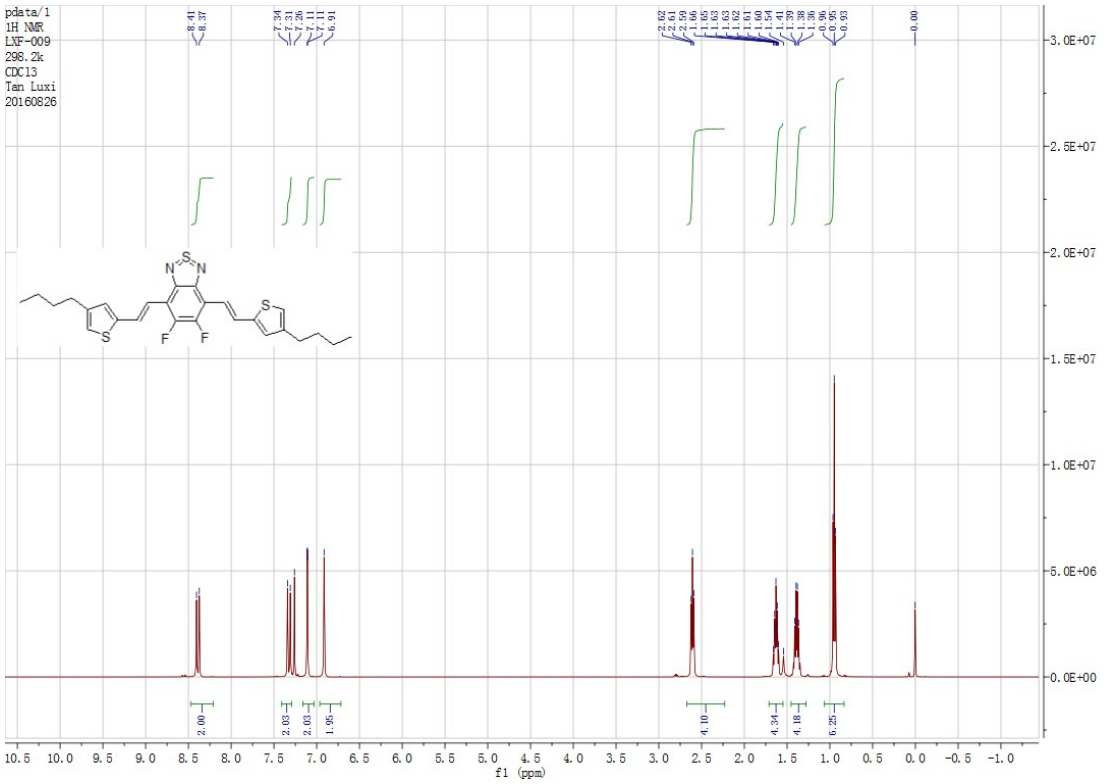

Figure S12. ^{1}H NMR spectra of **DVFBT** (600 MHz, $CDCl_3$)

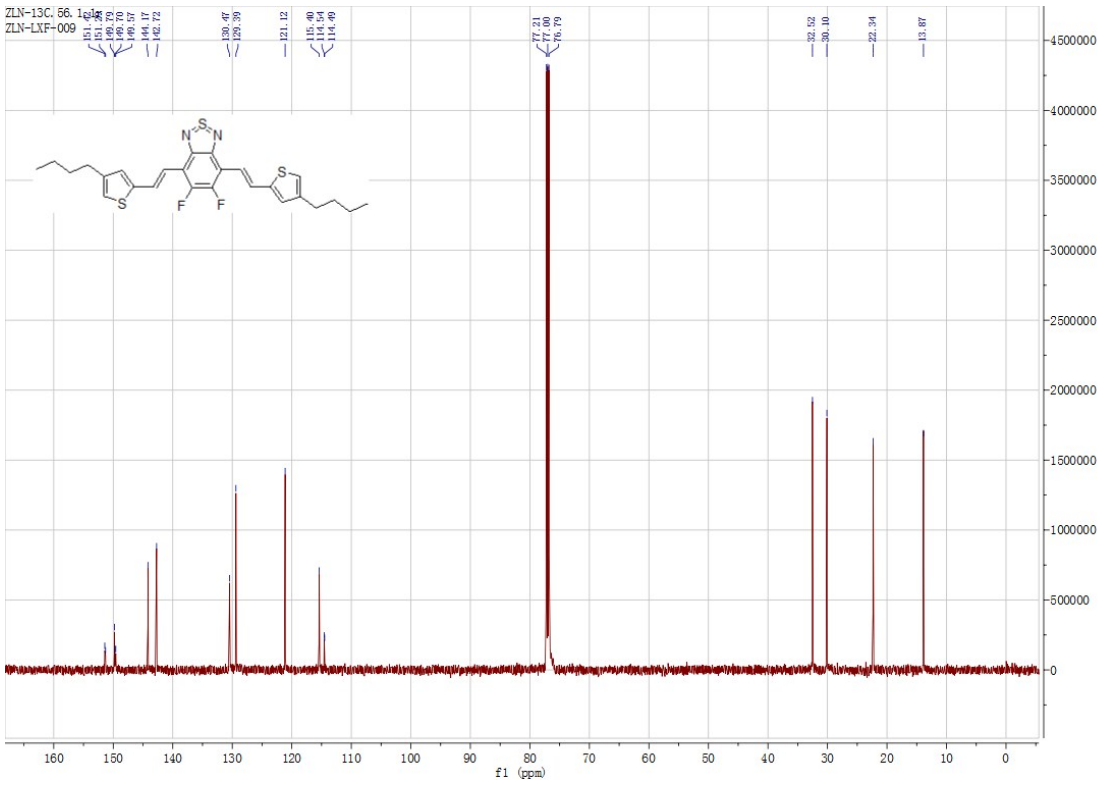

Figure S13. ^{13}C NMR spectra of **DVFBT** (151 MHz, $CDCl_3$)

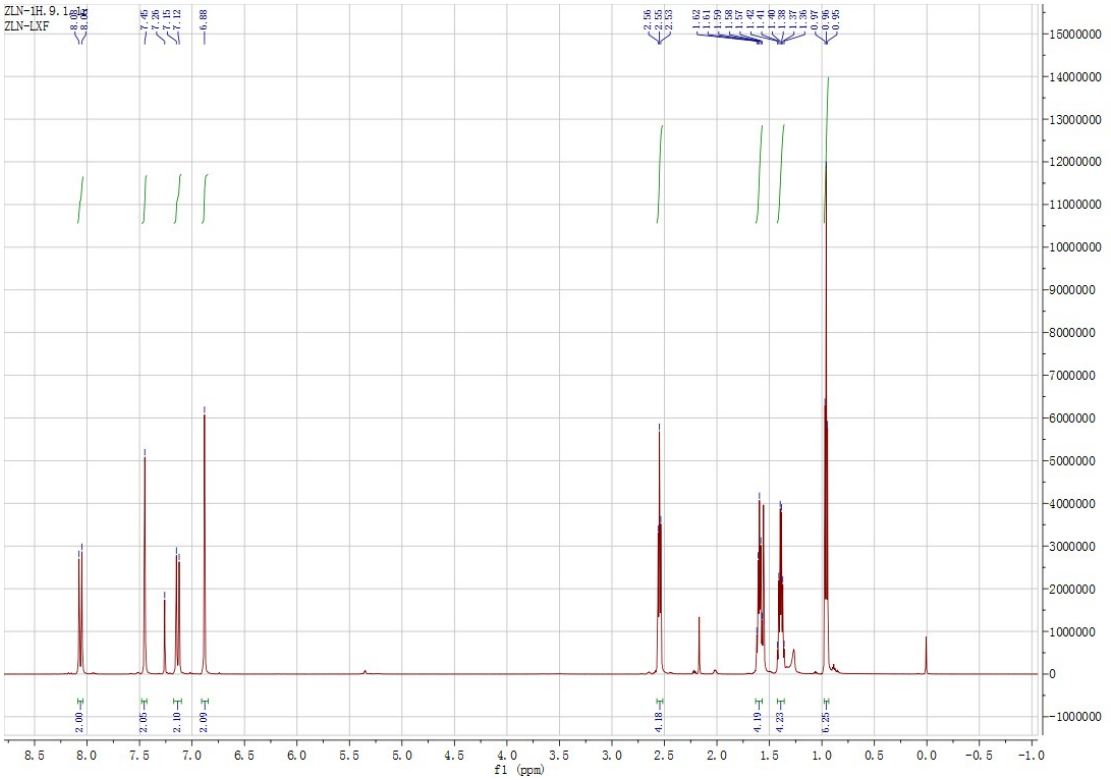

Figure S14. ^{1}H NMR spectra of **DVBT** (600 MHz, $CDCl_3$)

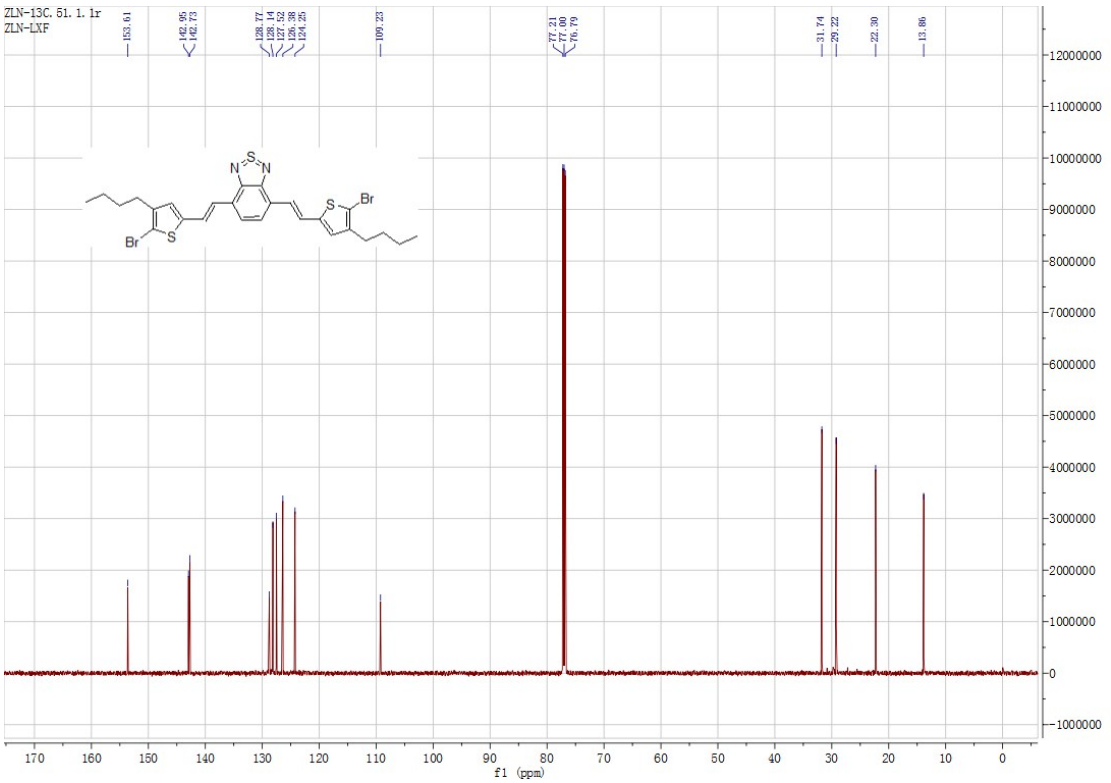

Figure S15. ^{13}C NMR spectra of **DVBT** (151 MHz, $CDCl_3$)