

Supporting Information

High Performance Achieved via Core Engineering and Side-Chain Engineering in Organic Solar Cells Based on Penta-Fused-Ring

Acceptor

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Experimental Section

1. Materials

PM6 and TPBT-CHO was purchased from Derthon. 4,7-Dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole and the terminal unit DPBT-2Cl, 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile, was purchased from Wuxi Seniormaterial, Other drugs used were purchased from Innochem without further purification.

2. Fabrication of OPVs

OPVs were fabricated in the conventional device architecture of ITO/PEDOT:PSS/Active layer/PFN-Br/Al. A 40 nm thin layer of PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron PVP Al 4083) was coated on the pre-cleaned ITO substrates, and baked at 150 °C for 15 min in the air. PM6: DPBT-2Cl was dissolved in chloroform (CF) and spin-cast at 3,000 rpm for 30 s onto the PEDOT: PSS layer, and thermal annealed (TA) at 110 °C for 10 min. The thickness of the photoactive layer is about 100 nm measured by ambios technology XP-2 profilometer. A thin layer of PFN-Br (about 5 nm) was coated onto the active layers from its ethyl alcohol solution (0.5 mg/mL). Subsequently, Al (about 150 nm) was thermally evaporated deposited atop under a shadow mask with a base pressure of ca. 10^{-5} Pa. The active area of 4 mm² was used in the *J-V* measurements.

Table S1 Condition with different ratio of PM6: DPBT-2Cl (D:A), and total of 16 mg/ml, dissolved in CF at 40 °C for 4h, TA at 110 °C for 10min.

D:A	V_{oc} (V)	J_{sc}/EQE (mA/cm ²)	FF (%)	PCE (%)	Thickness (nm)
1:1.0	0.807	21.37	58.6	10.11	
	0.811	21.08/20.56	59.6	10.20	98
	0.805	20.86	58.4	9.80	
1:1.2	0.810	21.70/21.02	59.9	10.52	
	0.807	21.68	60.2	10.54	93
	0.811	21.21	60.0	10.33	
1:1.4	0.805	21.78	54.0	9.47	
	0.805	21.95/21.31	58.1	10.26	101
	0.807	21.63	57.5	10.03	

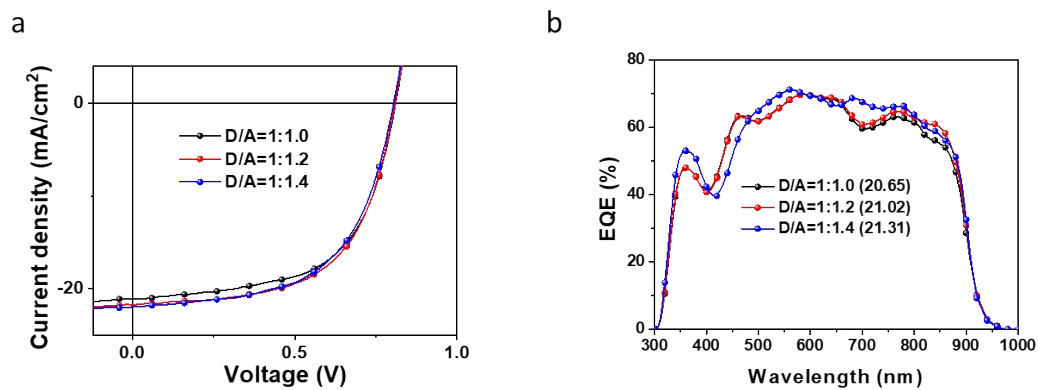


Figure S1 a. J - V and b. EQE curves with different ratio of PM6/ DPBT-2Cl.

Table S2 Condition with different ratio of additive, and PM6: DPBT-2Cl=1:1.2, total of 16 mg/ml, dissolved in CF at 40 °C for 4h, TA at 110 °C for 10 min.

Additive	V_{oc} (V)	J_{sc}/EQE (mA/cm ²)	FF (%)	PCE (%)	Thickness (nm)
0.50% CN	0.774	23.00	62.9	11.21	
	0.778	23.05/22.83	62.8	11.28	97
	0.778	22.22	63.6	11.02	
0.75% CN	0.770	22.78	63.8	11.20	
	0.776	23.08/22.98	64.0	11.49	98
	0.772	22.96	63.7	11.31	
1.00% CN	0.773	23.06	62.4	11.14	
	0.772	22.70/22.24	64.9	11.40	94
	0.769	23.00	62.8	11.13	
0.50% DIO	0.701	9.18	44.7	2.88	
	0.702	9.34/3.41	45.7	3.00	101
	0.701	9.20	44.2	2.86	

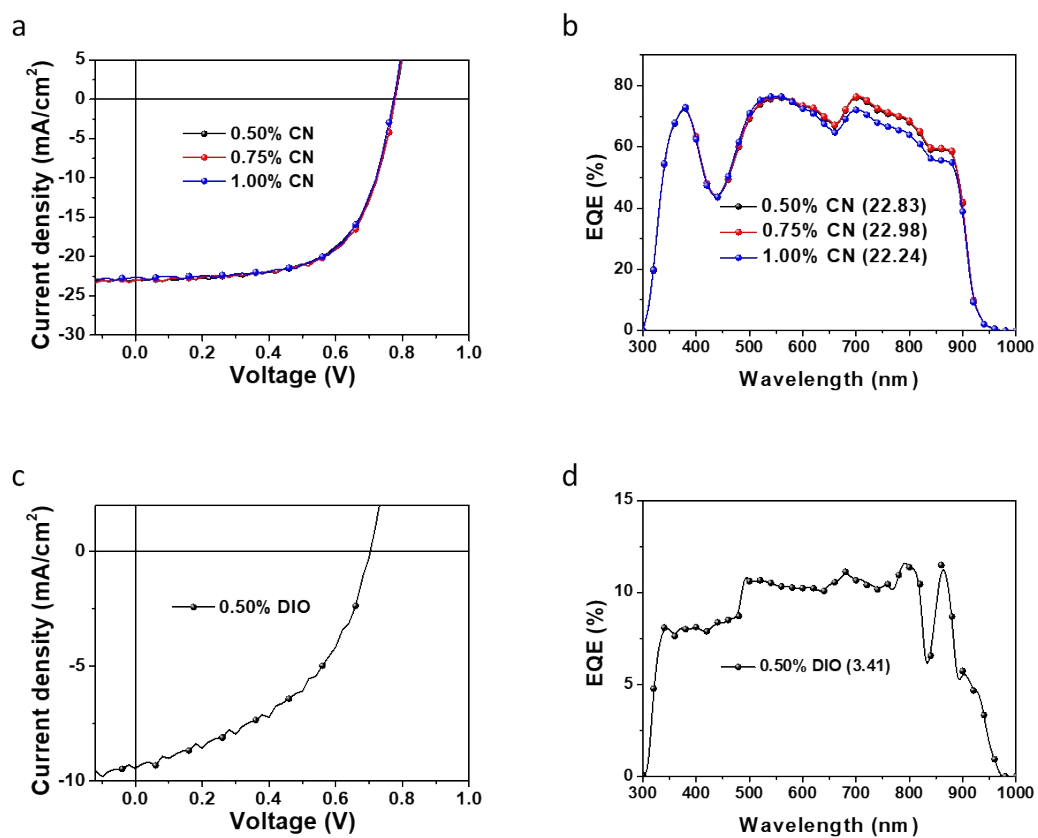


Figure S2 J - V and EQE curves of PM6/ DPBT-2Cl with different additive.

Table S3. TA at 110°C or as-cast, and PM6: DPBT-2Cl = 1:1.2, total of 16 mg/ml, dissolved in CF at 40°C for 4h, with additive CN 0.75 %.

TA/as-cast	V_{oc} (V)	J_{sc}/EQE (mA/cm ²)	FF (%)	PCE (%)	Thickness (nm)
as-cast	0.818	16.81/16.70	60.3	8.27	
	0.817	16.63/15.39	61.2	8.28	95
	0.814	16.46	60.2	8.04	
TA	0.770	22.78	63.8	11.20	
	0.776	23.08/22.98	64.0	11.49	98
	0.772	22.96/22.87	63.7	11.31	

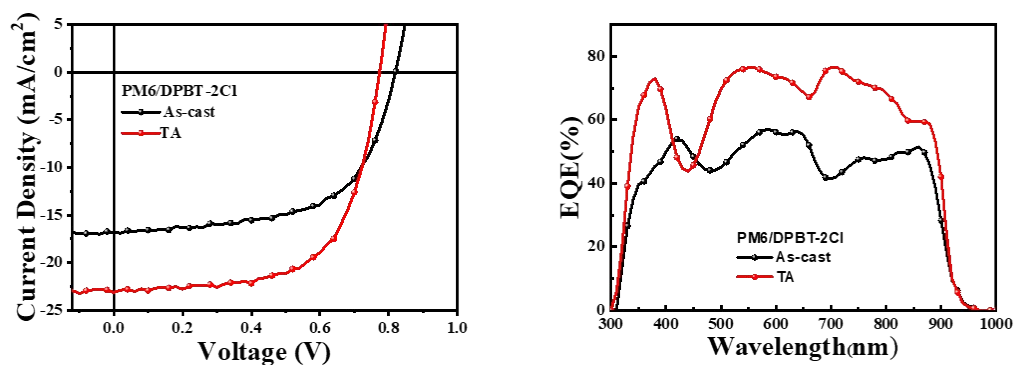


Figure S3 J - V and EQE curves of PM6/ DPBT-2Cl with TA or as-cast.

Table S4 TA at 110°C or as-cast and with or without additive CN, PM6: TPBT-2Cl = 1:1.2, total of 14 mg/ml, dissolved in CF at 40°C for 4h.

D/A	TA (°C)	Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Thickness (nm)
PM6:TPBT-2Cl	As-cast	0	0.74	3.56	36.4	0.95	96
PM6:TPBT-2Cl	110	0	0.68	2.47	0.37	0.70	96
PM6:TPBT-2Cl	As-cast	0.5%	0.69	2.02	47.0	0.65	98
PM6:TPBT-2Cl	110	0.5%	0.68	1.89	0.41	0.52	97

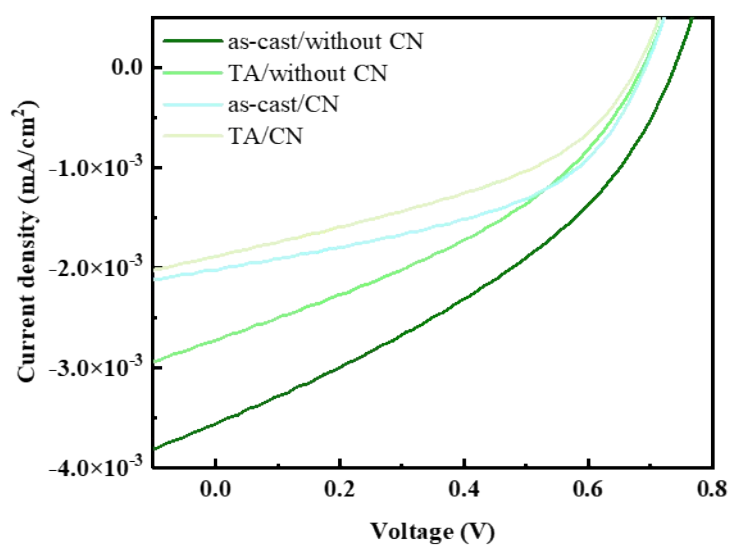


Figure S4 J - V curves of PM6/ TPBT-2Cl with TA/as-cast and with/without CN.

3. Characterization of Materials

Unless otherwise noted, Bruker AV-400 spectrometer was used to record ^1H and ^{13}C NMR spectra in deuterated chloroform solution at 298K. Chemical shifts are reported as δ values (ppm) and tetramethylsilane (TMS) is used as an internal reference. The molecular mass was confirmed by Autoflex III matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOF-MS). The Thermogravimetric analysis (TGA) data were obtained by testing on the TG-209F3 instrument at the National Center for Nanoscience and Technology.

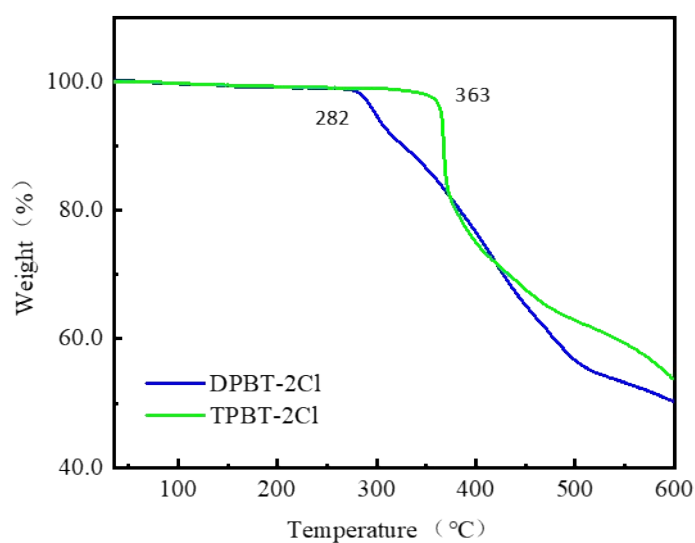


Figure S5. The TGA curves of DPBT-2Cl and TPBT-2Cl.

4. Instruments and Measurements

UV-Vis absorption spectra were recorded on the SHIMADZU UV-1800 spectrophotometer, and the scanning range was set to 350–1000 nm. For the solution measurements, PM6, DPBT-2Cl and TPBT2Cl were dissolved in CHCl_3 . For the solid-state measurements, PM6/DPBT-2Cl and PM6/TPBT-2Cl solutions in chloroform were spin coated on quartz plates to form relevant blend films.

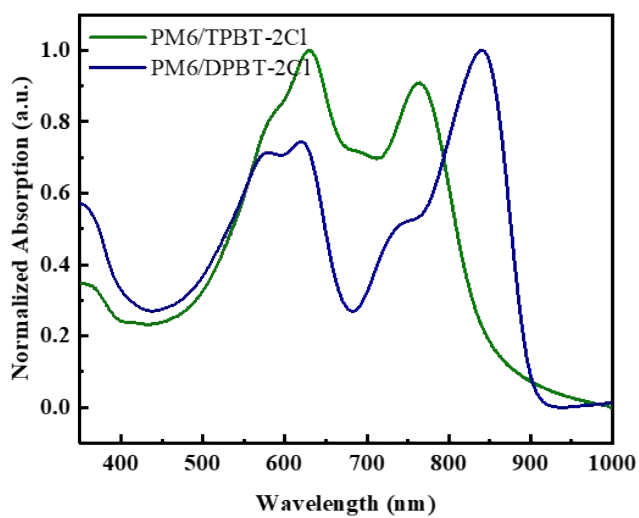


Figure S6 The blend film absorption spectra of PM6/DPBT-2Cl and PM6/TPBT-2Cl.

Cyclic voltammetry results were obtained with a computer-controlled CHI 660E electrochemical workstation using acceptor films on platinum (1.0 mm²) as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous argon saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile, at a scanning rate of 50 mV/s. Electrochemical onsets were determined at the position where the current started to rise from the baseline.

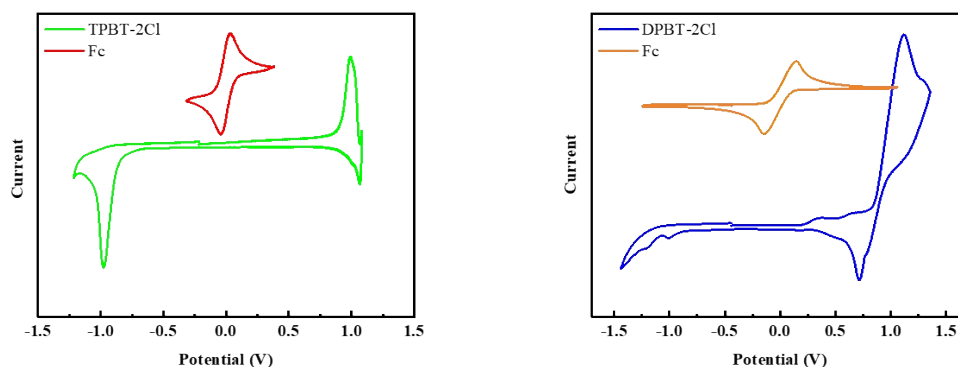


Figure S7. Cyclic voltammetry curves of DPBT-2Cl and TPBT-2Cl based on ferrocene (Fc) correction.

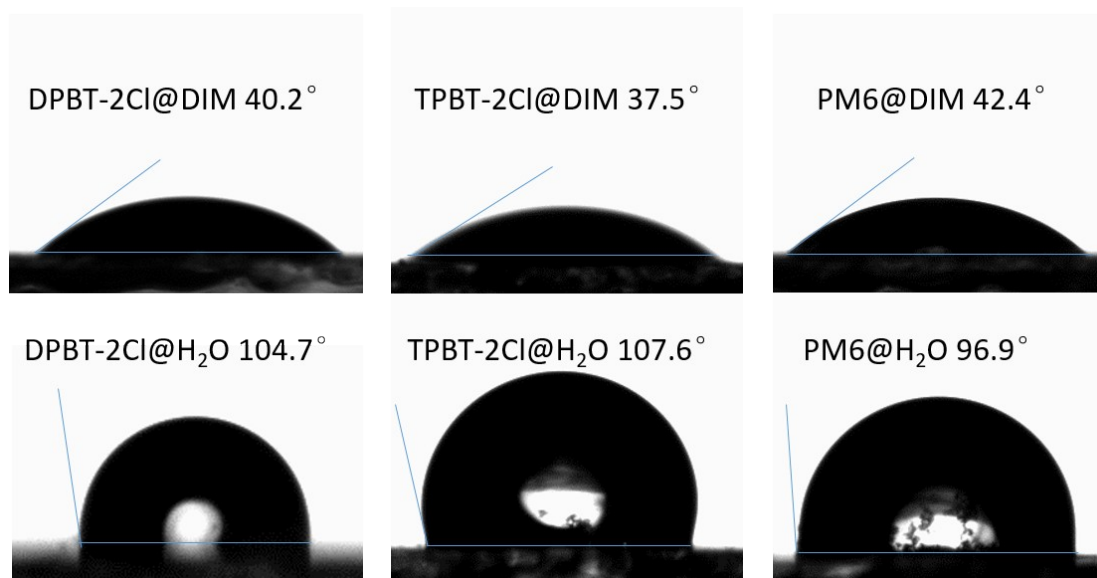


Figure S8. Contact angles of DPBT-2Cl, TPBT-2Cl and PM6 on H₂O and DIM.

Table S5. Surface energy characteristics of PM6, TPBT-2Cl and DPBT-2Cl pristine films.

Materials	$\theta_{\text{CH}_2\text{I}_2}/^\circ$	$\theta_{\text{H}_2\text{O}}/^\circ$	γ/mNm^{-1}	γ^p/mNm^{-1}	γ^d/mNm^{-1}
PM6	42.40	96.90	39.00	0.30	38.70
TPBT-2Cl	37.50	107.60	45.05	0.41	44.64
DPBT-2Cl	40.20	104.70	42.27	0.08	42.19

The J - V measurements were performed on the solar simulator along with AM 1.5G spectra (100 mW/cm²). The EQE measurements were tested on the solar cell spectral response measurement system. AFM (with Nanoscope AFM microscope (Bruker)) and GIWAXS (with XEUSS SAXS/WAXS system (XENOCSS, France)) measurements were performed at Engineering Plastics Laboratory, Institute of Chemistry, Chinese Academy of Sciences (ICCAS, Beijing). The transmission electron microscopy (TEM) were obtained on the field emission transmission electron microscope JEM-F200 at the Beijing Regional Center for Matter and Nanoscience.

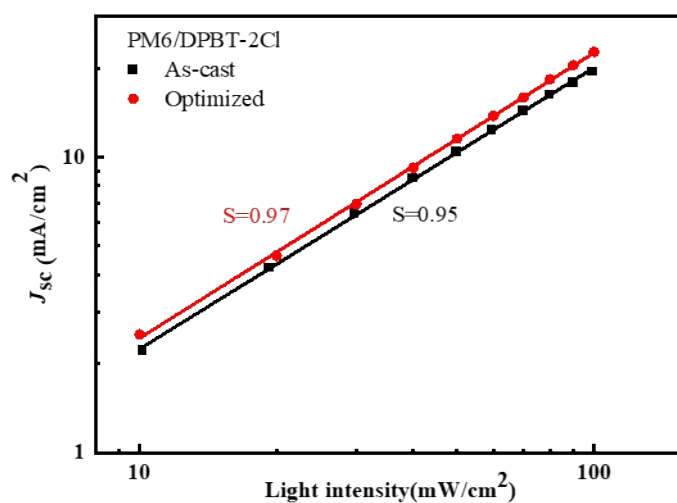


Figure S9. J_{sc} vs light intensity of PM6/DPBT-2Cl based on as-cast or optimized.

Table S6. Mobilities of as-cast and optimized blend films of PM6:P4-IC2Cl.

Conditions	μ_h [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_e [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	μ_h/μ_e
As-cast	3.2×10^{-4}	2.3×10^{-4}	1.39
Optimized	5.9×10^{-4}	5.3×10^{-4}	1.11

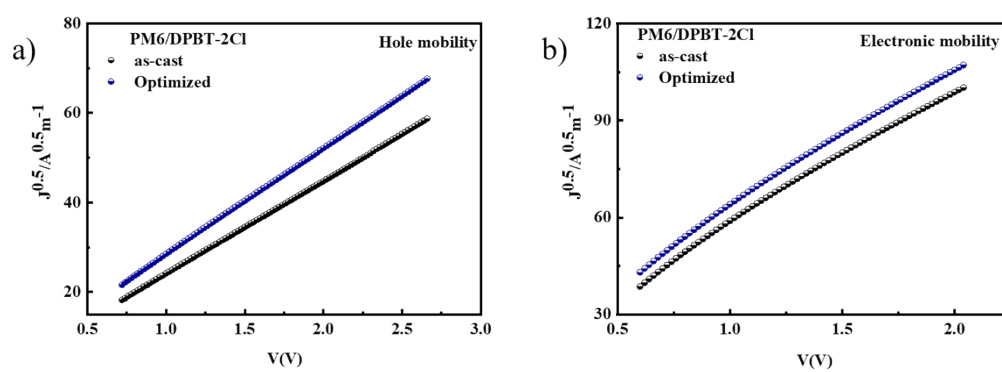


Figure S10. Hole/electronic mobility of PM6/DPBT-2Cl in as-cast and optimized blend films.

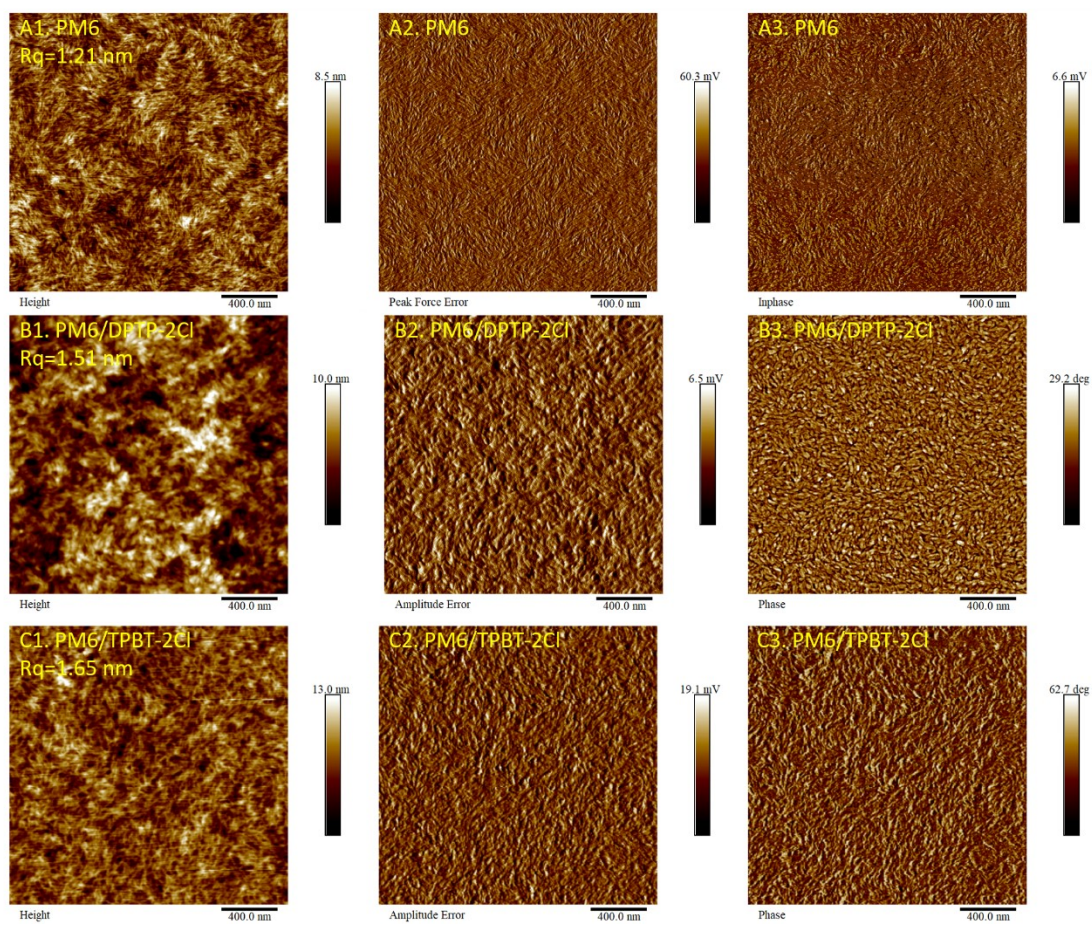
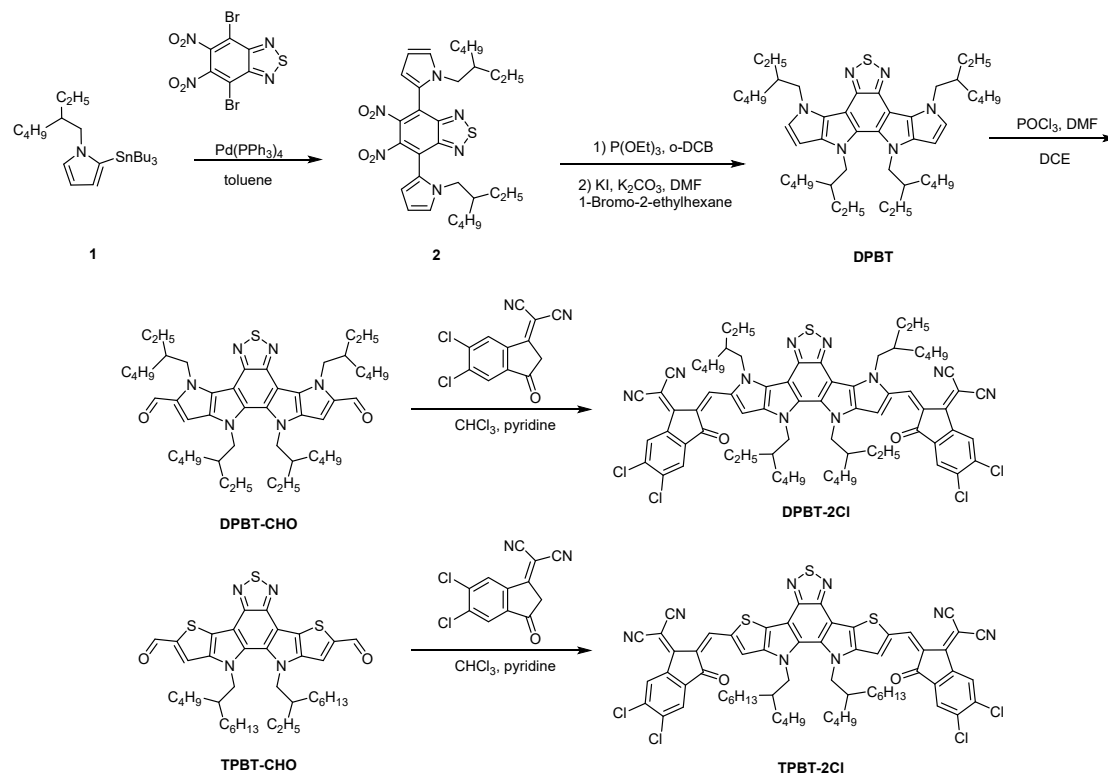


Figure S11 AFM height/amplitude error/phase patterns of films for A1/A2/A3 (PM6), B1/B2/B3 (PM6/DPBT-2Cl), and C1/C2/C3 (PM6/TPBT-2Cl).

5. Synthesis



Scheme S1. Synthetic routes of DPBT-2Cl and TPBT-2Cl.

Synthesis of compound **2**

A mixture of compound **1** (9.38 g, 20 mmol), 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole (3.80 g, 9.95 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (460 mg, 0.40 mmol) were dissolved in dry toluene (100 mL) under argon atmosphere, stirred and heated at 110 °C for 16 h. After being cooled to room temperature, the reaction mixture was extracted by ethyl acetate three times. The combined organic phase was dried over anhydrous Na_2SO_4 , filtered, and concentrated by reduced pressure rotary evaporation. The compound **2** was obtained from silica-gel column chromatography as a dark red solid which was directly used in the next experiment (5.22 g, 90% yield).

^1H NMR (300 MHz, Chloroform-*d*) δ 7.09 – 6.44 (m, 4H), 6.23 – 6.04 (m, 2H), 4.02 (d, $J = 7.5$ Hz, 4H), 1.83 – 1.66 (m, 2H), 1.28 – 1.20 (m, 16H), 0.99 – 0.77 (m, 12H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 127.82, 121.98, 121.07, 108.00, 107.64, 83.04, 53.27, 41.66, 30.51, 28.60, 23.66, 23.13, 14.10, 10.49.

Synthesis of DPBT

A mixture of compound **2** (4.0 g, 6.89 mmol) and $\text{P}(\text{OEt})_3$ (20 mL) were dissolved in *o*-DCB (20 mL) under argon atmosphere, heated at 180 °C for 18 h. After cooling to room temperature, the reaction mixture was extracted by CHCl_3 three times. The combined organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated by reduced pressure rotary evaporation. The residue, 1-bromo-2-ethylhexane (3.84 g, 20 mmol), KOH (1.12 g, 20 mmol), KI (16.5 mg, 0.1 mmol), and DMF (50 mL) were added into a three-necked round bottom flask, then deoxygenated with argon

for 20 min. Heated and stirred at 80 °C for 18 h. After cooling to room temperature, the mixture was extracted with CH₂Cl₂ and brine, dried over Na₂SO₄, filtered and concentrated by reduced pressure rotary evaporation. The crude product of DPBT (2.0 g, about 2.7 mmol, 40 % yield) was directly used in the next reaction after passing through a fast silica gel column with CH₂Cl₂ : Petroleum ether = 1: 2. HR-MS (MALDI-TOF) m/z calcd. for (C₄₆H₇₂N₆S): 740.5531. Found: 740.5534.

Synthesis of DPBT-CHO

To a solution of crude DPBT (1.00 g, about 1.35 mmol) in dry 1,2-dichloroethane (DCE) (100 mL) were added POCl₃ (562 mg, 3.70 mmol) and DMF (270 mg, 3.70 mmol) under argon atmosphere. The reaction mixture was stirred in an ice bath for 5 h, and then heated at 85 °C for 12 h. After cooling to room temperature, the reaction mixture was extracted by CHCl₃ three times. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated by reduced pressure rotary evaporation. The pure DPBT-CHO was obtained from silica gel column chromatography as an orange solid (860 mg, about 80 % yield).

¹H NMR (300 MHz, Acetone-*d*₆) δ 9.70 (s, 2H), 7.17 (s, 2H), 5.47 – 5.14 (m, 4H), 4.59 (d, *J* = 7.4 Hz, 4H), 2.07 (d, *J* = 7.7 Hz, 4H), 1.34 (m, 8H), 1.17 – 0.80 (m, 32H), 0.78 – 0.42 (m, 24H). ¹³C NMR (75 MHz, Acetone-*d*₆) δ 179.23, 147.35, 136.71, 135.39, 134.07, 103.30, 51.95, 41.40, 38.66, 30.04, 27.37, 23.53, 22.90, 22.85, 22.55, 13.48, 13.18, 10.46, 9.61.

Synthesis of DPBT-2Cl

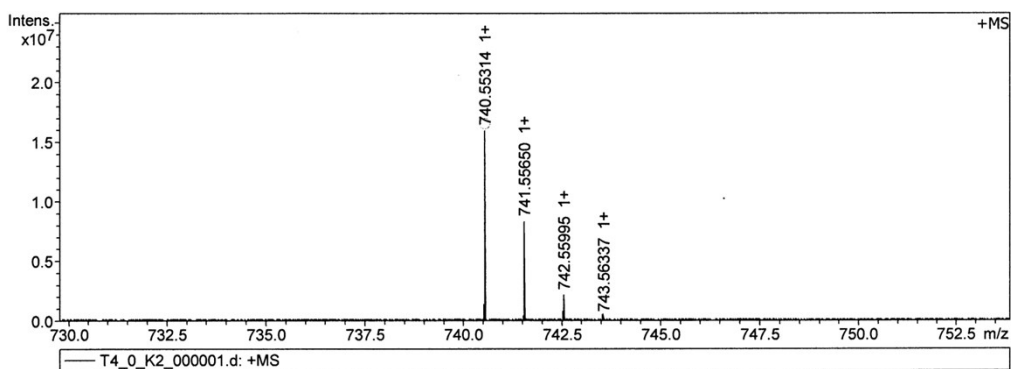
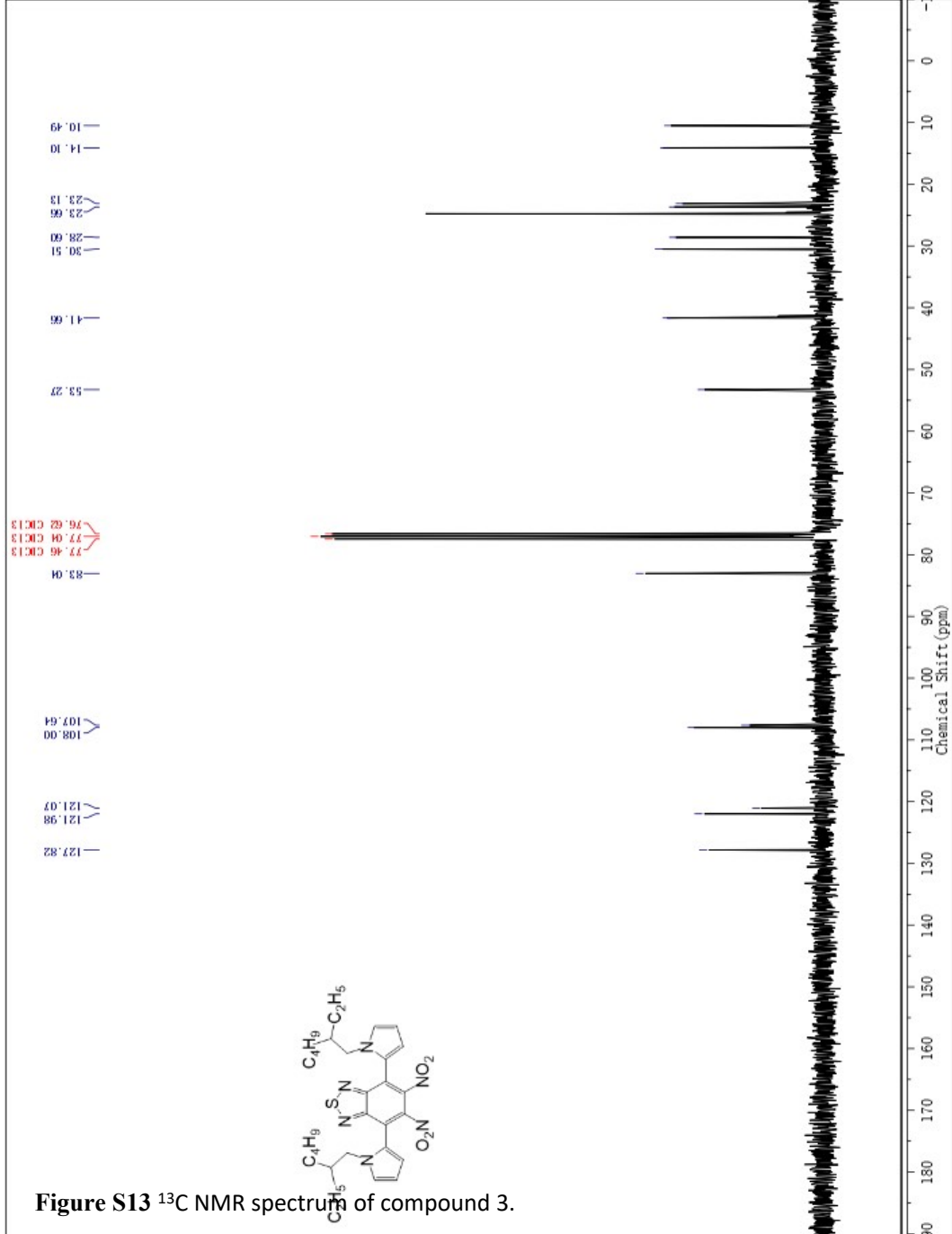
Compound DPBT-CHO (600 mg, 0.75 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC2Cl) (589 mg, 2.25 mmol) were dissolved in dry chloroform (80 mL) under argon atmosphere. Added pyridine (0.1 mL), stirred for 24 h at 65 °C. After cooling to room temperature, the reaction mixture was extracted by CHCl₃ three times. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated by reduced pressure rotary evaporation. The pure DPBT-2Cl was obtained from silica gel column chromatography as a black solid (578 mg, 60% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 1H), 8.63 (s, 2H), 7.88 (s, 1H), 5.14 (br. s, 2H), 4.43 (d, *J* = 7.6 Hz, 2H), 2.19–2.04 (m, 1H), 2.03–1.91 (m, 1H), 1.38–1.24 (m, 4H), 1.22–0.87 (m, 12H), 0.86–0.65 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 185.05, 159.99, 147.04, 140.23, 138.56, 138.45, 138.41, 136.72, 136.67, 136.52, 129.68, 126.27, 124.58, 119.09, 115.76, 115.15, 108.63, 104.60, 66.34, 54.19, 51.07, 42.42, 42.31, 38.65, 29.97, 29.87, 28.39, 28.31, 27.84, 23.55, 23.30, 23.24, 23.06, 23.01, 22.76, 13.92, 13.76, 10.78, 10.74, 10.03. HR-MS (MALDI-TOF) m/z calcd. for (C₅₈H₈₂N₄O₂S₅): 1284.4622. Found: 1284.4622.

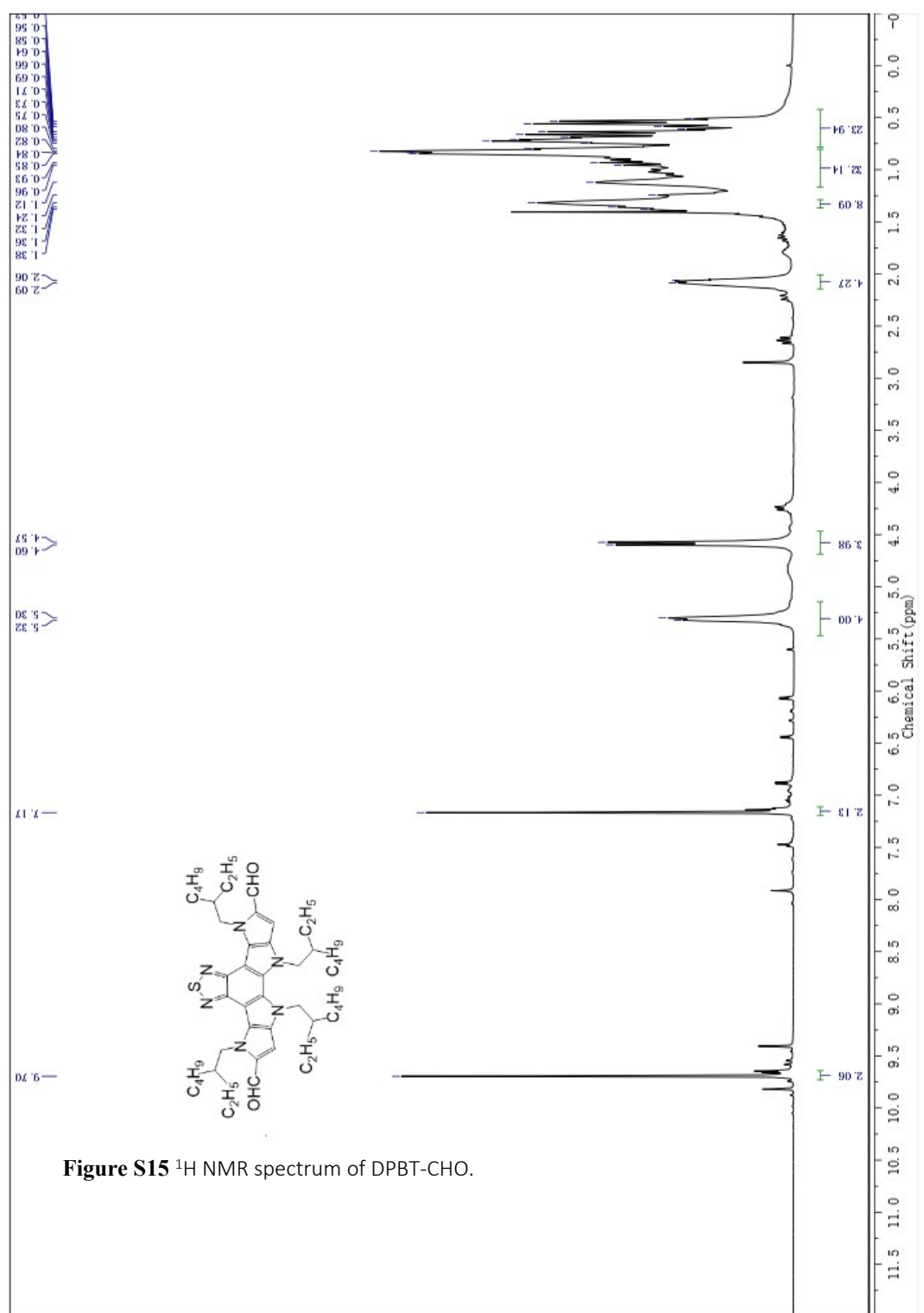
Synthesis of TPBT-2Cl

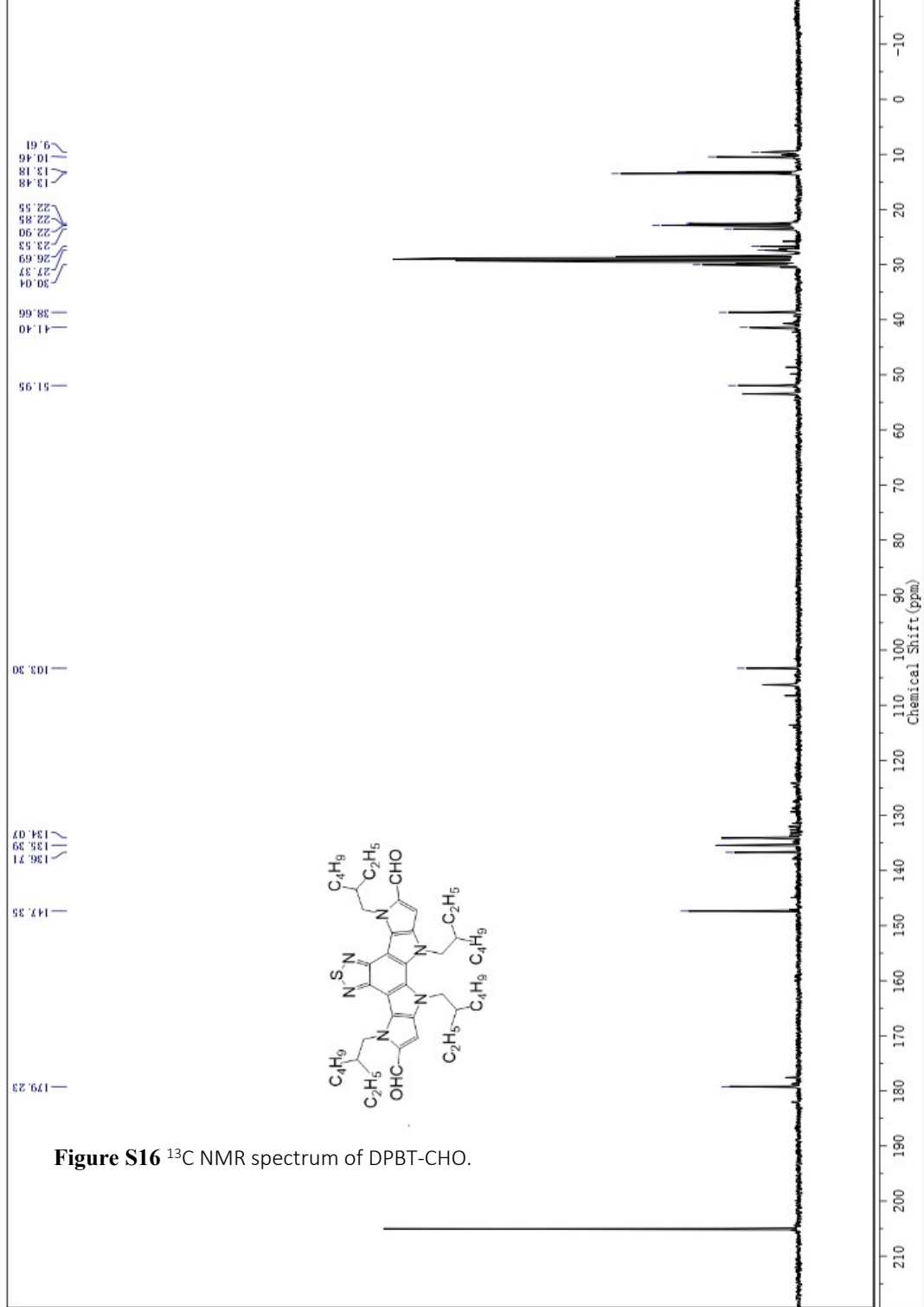
Compound TPBT-CHO (718 mg, 1.00 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC2Cl) (789 mg, 3.00 mmol) were dissolved in dry chloroform (80 ml) under argon atmosphere. Added pyridine (0.1 ml), stirred for 24 h at 65 °C. After cooling to room temperature, the reaction mixture was extracted by CHCl₃ three times. The combined organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated by reduced pressure rotary evaporation. The pure DPBT-2Cl was obtained from silica gel column chromatography as a dark blue solid (578 mg, 60% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.75 (s, 1H), 7.97 (s, 1H), 7.975 (s, 1H), 4.58 (d, *J* = 8.0 Hz, 2H), 2.16–2.09 (m, 1H), 1.18–0.86 (m, 16H), 0.77–0.66 (m, 6H). ¹³C NMR (175 MHz, Chloroform-*d*) δ 185.55, 158.17, 147.45, 146.89, 140.31, 139.83, 139.66, 138.99, 138.71,



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
740.553141	1	C ₄₆ H ₇₂ N ₆ S	100.00	740.553369	0.3	0.2	86.0	14.0	odd	ok





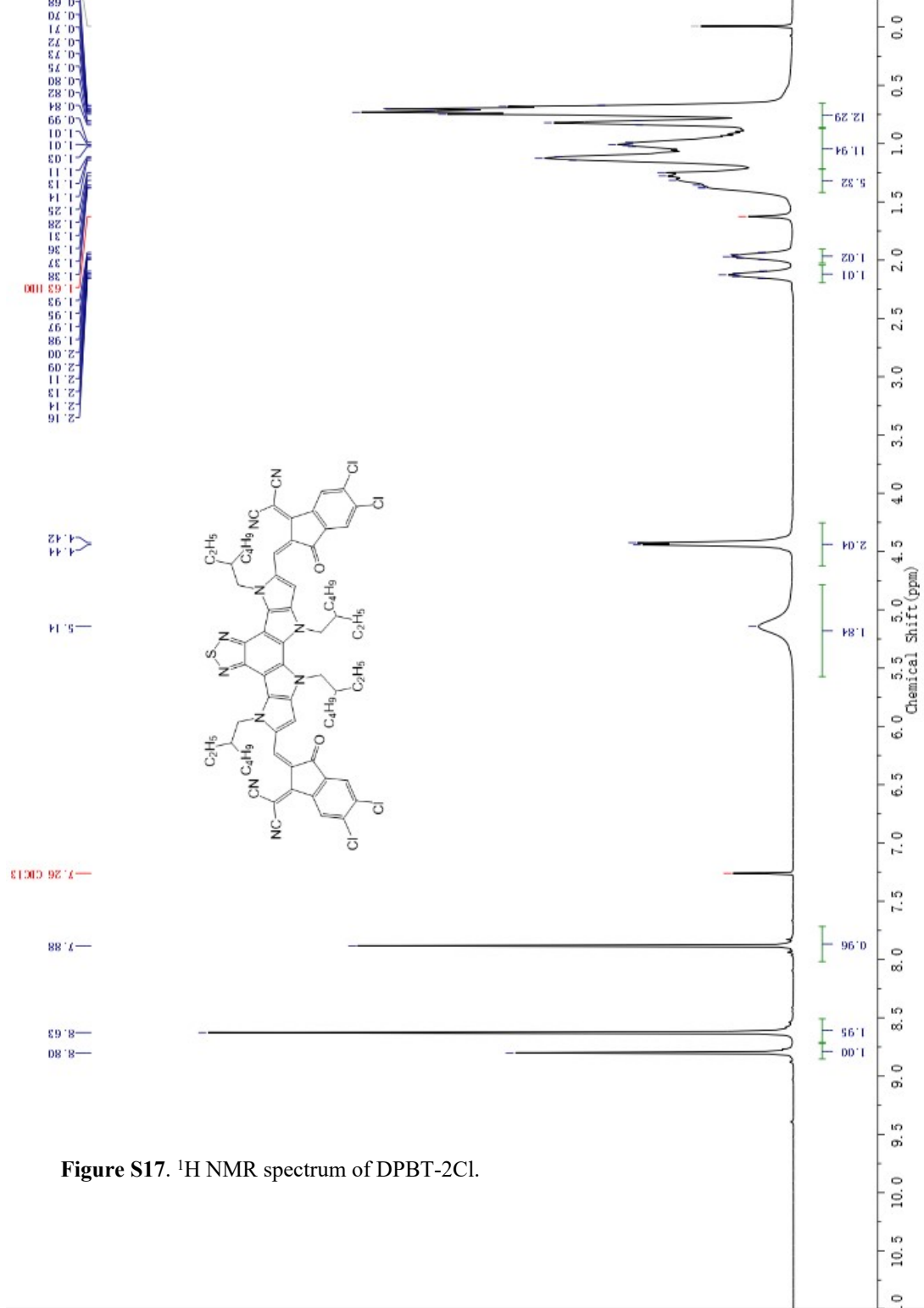


Figure S17. ^1H NMR spectrum of DPBT-2Cl.

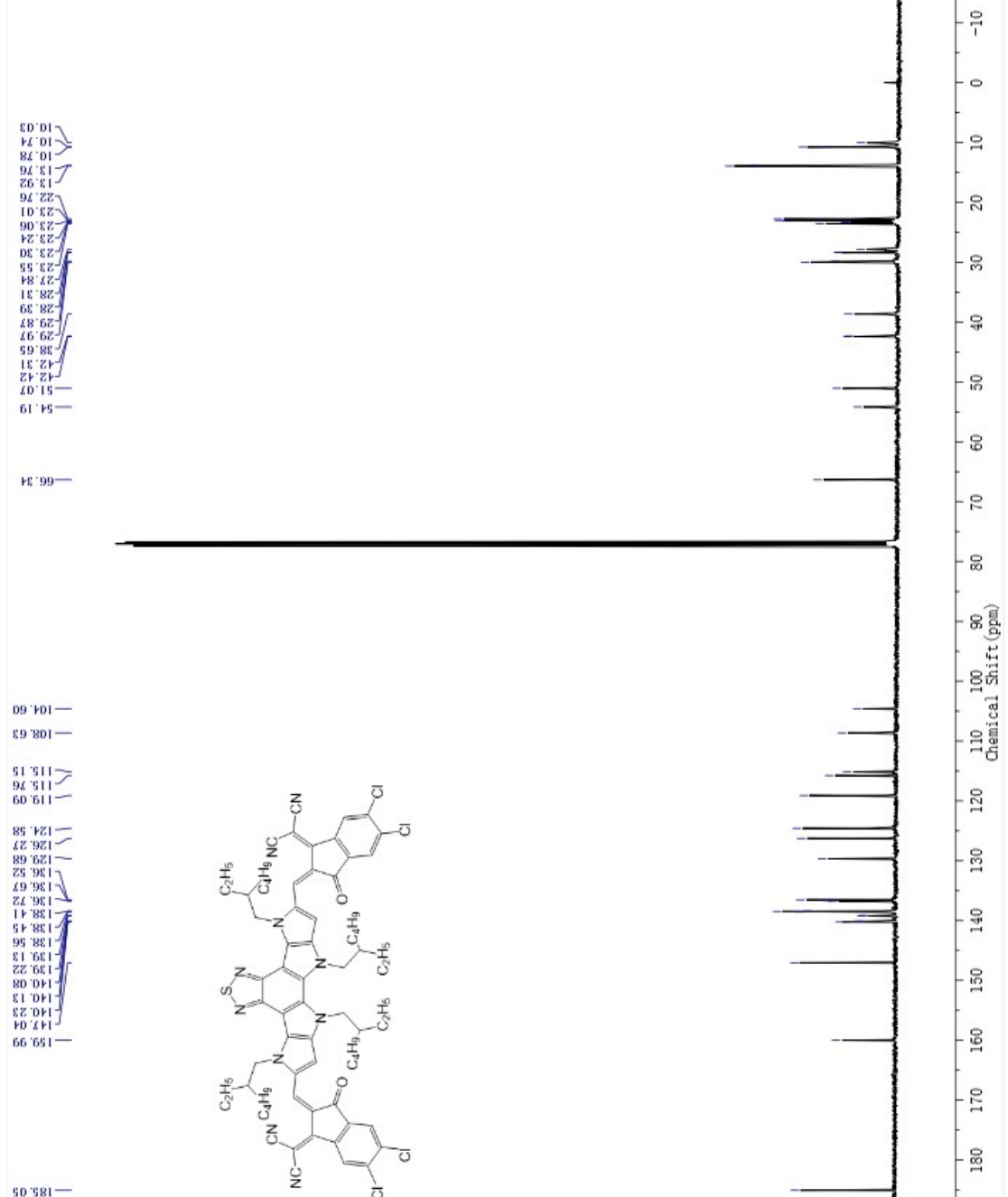
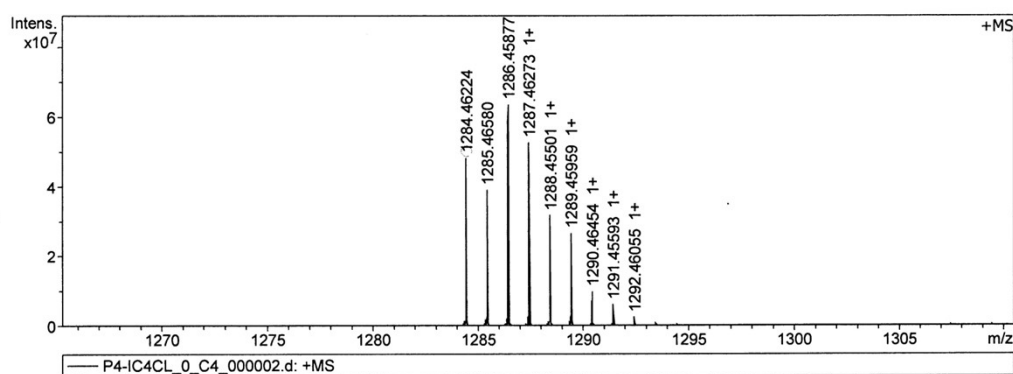
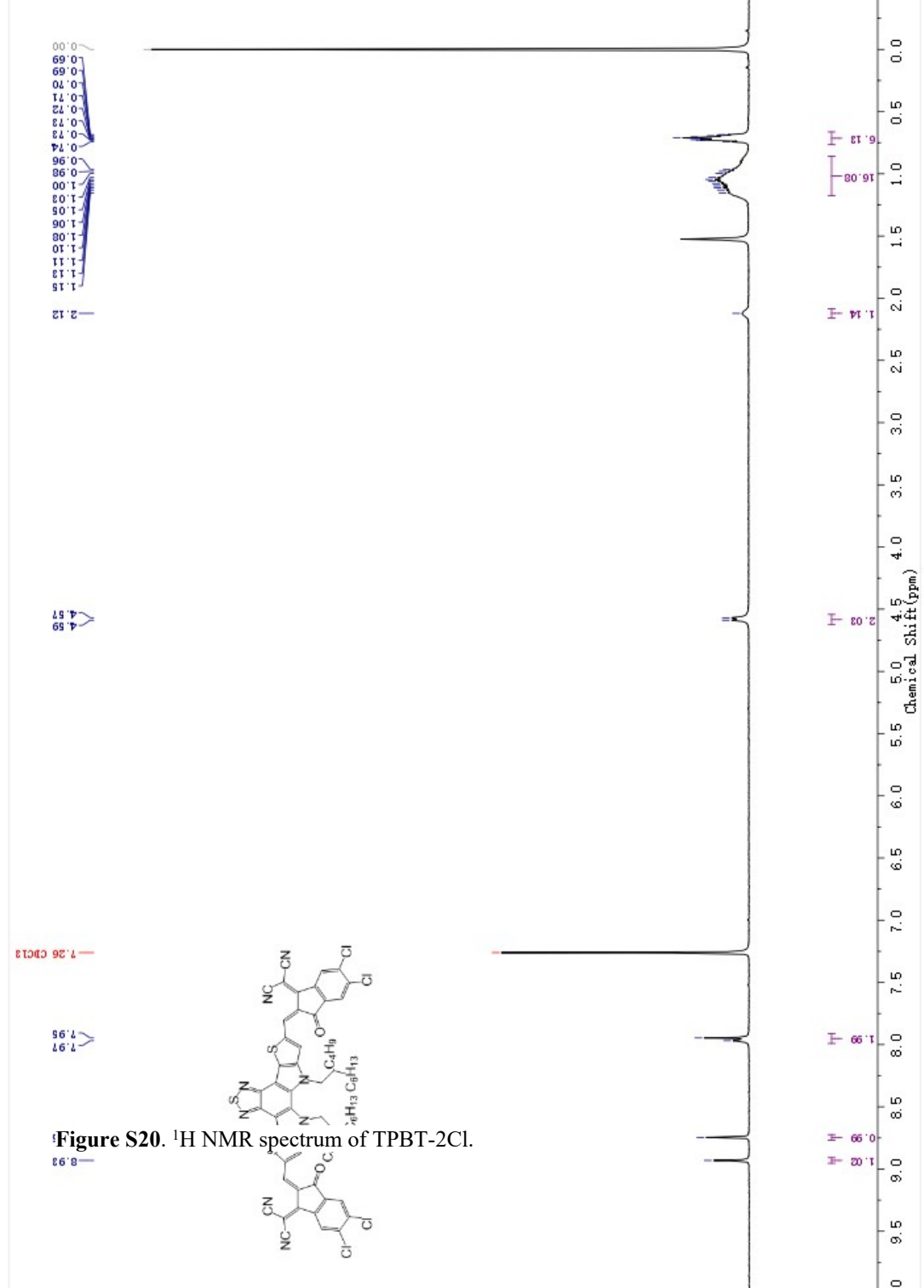


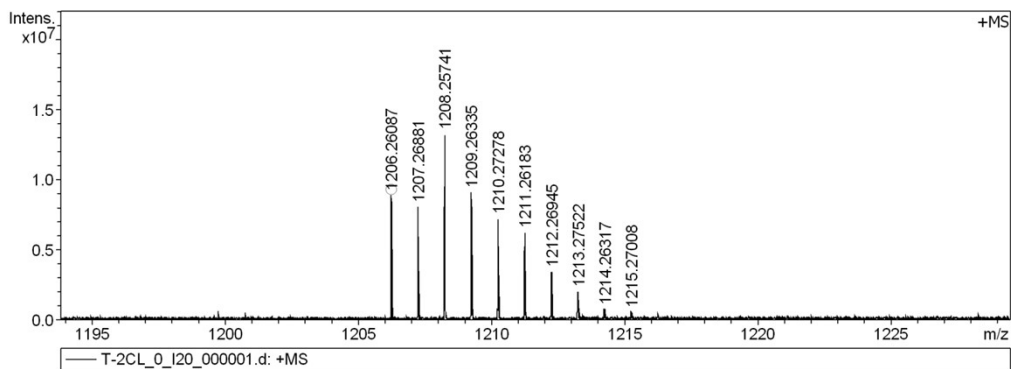
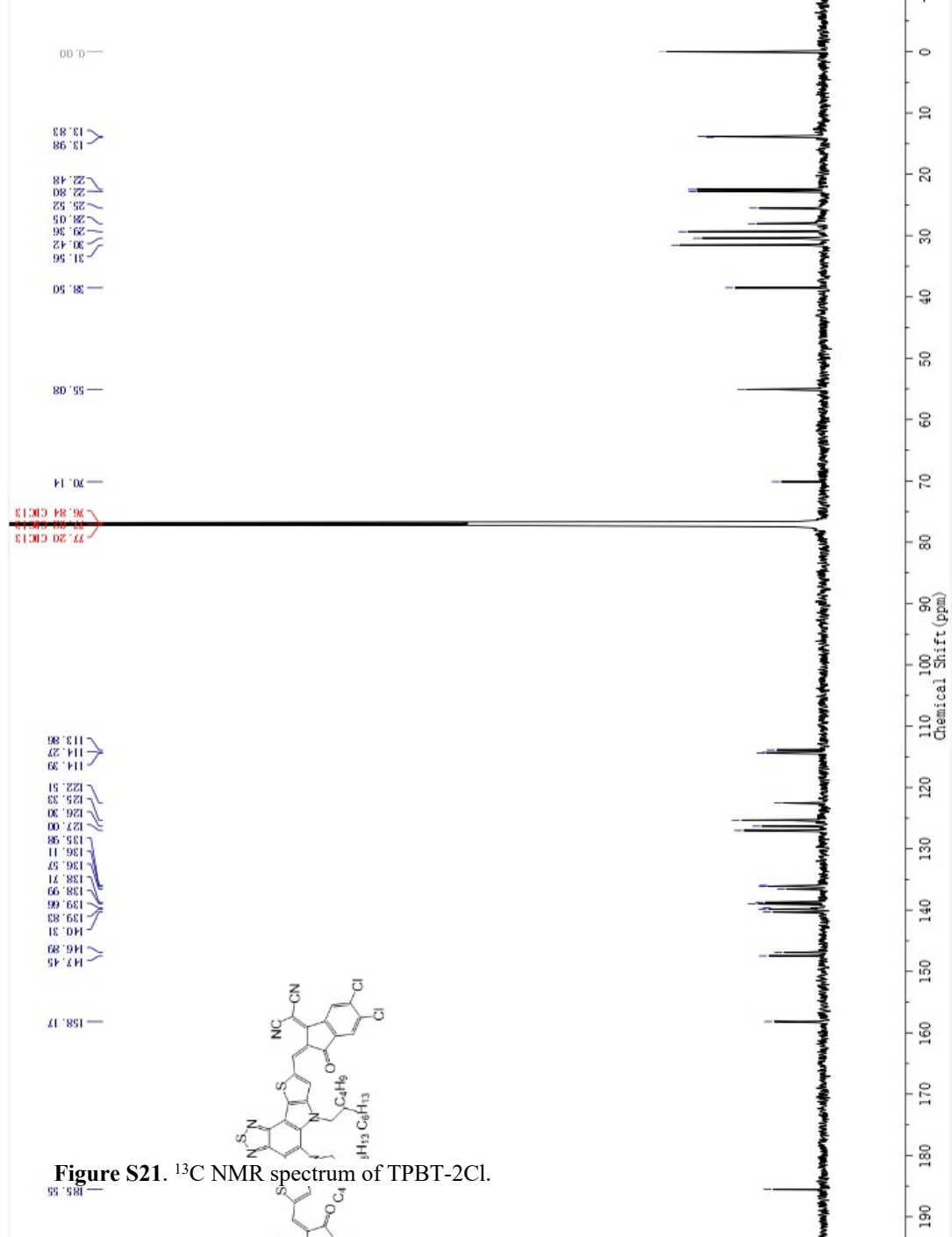
Figure S18. ¹³C NMR spectrum of DPBT-2Cl.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdB	e ⁻ Conf	N-Rule
1284.462241	1	C72H76Cl4N10O2S	100.00	1284.462205	-0.0	0.8	94.9	38.0	odd	ok

Figure S19. HR-MS (MALDI-TOF) spectrum of DPBT-2Cl.





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1206.260873	1	C ₆₄ H ₅₈ Cl ₄ N ₈ O ₂ S ₃	100.00	1206.259348	-1.3	-1.6	115.5	38.0	odd	ok

Figure S22. HR-MS (MALDI-TOF) spectrum of TPBT-2Cl.