Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Highly planar cross-conjugated alternating polymers with multiple conformational locks: synthesis, characterization and their field-effect properties

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1. Thermal properties of the polymers PDTO-C1 and PDTO-C3

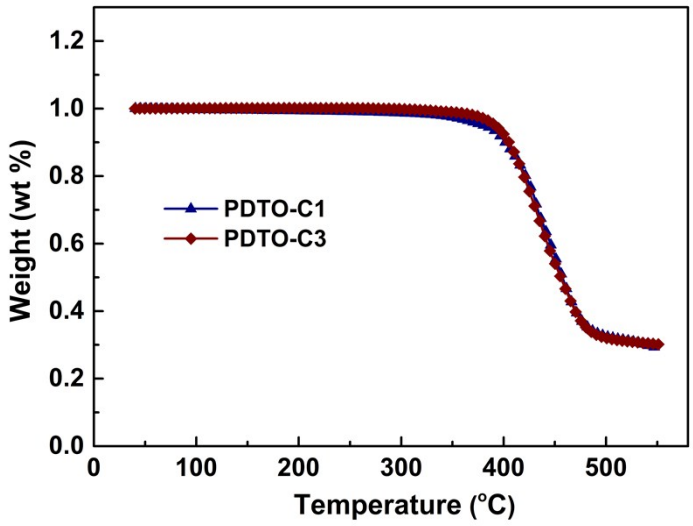


Fig. S1 TGA curves of the polymers PDTO-C1 and PDTO-C3.

2. The electrochemical properties of the polymers PDTO-C1 and PDTO-C3.

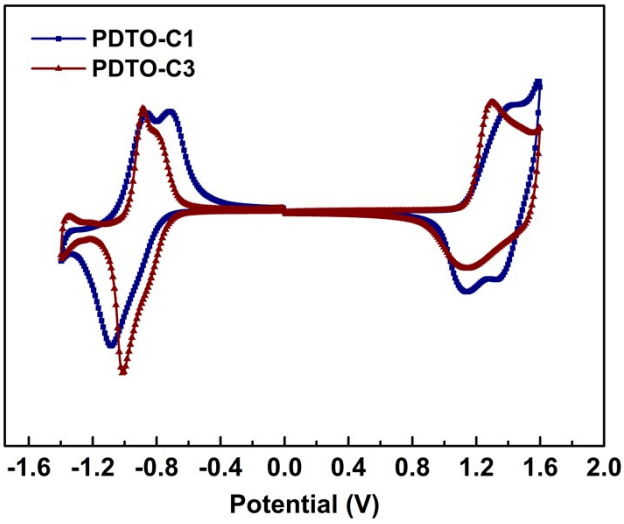


Fig. S2 CV traces of the polymers PDTO-C1 and PDTO-C3.

3. Typical transfer and output characteristics of the OFETs based on PDTO-C1.

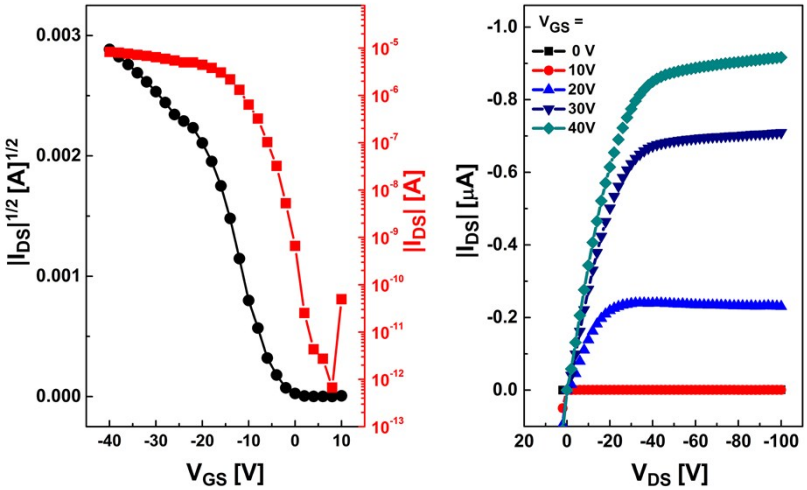
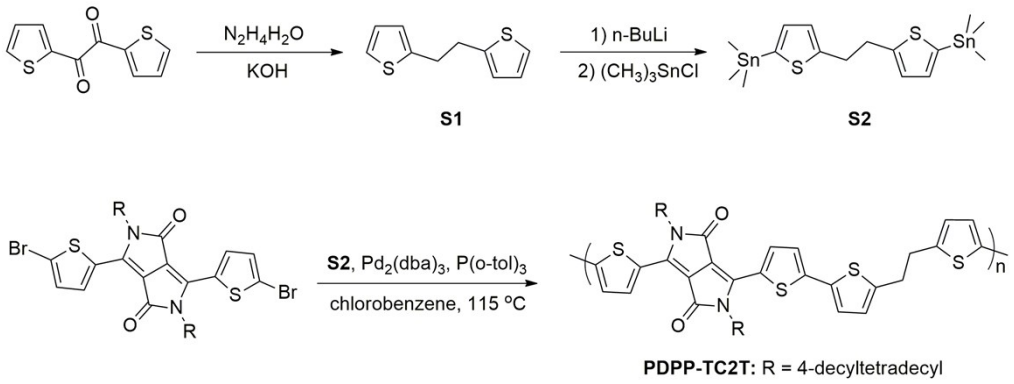


Fig. S3. The typical transfer and output characteristics of the OFETs based on PDTO-C1.

4. Synthetic procedures of PDPP-TC2T and PDPP-DTE.

For obtaining better comparisons, PDPP-TC2T sample was also synthesized according to reported methods (Scheme S1).[1] The PDPP-DTE sample was

synthesized based on previous literature.[2]



Scheme S1 Synthetic routes of alternating polymers PDTO-TC2T.

1,2-di(thiophen-2-yl)ethane (**S1**): An established method was adopted using 1,2-di(thiophen-2-yl)ethane-1,2-dione (1.00 g), 85% hydrazine hydrate (1.3 mL), KOH (1.8 g), and ethylene glycol (15 mL) to give the title compound as a colorless crystal (340 mg, 39 %). ^{1}H NMR (300 MHz, CD_2Cl_2): 7.16 (dd, J = 5.1 Hz, J = 0.9 Hz, 2H), 6.84 (dd, J = 5.1 Hz, J = 3.3 Hz, 2H), 6.73 (d, J = 3.0 Hz, 2H), 3.10 (s, 4H). HRMS: Calcd. for $[C_{10}H_{10}S_2]^+$: 194.0224; Found: 194.0221.

1,2-bis((5-trimethylstannyl)thiophen-2-yl)ethane (**S2**): An established method was adopted using S1 (300 mg, 1.54 mmol), 2.5 M n-BuLi in hexanes (1.8 mL, 4.6 mmol), 1.0 M trimethyltin chloride in hexanes (4.8 mL, 4.8mmol), and anhydrous tetrahydrofuran (15 mL) affording the title compound as a white solid (224 mg, 28 %). ^{1}H NMR (300 MHz, CD_2Cl_2): 6.93 (d, J = 3.3 Hz, 2H), 6.85 (d, J = 3.3 Hz, 2H), 3.13 (s, 4H), 0.25 (s, 18H). HRMS: Calcd. for $[C_{16}H_{26}S_2Sn_2]^+$: 519.9514; Found: 519.9518.

PDPP-TC2T. An established method was adopted using S2 (0.2 mmol), dibromo-DPPs (0.2 mmol), $Pd_2(dba)_3$ (6 mg) and P(*o*-tol)$_3$ (17 mg) and chlorobenzene (5.0 mL)

to afford the desired polymer martial (193 mg, 84 %). GPC: M_n = 14.3 kDa, M_w = 40.0 kDa, PDI = 2.34. Elemental Anal. Calcd. for $C_{72}H_{112}N_2O_4S_4$: C, 74.17; H, 9.68; N, 2.40; Found: C 72.79, H 9.19, N 2.52.

1. X. K. Zhao, Y. Zhao, Q. Ge, K. Butrouna, Y. Diao, K. R. Graham and J. G. Mei, *Macromolecules*, 2016, **49**, 2601−2608.

2. H. J. Chen, Y. L. Guo, G. Yu, Y. Zhao, J. Zhang, D. Gao, H. T. Liu and Y. Q. Liu, *Adv. Mater.*, 2012, **24**, 4618−4622.

5. Typical transfer and output characteristics of the OFETs based on PDPP-TC2T and PDPP-DTE.

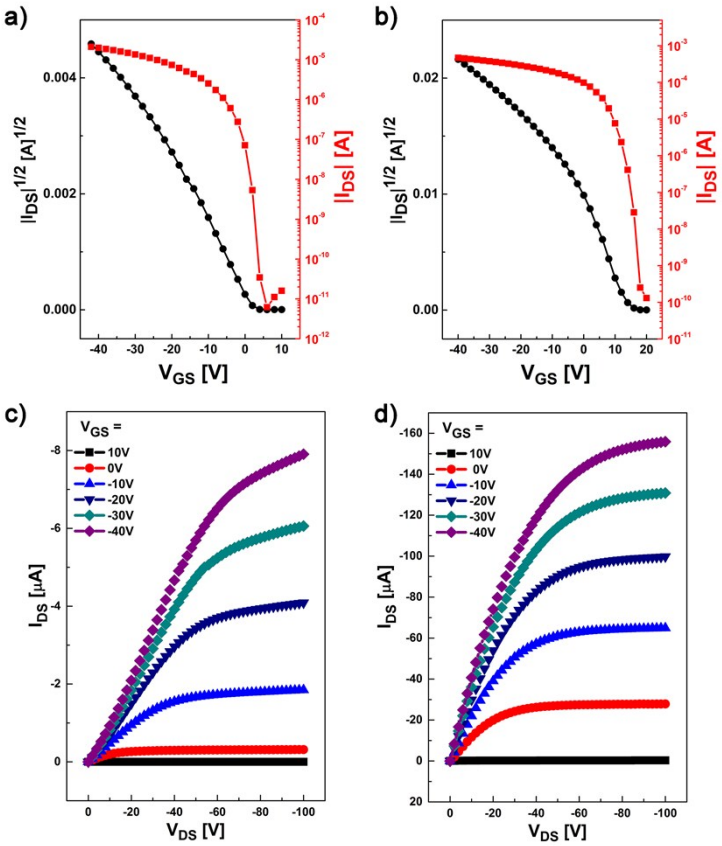


Fig. S4 The typical transfer and output characteristics of the FET devices based on PDPP-TC2T and PDPP-DTE. (a), (c) PDPP-TC2T after annealing at 100 °C; (b), (d) PDPP-DTE after annealing at 180 °C.

6. X-ray crystallographic data

Table S1. Crystal data and structure refinement for dibromo-DTO, **3**.

Identification code	sa3394
Empirical formula	$C_{10}H_4Br_2O_2S_2$
Formula weight	380.07
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 5.7908(6) Å α = 90°
	b = 11.3325(13) Å β = 90°
	c = 17.3880(19) Å γ = 90°
Volume	1141.1(2) $Å^3$
Z	4
Density (calculated)	2.212 mg/m^3
Absorption coefficient	7.448 mm^{-1}
F(000)	728
Crystal size	0.69 × 0.18 × 0.1 mm^3
Theta range for data collection	3.596 to 27.480°
Index ranges	-7<=h<=7, -12<=k<=14, -12<=l<=22
Reflections collected	4648
Independent reflections	2548 [R(int) = 0.0264]
Completeness to theta = 26.000°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.3890
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2548 / 0 / 145
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0571
R indices (all data)	R1 = 0.0297, wR2 = 0.0582
Absolute structure parameter	0.023(9)

Extinction coefficient	n/a
Largest diff. peak and hole	0.319 and −0.555 e.Å^{-3}

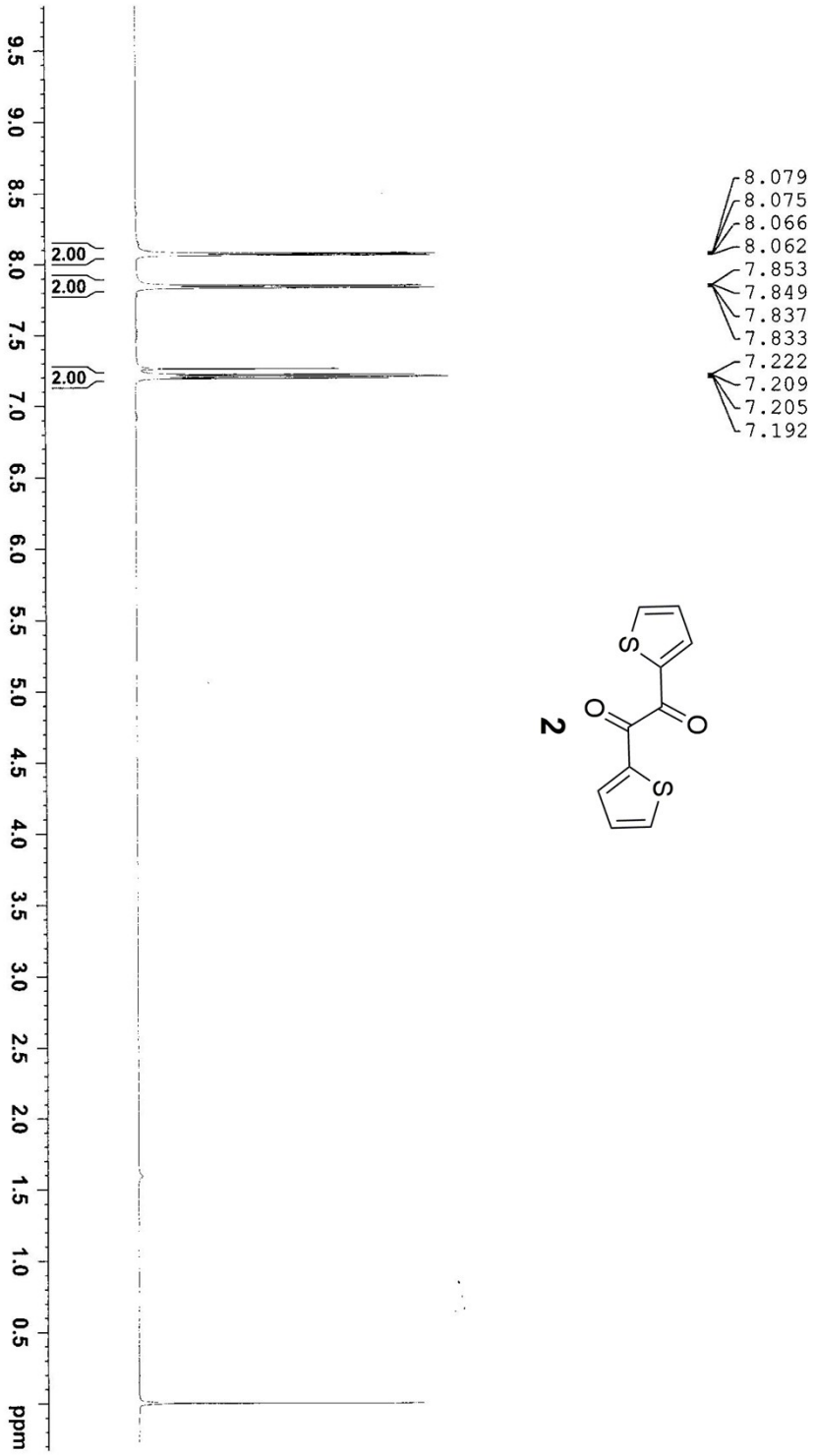
7. The annealing temperature-dependent mobilities of PDTO-C1 and PDTO-C3-based devices.

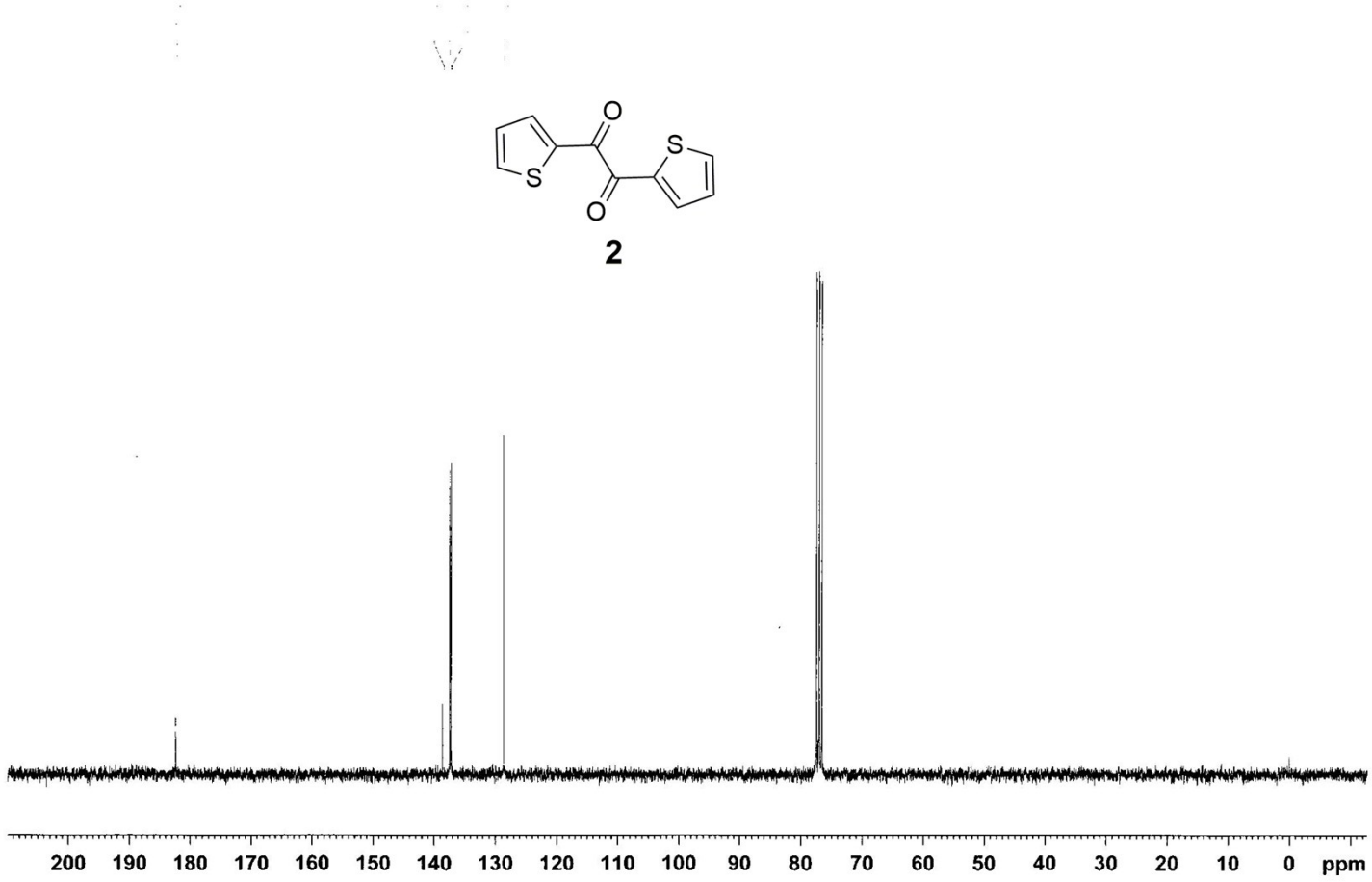
Table S2. The mobilities of PDTO-C1 and PDTO-C3-based FET devices before and after annealed at different temperatures.

Polymer	T_{an}[a]	μ	I_{on}/I_{off}	V_{th}
	°C	cm^2 V^{-1} s^{-1}		V
PDTO-C1	25	0.02[b] (0.028)[c]	>10^4	5~-5
	60	0.05 (0.070)	>10^5	-5~-10
	100	0.08 (0.095)	>10^6	-5~-10
	120	0.11 (0.14)	>10^6	-5~-10
	140	0.18 (0.22)	>10^6	-5~-10
	160	0.13 (0.16)	>10^6	-5~-10
PDTO-C3	25	0.08 (0.10)	>10^4	-5~-10
	60	0.21 (0.24)	>10^5	0~-10
	100	0.28 (0.40)	>10^6	0~-10
	120	0.36 (0.54)	>10^6	0~-10
	140	0.31 (0.43)	>10^6	0~-10

[a]Annealing temperature. [b]Average mobility. [c]The highest mobility.

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

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S
S
O
2
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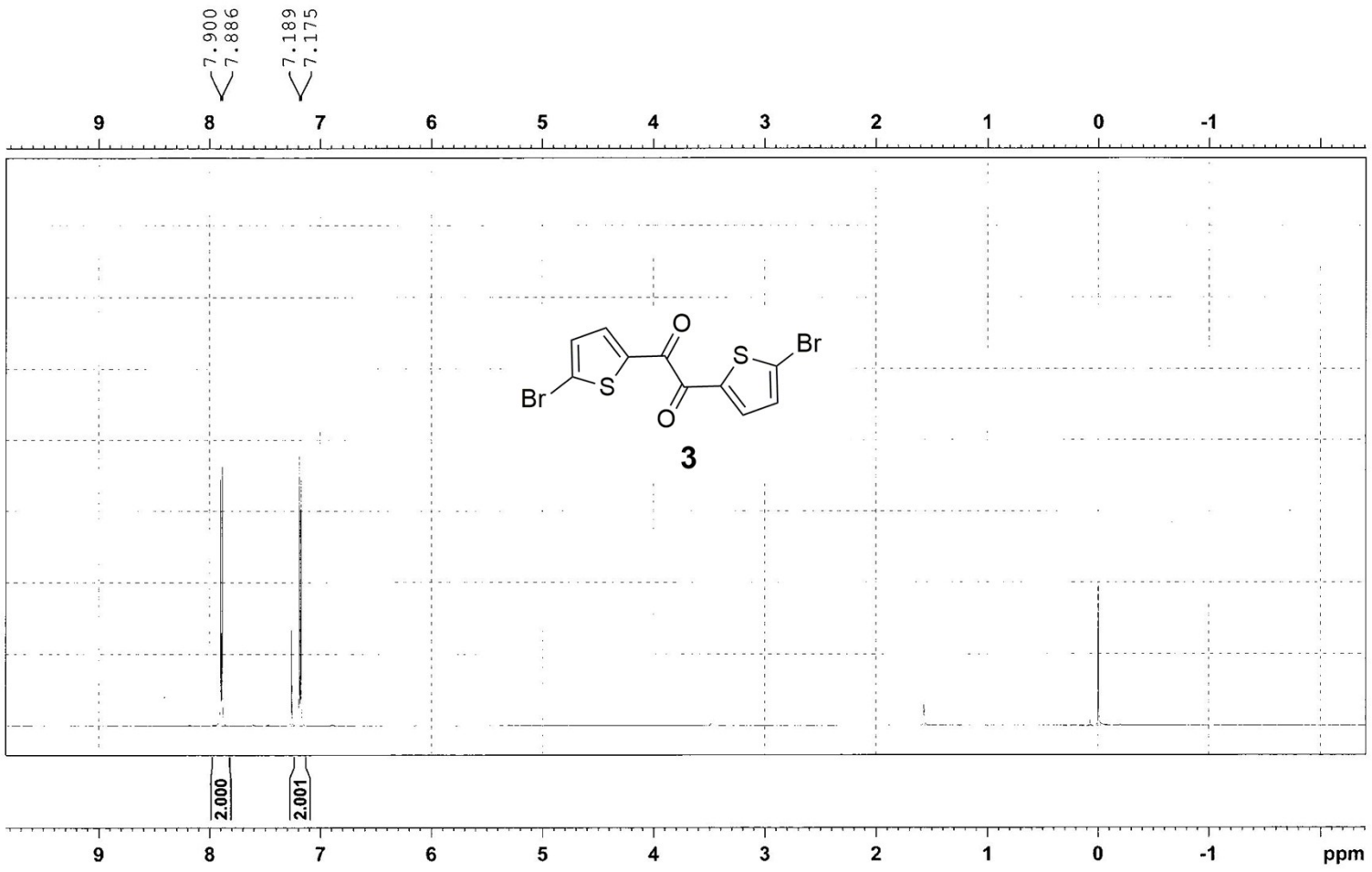
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7.175
9
8
7
6
5
4
3
2
1
0
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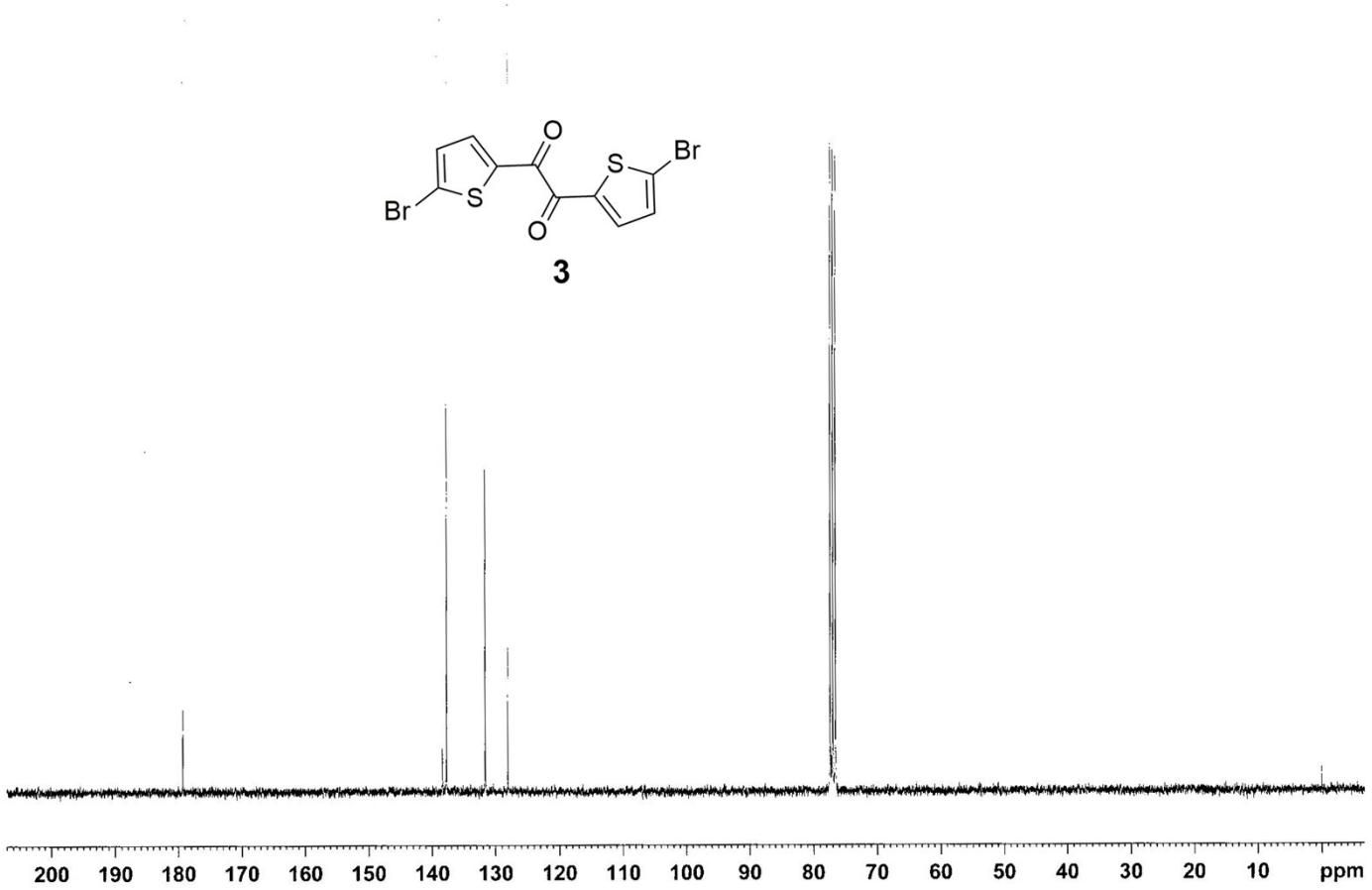
Br
S
O
O
S
Br
3
2.000
2.001
ppm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S
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Br
O
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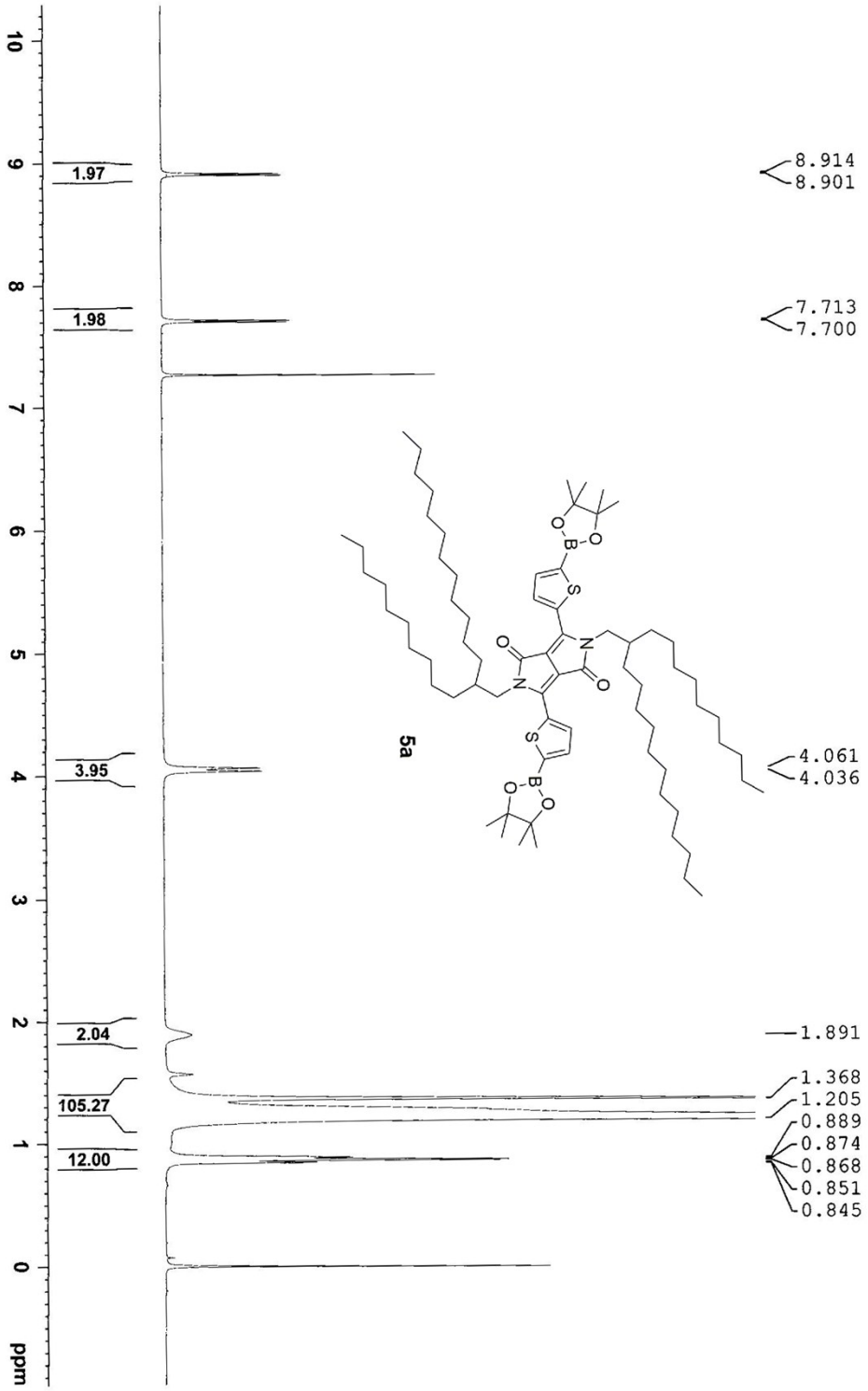
20
10
ppm

3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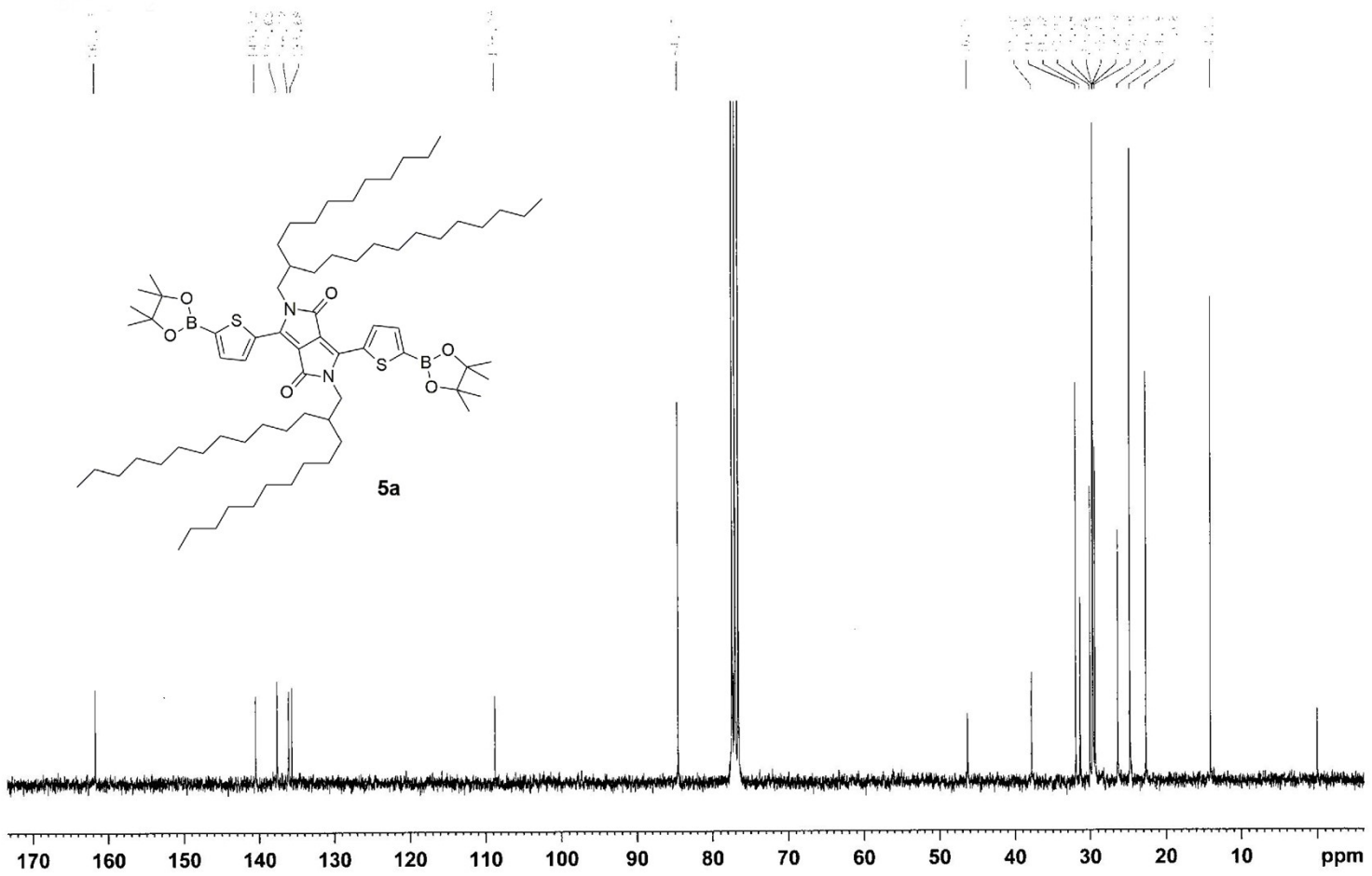
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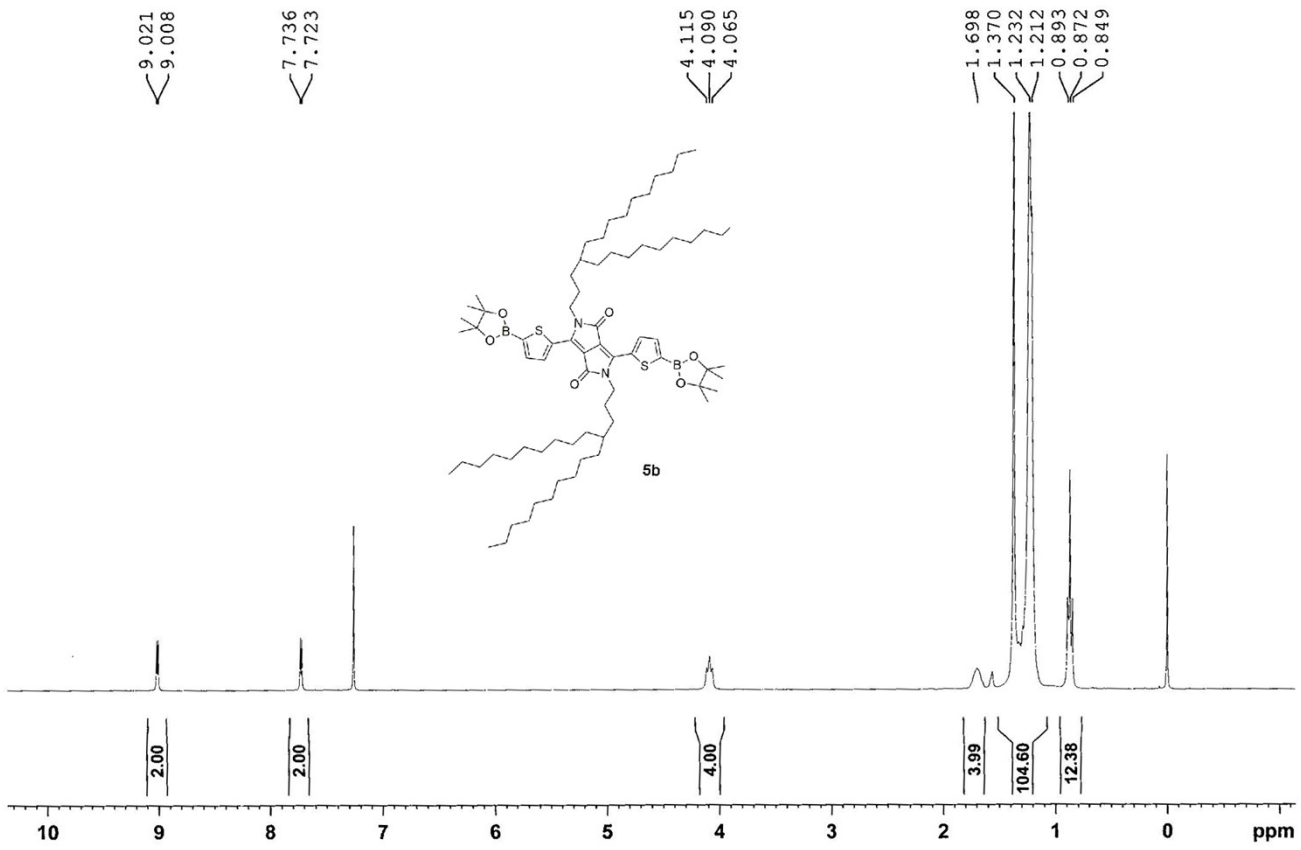
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5b
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2.00
4.00
3.99
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10
9
8
7
6
5
4
3
2
1
0
ppm

DPP-B320