Supporting Information

Methoxylation of Quinoidal Bithiophene as Single Regioisomer Building Block for Narrow-Bandgap Conjugated Polymers and High-Performance Organic Field-Effect Transistors

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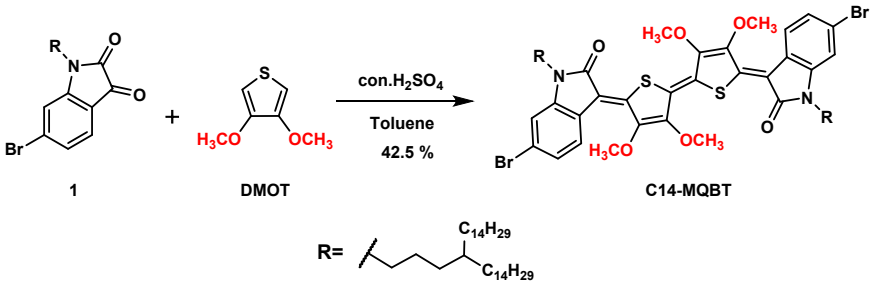
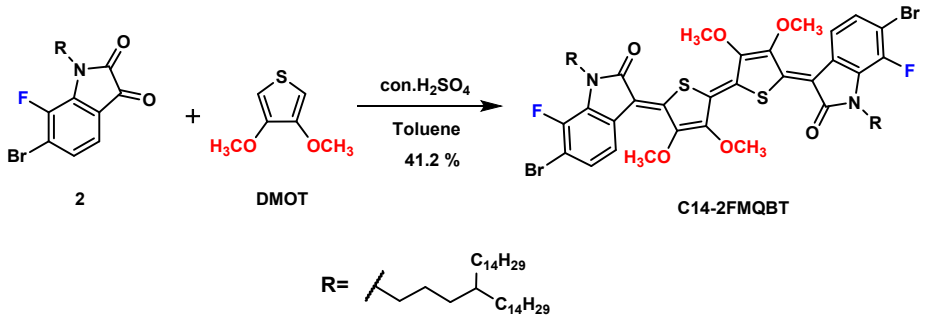
1. Synthetic procedures and characterization

Compound **1, 2** and **3** were synthesized according to the previous report.[1,2]



Synthesis of C14-MQBT

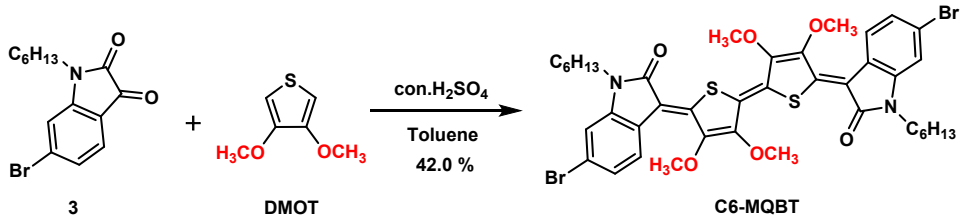
1 (500 mg, 0.75 mmol, 1.0 equiv.) and 3,4-dimethoxythiophene (220 mg, 1.52 mmol, 2.03 equiv.) were dissolved and stirred in toluene (15.0 mL) at room temperature, to which was slowly added concentrated sulfuric acid (0.6 mL). After the mixture was stirred for 2 h at room temperature, the reaction was quenched by pouring into water (30 mL), extracted by DCM (3×30 mL) and dried by Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (PE/DCM from 1/8 to 1/10 (v/v)) to afford a bluish green solid (510 mg, yield: 42.5 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.91 (s, 2H), 4.22 (s, 6H), 3.85 (s, 6H), 3.71 (t, *J* = 7.7 Hz, 4H), 1.71−1.60 (m, 4H), 1.31−1.22 (m, 116H), 0.89−0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.60, 153.29, 148.45, 143.09, 142.23, 128.70, 125.88, 123.96, 120.75, 111.58, 110.88, 61.00, 60.47, 40.35, 37.25, 33.60, 31.93, 30.85, 30.14, 29.72, 29.67, 29.37, 26.74, 24.94, 22.69, 14.11. HR-MALDI-TOF calcd. for $C_{92}H_{149}Br_2F_2N_2O_6S_2$ $[M+H]^+$: 1599.9225; found: 1599.9206.



Synthesis of C14-2FMQBT

2 (500 mg, 0.72 mmol, 1.0 equiv.) and 3,4-dimethoxythiophene (210 mg, 1.46 mmol, 2.03 equiv.) were dissolved and stirred in toluene (14.4 mL) at room temperature, to which was slowly added concentrated sulfuric acid (0.57 mL). After the mixture was stirred for 2 h at room temperature, the reaction was quenched by pouring into water (30 mL), extracted by DCM (3 × 30 mL) and dried by Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (PE/DCM from 1/8 to 1/10 (v/v)) to afford a bluish green solid (486 mg, yield: 41.2 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.11 (t, *J* = 8.5 Hz, 2H), 4.24 (s, 6H), 3.90 (t, *J* = 7.7 Hz, 4H), 3.83 (s, 6H), 1.62−1.60 (m, 4H), 1.31−1.22 (m, 116H), 0.89−0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.39, 153.85, 148.28, 145.10−142.69 (t, $J_{F\text{-}C}{}^{1}$ = 243.0 Hz),

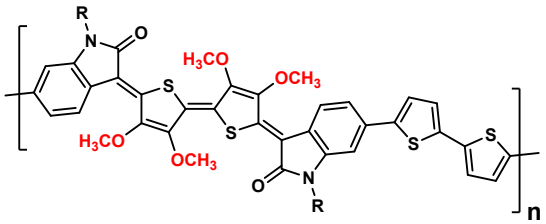
129.26, 128.90−128.80 (d, $J_{F\text{-}C^3}$ = 9.6 Hz), 124.86, 123.94−123.91 (d, $J_{F\text{-}C^4}$ = 3.4 Hz), 121.31, 111.58−111.55 (d, $J_{F\text{-}C^4}$ = 3.5 Hz), 108.51−108.32 (d, $J_{F\text{-}C^2}$ = 19.4 Hz), 63.61, 61.13, 60.53, 42.49, 37.26, 33.61, 31.93, 30.59, 30.14, 29.72, 29.67, 29.37, 26.71, 26.68, 22.69, 14.10. HR-MALDI-TOF calcd. for $C_{92}H_{147}Br_2F_2N_2O_6S_2$ $[M+H]^+$: 1635.9036; found: 1635.9012.



Synthesis of C6-MQBT

3 (600 mg, 1.93 mmol, 1.0 equiv.) and 3,4-dimethoxythiophene (565 mg, 3.92 mmol, 2.03 equiv.) were dissolved and stirred in toluene (35 mL) at room temperature, to which was slowly added concentrated sulfuric acid (3.1 mL). After the mixture was stirred for 2 h at room temperature, the reaction was quenched by pouring into water (40 mL), extracted by DCM (3 × 40 mL) and dried by Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (PE/DCM from 1/3 to 1/5 (v/v)) to afford a bluish green solid (706 mg, yield: 42.0 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.85 (s, 2H), 4.22 (s, 6H), 3.87 (s, 6H), 3.69 (t, *J* = 7.6 Hz, 4H), 1.69−1.61 (m, 4H), 1.39−1.30 (m, 12H), 0.91−0.88 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.74, 153.48, 148.49, 143.18, 142.36, 128.80, 125.97, 124.09, 120.85, 111.66, 110.92, 61.07, 60.47, 40.08, 31.54, 27.84, 26.71, 22.56, 14.03. HR-MALDI-TOF calcd. for $C_{40}H_{45}Br_2F_2N_2O_6S_2$ $[M+H]^+$: 871.1087; found: 871.1086.

General Procedures for Stille Polymerization and Polymer Purification.

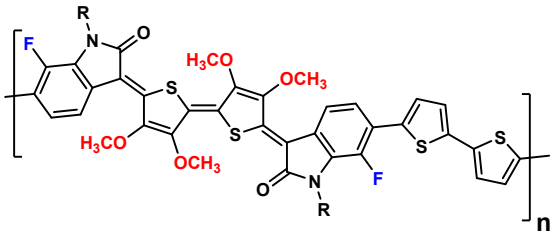


PMQBT-BT

Synthesis of PMQBT-BT

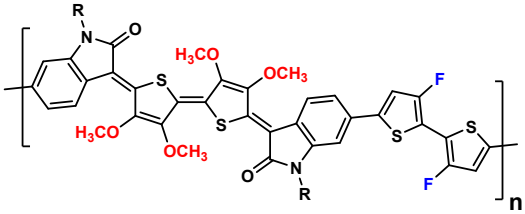
C14-MQBT (100 mg, 0.0625 mmol, 1.0 equiv.), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (31 mg, 0.0625 mmol, 1.0 equiv.), P(*o*-tol)$_3$ (4.6 mg, 0.015 mmol, 0.24 equiv.) and $Pd_2(dba)_3$ (1.8 mg, 0.00187 mmol, 0.03 equiv.) were added to an oven-dried Schlenk tube. Toluene (4 mL) was injected in one portion through syringe under N_2 protection. This tube was charged with N_2 through a freeze-pump-thaw cycle for three times. The solution was heated at 110 °C and stirred for 3 days. The reaction mixture was cooled down to room temperature and poured into methanol (100 mL) containing hydrochloric acid (5 mL). After

stirring for 3 h, the precipitates were collected by filtration and subject to consecutive Soxhlet extraction with methanol (10 h), acetone (10 h), hexane (10 h), and was finally collected with chloroform (10 h). The chloroform fraction was concentrated by evaporation, precipitated into methanol (100 mL) and filtered off to afford the target polymer (82 mg, 79.1%). HT-GPC: M_n = 13.9 kDa; $Đ_M$ = 2.07. Elemental Anal. calcd. for $C_{100}H_{154}N_2O_6S_4$: C 74.67, H 9.65, N 1.74. Found C 73.73, H 9.37, N 1.83.



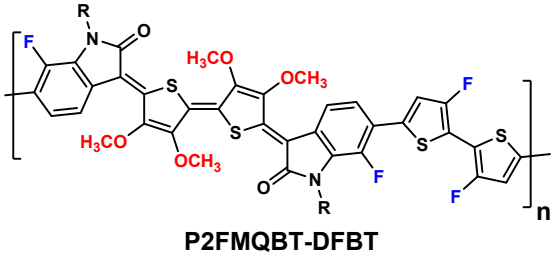
P2FMQBT-BT

P2FMQBT-BT. Synthetic procedure is similar as described for **PMQBT-BT** (chlorobenzene fraction: 80 mg, yield 79.6 %). HT-GPC: M_n = 55.9 kDa; $Đ_M$ = 1.35. Elemental Anal. calcd for $C_{100}H_{152}F_2N_2O_6S_4$: C 73.03, H 9.32, N 1.70, Found C 72.11, H 9.07, N 1.78.



PMQBT-DFBT

PMQBT-DFBT. Synthetic procedure is similar as described for **PMQBT-BT** (chlorobenzene fraction: 46 mg, 44.8 %). HT-GPC: M_n = 172.7 kDa; $Đ_M$ = 1.59. Elemental Anal. calcd for $C_{100}H_{152}F_2N_2O_6S_4$: C 73.03, H 9.32, N 1.70; Found C 72.52, H 9.29, N 1.74.



P2FMQBT-DFBT

P2FMQBT-DFBT. Synthetic procedure is similar as described for **PMQBT-BT** (chlorobenzene fraction: 60 mg, 58.4 %). HT-GPC: M_n = 100.8 kDa; $Đ_M$ = 1.98. Elemental Anal. calcd for $C_{100}H_{150}F_4N_2O_6S_4$: C 71.47, H 9.00, N 1.67, Found C 71.29, H 8.97, N 1.73.

2. Thin layer chromatography analysis results

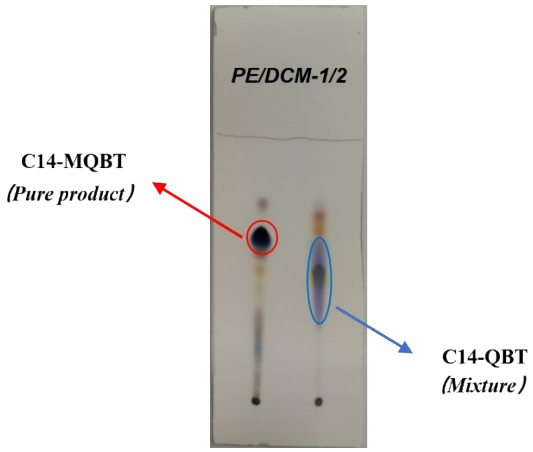


Figure S1. Thin layer chromatography (TLC) analysis of **C14-MQBT** and **C14-QBT** after stirred at room temperature for 4 hours by catalytic amount of concentrated sulphuric acid.

3. GPC curves of the four polymers

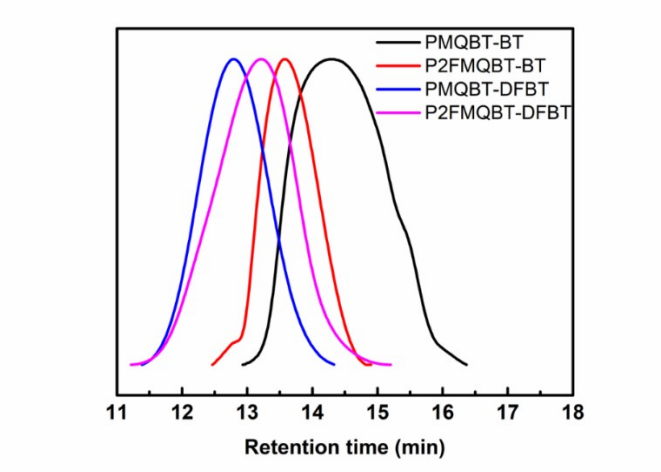


Figure S2. Overlay of GPC curves of four polymers.

4. Thermal analysis of four polymers

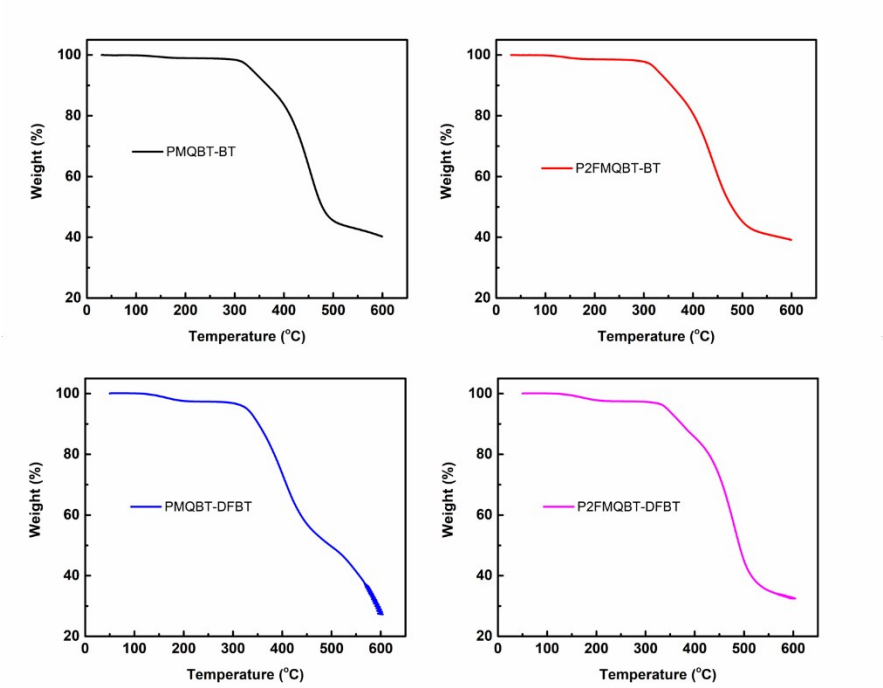


Figure S3. TGA curves of **PMQBT-BT** (black), **P2FMQBT-BT** (red), **PMQBT-DFBT** (blue), **P2FMQBT-DFBT** (magenta).

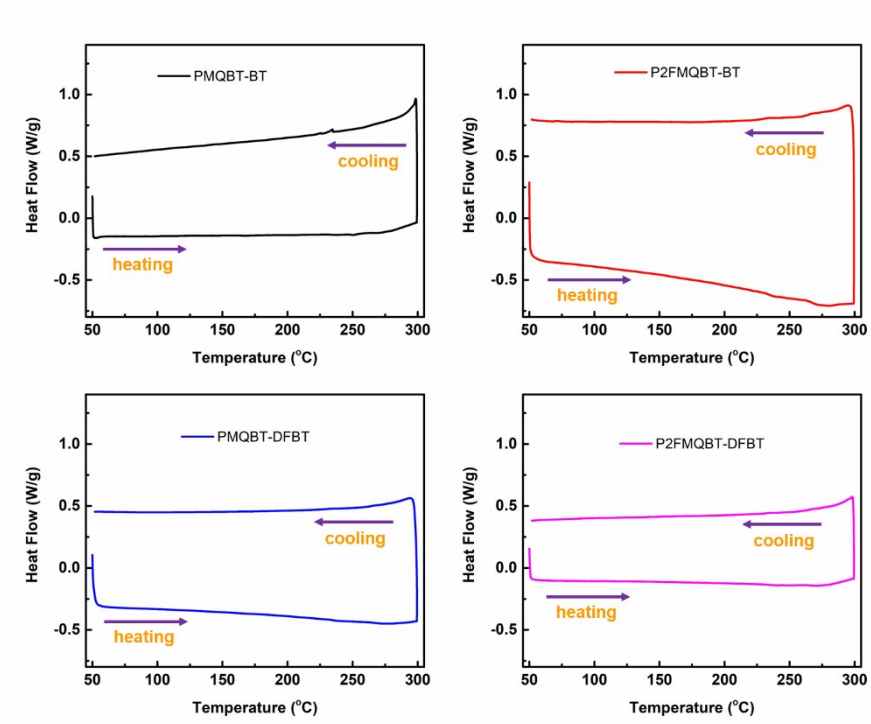


Figure S4. DSC curves of **PMQBT-BT** (black), **P2FMQBT-BT** (red), **PMQBT-DFBT** (blue), **P2FMQBT-DFBT** (magenta).

5. Density functional theory calculations results

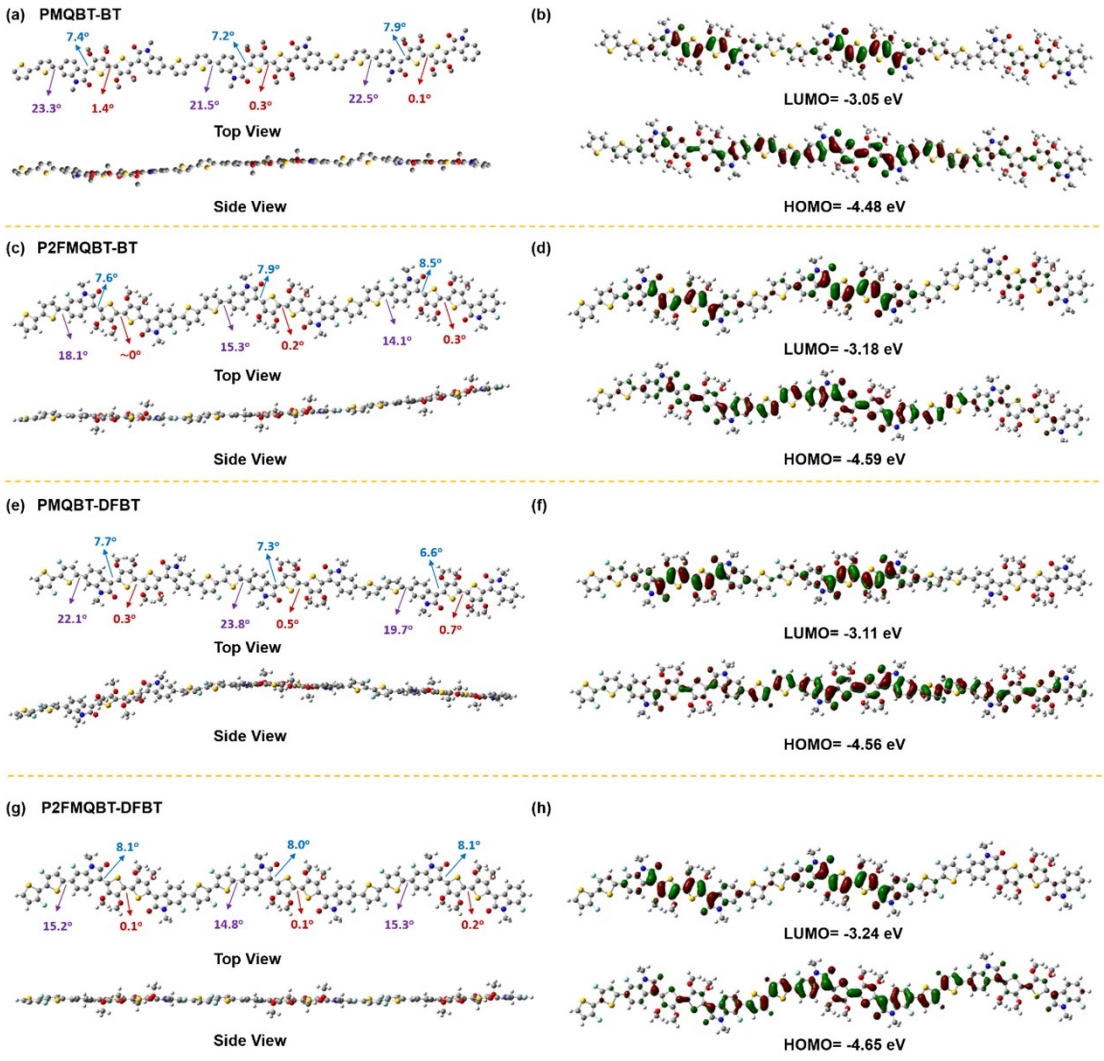


Figure S5. DFT optimized geometries and complete FMO modeling for model structures (a, b) **PMQBT-BT**, (c, d) **P2FMQBT-BT**, (e, f) **PMQBT-DFBT**, and (g, h) **P2FMQBT-DFBT** trimers at B3LYP/6–31G(d) level, respectively.

6. OFET performances of the four copolymers

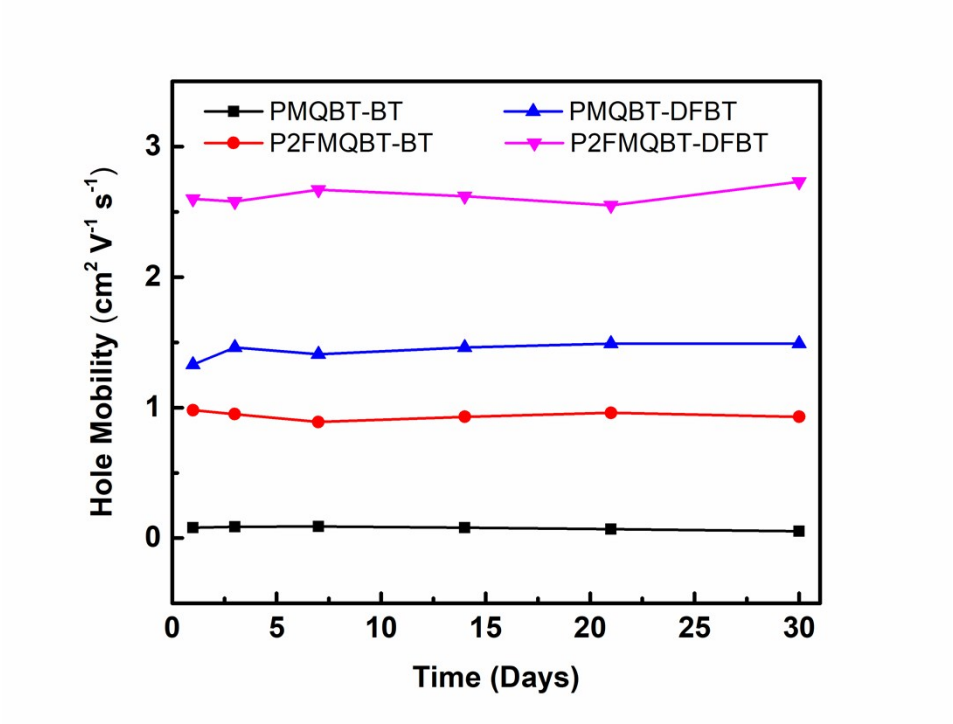


Figure S6. The hole mobility as a function of time for devices stored for 30 days in air under ambient conditions.

7. X-ray crystallographic analysis of C6-MQBT

Table S1. X-ray Crystallographic Data of **C6-MQBT**.

Compound	**C6-MQBT**
Empirical formula	$C_{30}H_{22}BrNO_3S$
Formula weight	556.45
Temperature/K	169.99(14)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.6100(4)
b/Å	4.47950(10)
c/Å	33.0164(7)
α/°	90
β/°	104.647(2)
γ/°	90
Volume/Å^3	2519.83(10)
Z	4
ρ_{calc}g/cm^3	1.467
μ/mm^{-1}	3.265
F(000)	1136
Crystal size/mm^3	0.15 × 0.012 × 0.011
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.186 to 151.402
Index ranges	$-22 \le h \le 21$, $-5 \le k \le 5$, $-40 \le l \le 37$
Reflections collected	15700
Independent reflections	5040 [R_{int} = 0.0421, R_{sigma} = 0.0404]
Data/restraints/parameters	5040/0/238
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.1201
Final R indexes [all data]	R_1 = 0.0584, wR_2 = 0.1295
Largest diff. peak/hole / e Å^{-3}	1.03/–0.69

8. ^{1}H and ^{13}C NMR spectra

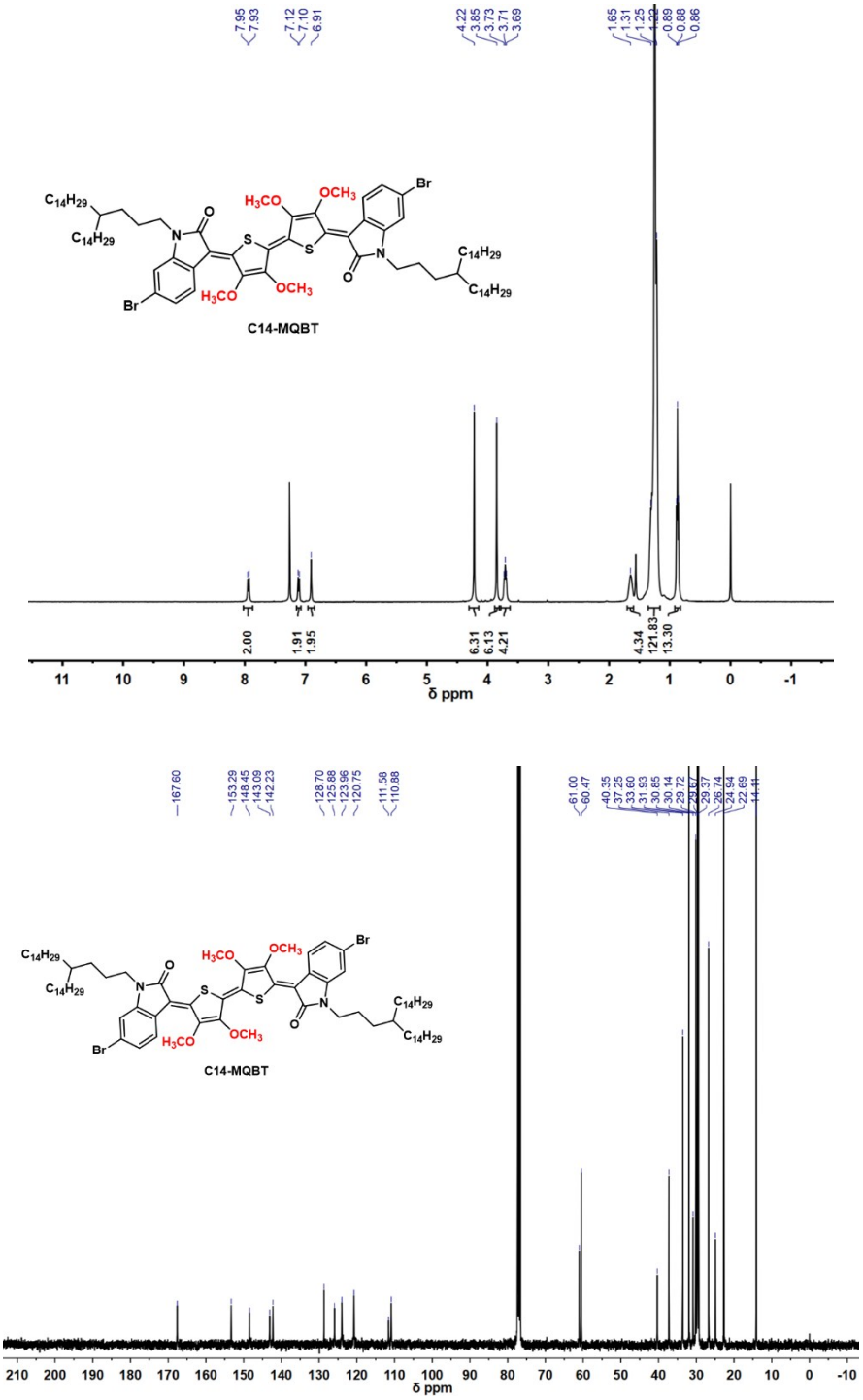


Figure S7. ^{1}H and ^{13}C NMR spectra of **C14-MQBT** in $CDCl_3$ (400 MHz).

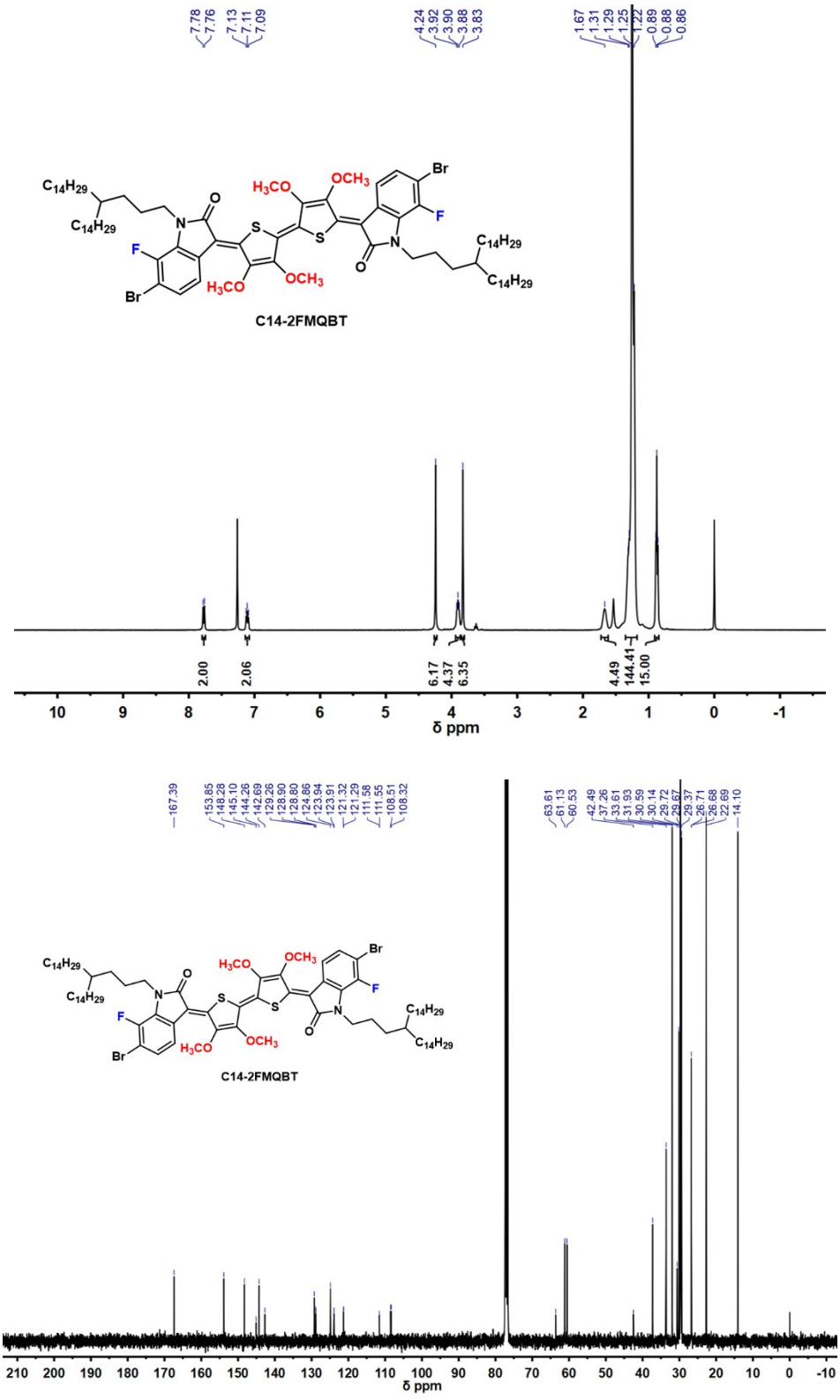


Figure S8. ^{1}H and ^{13}C NMR spectra of **C14-2FMQBT** in $CDCl_3$ (400 MHz).

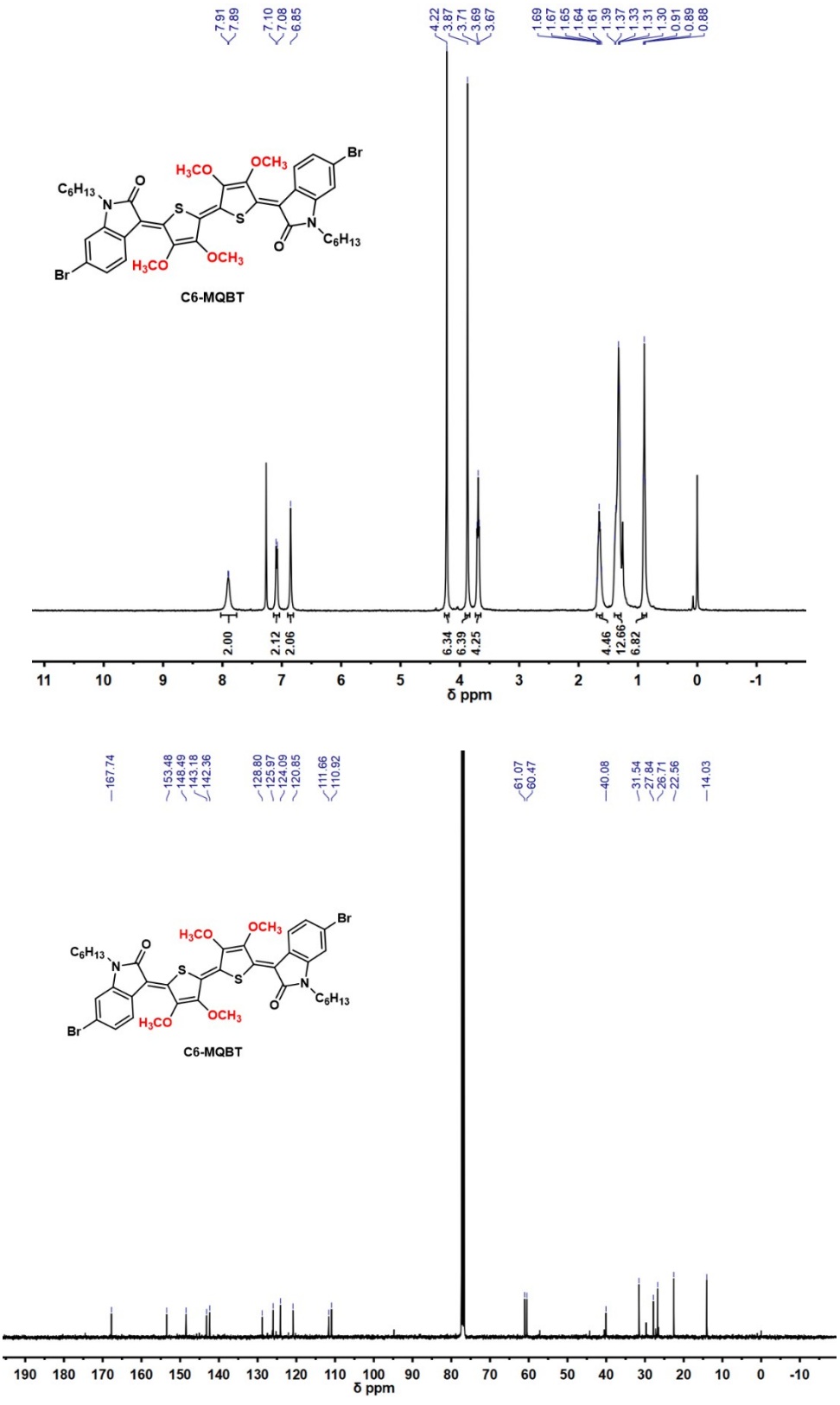


Figure S9. ^{1}H and ^{13}C NMR spectra of **C6-MQBT** in $CDCl_3$ (400 MHz).

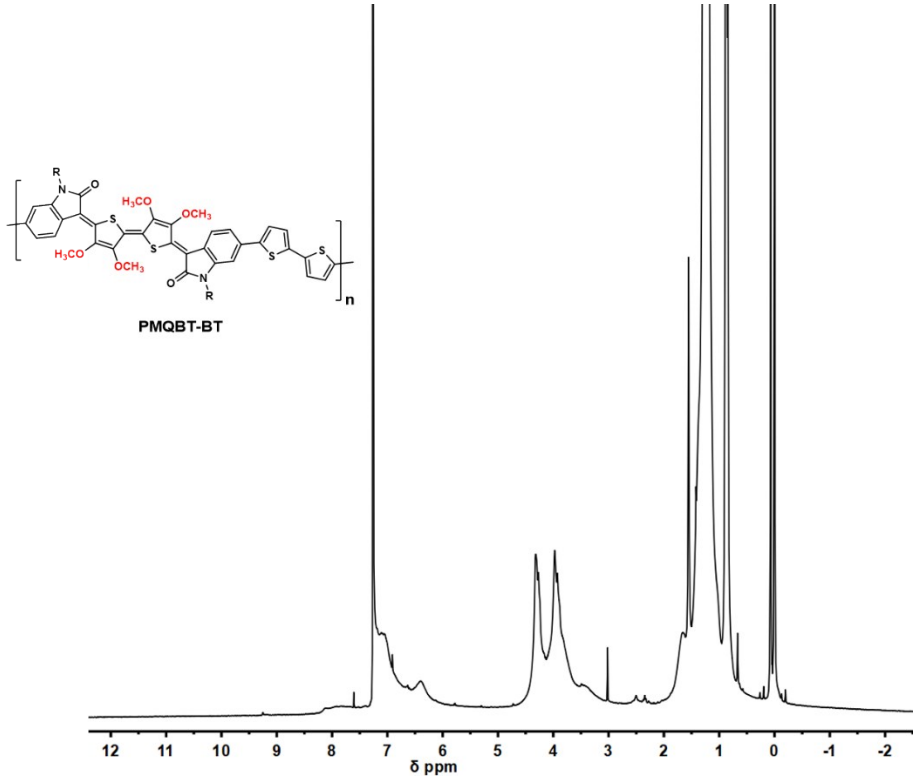


Figure S10. ^{1}H spectrum of **PMQBT-BT** in $CDCl_3$ (300 MHz).

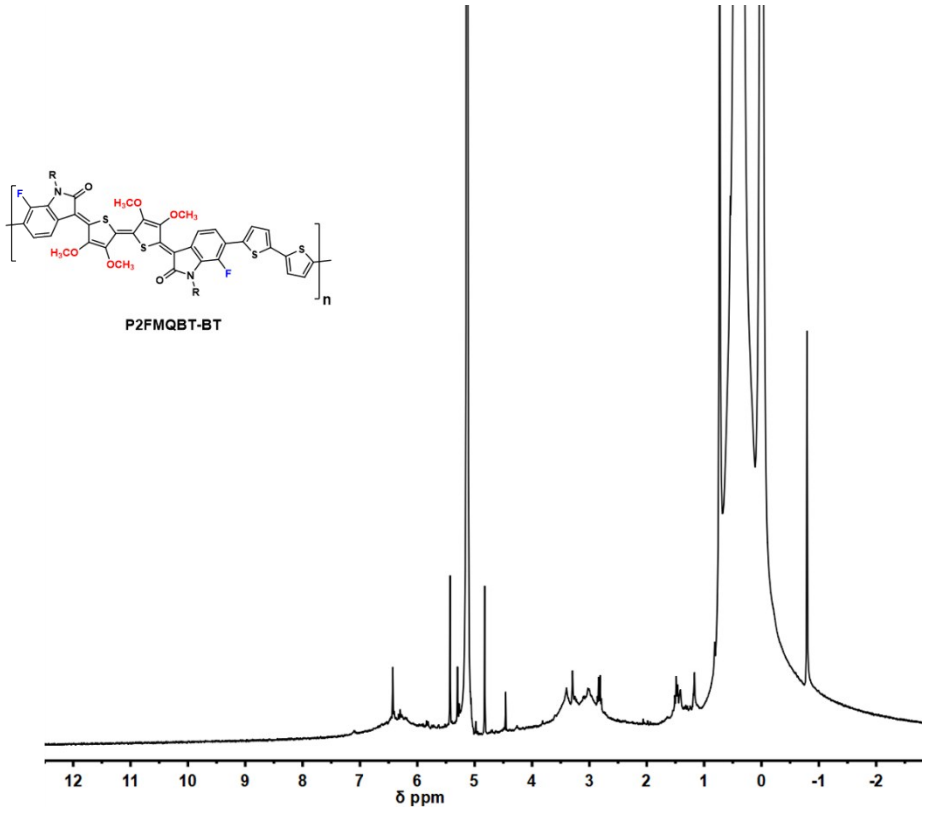


Figure S11. ^{1}H spectrum of **P2FMQBT-BT** in 1,1,2,2-tetrachloroethane-d_2 (300 MHz).

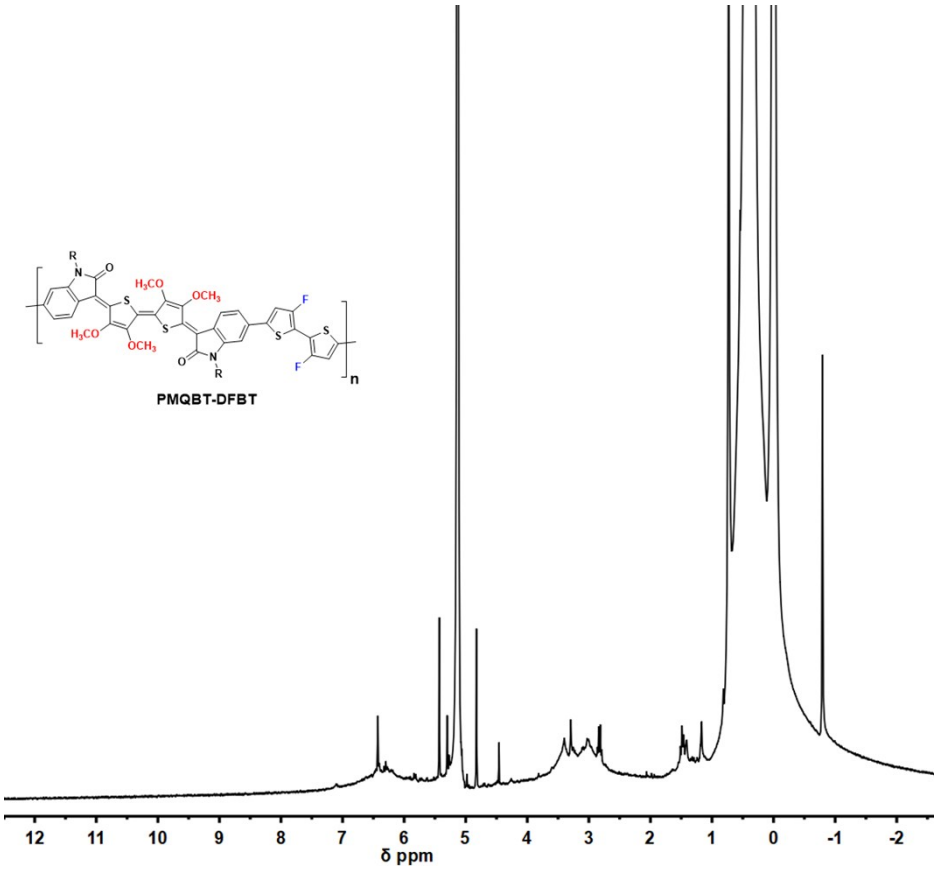


Figure S12. ^{1}H spectrum of **PMQBT-DFBT** in 1,1,2,2-tetrachloroethane-d_2 (300 MHz).

We failed to obtain ^{1}H spectrum of **P2FMQBT-DFBT** on account of low solubility in 1,1,2,2-tetrachloroethane-d_2 at 90 ^{o}C.

References:

1. T. Lei, X. Xia, J. Y. Wang, C. J. Liu and J. Pei, *J. Am. Chem. Soc.*, 2014, **136**, 2135−2141.

2. Y. Deng, B. Sun, Y. He, J. Quinn, C. Guo and Y. Li, *Angew. Chem. Int. Ed. Engl.*, 2016, **55**, 3459−3462.