Supporting Information

Synthesis and Characterization of Electron-Deficient Conjugated Polymer Based on Pyridine-Flanked Diketopyrrolopyrrole

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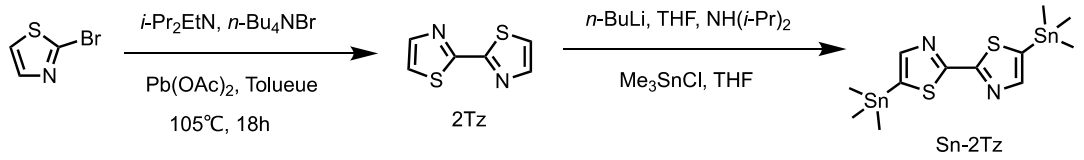
General procedures and experimental details

All chemical reagents were purchased and used as received unless otherwise indicated. All air and water sensitive reactions were performed under nitrogen atmosphere. Dichloromethane, tetrahydrofuran, toluene and *N,N*-Dimethylformamide were dried by a JC Meyer solvent drying system prior to use.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). ^{1}H NMR chemical shifts were referenced to $CDCl_3$ (7.26 ppm) and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.16 ppm). Mass spectra were recorded on an AB Sciex-5800 MALDI-TOF mass spectrometer and a Bruker Solarix XR mass spectrometer. Elemental analyses were performed on Vario EL elemental analyzer. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) performed on Polymer Laboratories PL-GPC220 at 150 ^{o}C using 1,2,4-tricholorobenzene (TCB) as eluent. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 SDT analyzer, and a METTLER TOLEDO Instrument DSC822 calorimeter was used for differential scanning calorimetry (DSC) analysis. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis spectrometer, and temperature-depending absorption spectra were recorded on Shimadzu UV3600Plus UV-vis-NIR spectrometer. The doping samples were encapsulated to avoid exposure to ambient air during measurement. Cyclic voltammetry (CV) was performed on BioLogic SP-300 workstation. Thin film measurements were carried out in acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum wire as a counter electrode, and all potentials were recorded versus AgCl/Ag (saturated) as a reference electrode (scan rate: 50 mV s^{-1}).

The geometries of P(PyDPP2OD-2Tz) and P(PyDPP2OD-2T) trimer were optimized at the B3LYP/6-311G (d, p) level, and the HOMOs and LUMOs were also calculated with the 6-311G(d, p) basis set, using the Gaussian 09 software package.

Synthetic Route for Preparing Sn-2Tz



Synthesis of 2Tz

2-bromothiazole (3.50 g, 21.34 mmol), N, N-diisopropylethylamine (2.76 g, 21.34 mmol), tetra-n-butylammonium bromide (6.88 g, 10.67 mmol), palladium acetate (0.35 g, 2.13 mmol) and toluene (14 mL) were added to a 50 mL Schlenk bottle in turn at -78 °C under nitrogen and warmed to room temperature. The reaction mixture was slowly warmed to 105 °C and stirred for 18 h. After the reaction, deionized water was added to the reaction solution to quench and the resulting mixture was extracted with dichloromethane (50 mL × 3). The organic phase was combined, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (petroleum ether/dichloromethane = 6:1) Pale yellow solid powder (970 mg, yield 54%) was obtained, which was compound 2Tz. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.90 (d, J = 3.2 Hz, 2H), 7.45 (d, J = 0.008Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.77, 144.06, 121.10; ESI MS calcd. For [M + H] +: 168.0; Found: 169.0.

Synthesis of Sn-2Tz

Under nitrogen protection, 3 mL of dry tetrahydrofuran (THF) was added to a 50 mL double-necked round bottom flask. After cooling to -78 °C, *n*-BuLi (1.8 mL, 4.33 mmol) was added and NH(*i*-Pr)$_2$ (437.85 mg, 4.33 mmol) was added dropwise, stirring the reaction at -78 °C for 30 min to prepare the lithium diisopropylamide (LDA) solution. Under the protection of nitrogen, 2Tz (200 mg, 1.19 mmol) and 16 mL tetrahydrofuran (THF) were added to another 100 mL three-necked round bottom flask, and the reaction mixture was cool to -78 °C. One-third of the LDA solution prepared above was slowly added dropwise to the flask. The reaction solution turned orange-yellow. After stirring for 40 min at -78 °C, Me_3SnCl solid (291.40 mg, 1.46 mmol) was added to the reaction system. Then another third of the LDA solution was slowly dripped and the reaction solution turned orange-red. After stirring the reaction at -78 °C for 40 minutes, Me_3SnCl solid (291.40 mg, 1.46 mmol) was added to the reaction system slowly. The last third of the LDA solution was added after 40 minutes, stirring the reaction at -78 °C for 40 min and Me_3SnCl solid (291.40 mg, 1.46 mmol) was added. Then the reaction mixture was warmed to room temperature and stirred for 2 h. After the reaction, the liquid was cooled, and deionized water was slowly added. a large amount of deionized water was added to quench the reaction if the reaction liquid had no reaction, and the reaction mixture was extracted with dichloromethane. The lower organic phase was dried over anhydrous Na_2SO_4 and concentrated to obtain the crude yellow solid product. The product was purified by gel permeation chromatography (GPC) and concentrated to obtain a pale yellow powdered solid (389 mg, yield 66%), which is compound Sn-2Tz. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80

(s, 2H), 0.44 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 166.33, 150.23, 132.22, -7.88. ESI MS calcd. For [M - H]-: 495.9; Found: 494.9.

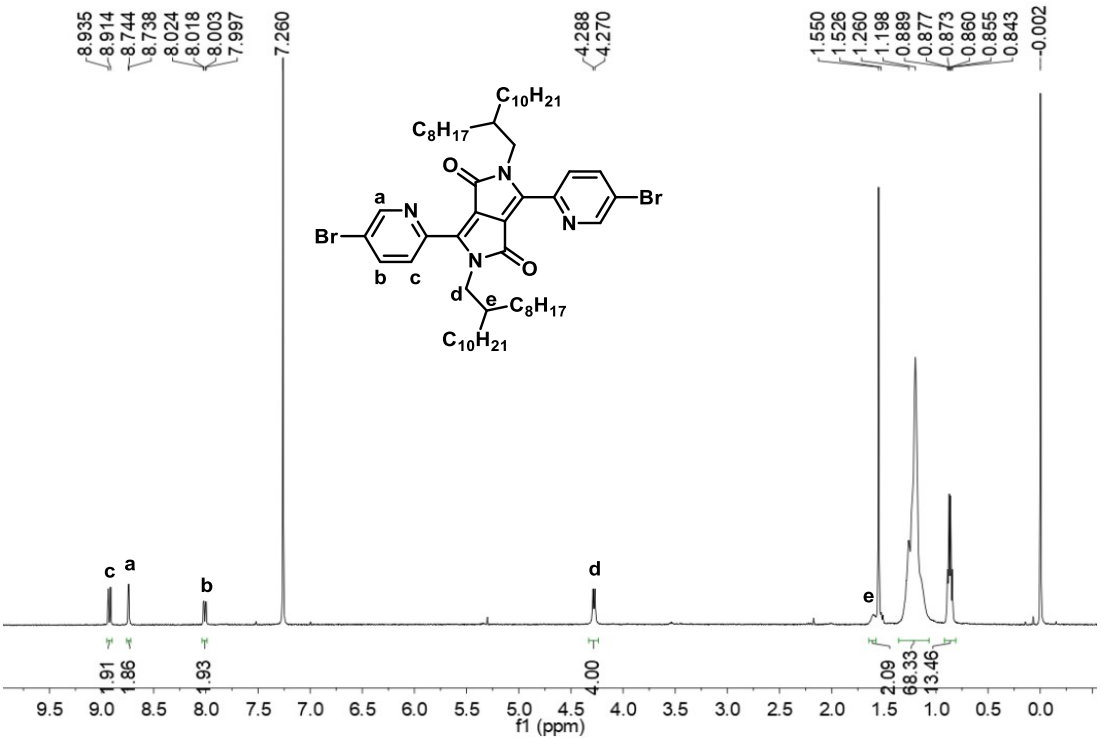


Figure S1. ^{1}H NMR spectrum of PyDPP2OD in $CDCl_3$

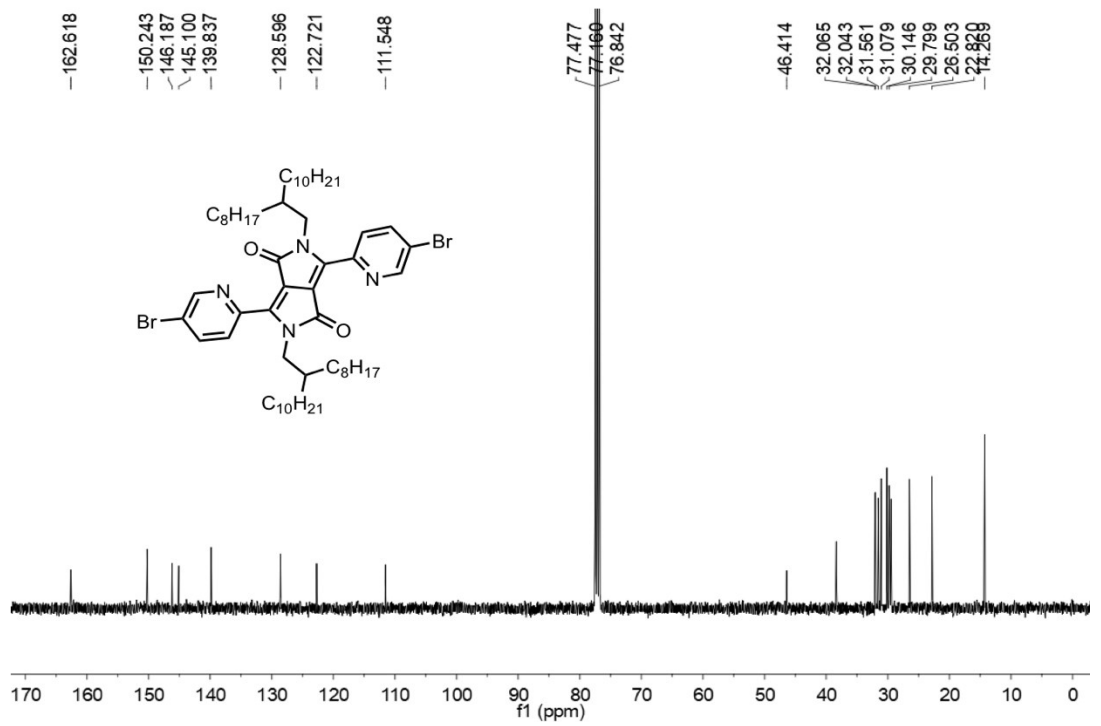


Figure S2. ^{13}C NMR spectrum of PyDPP2OD in $CDCl_3$

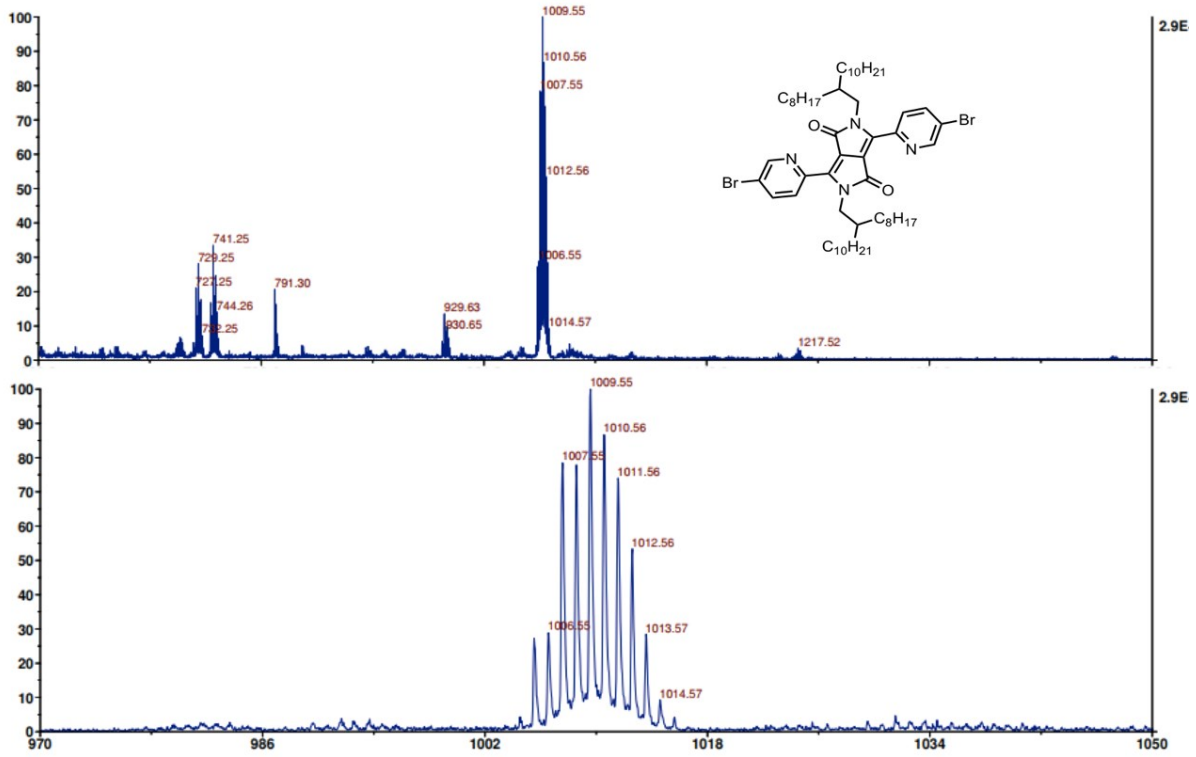


Figure S3. Mass spectrum of PDBPyBTz

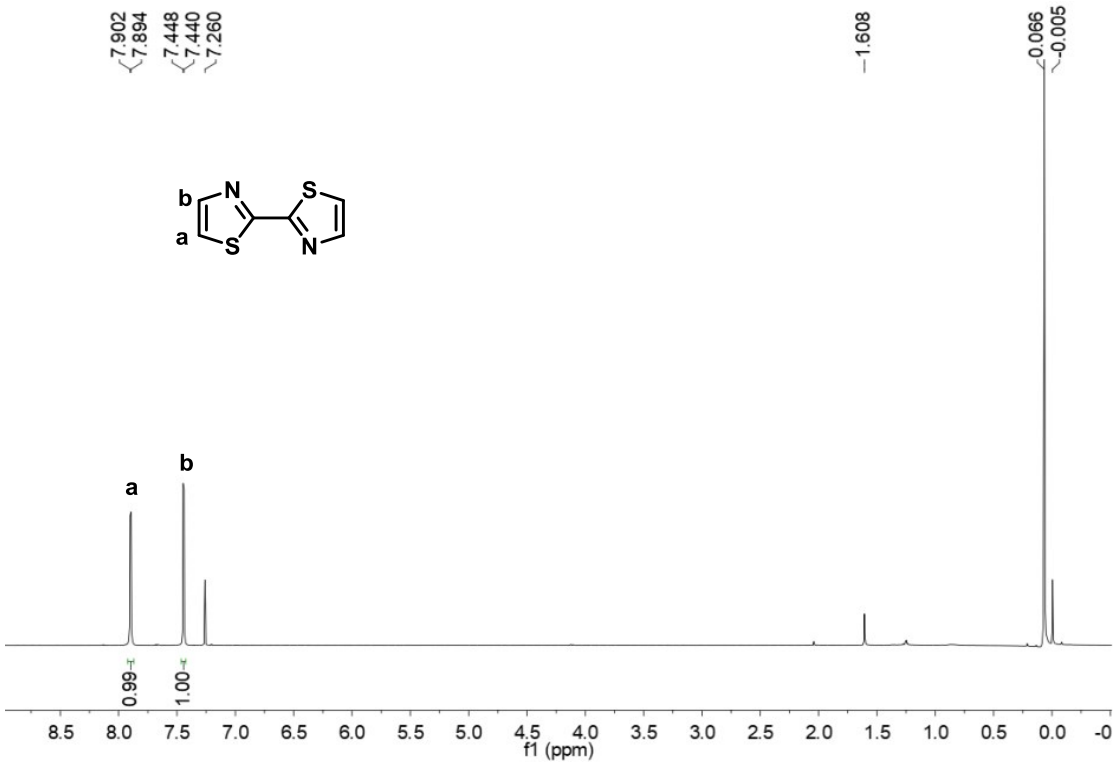


Figure S4. ^{1}H NMR spectrum of 2Tz in $CDCl_3$

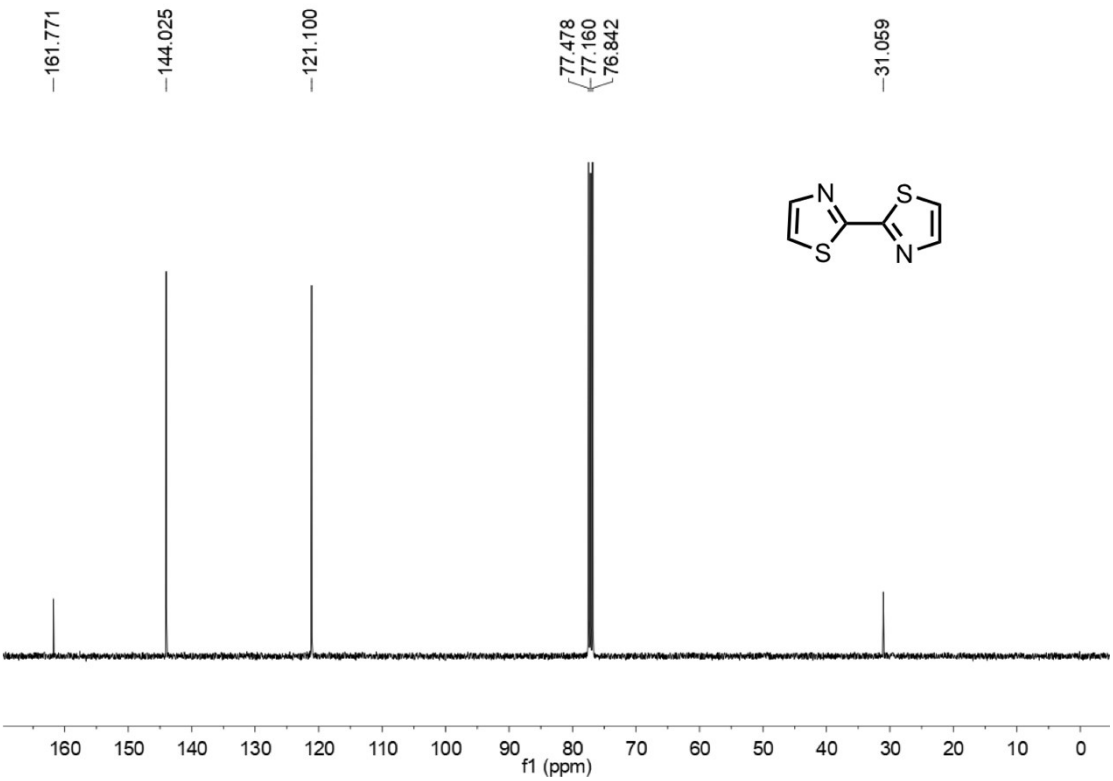


Figure S5. ^{13}C NMR spectrum of 2Tz in $CDCl_3$

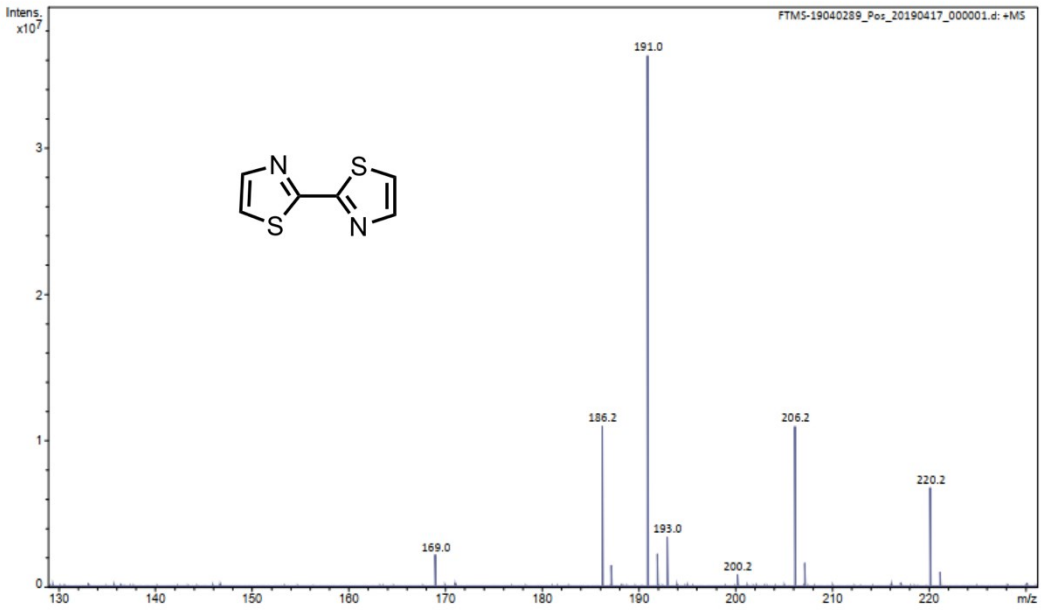


Figure S6. Mass spectrum of 2Tz

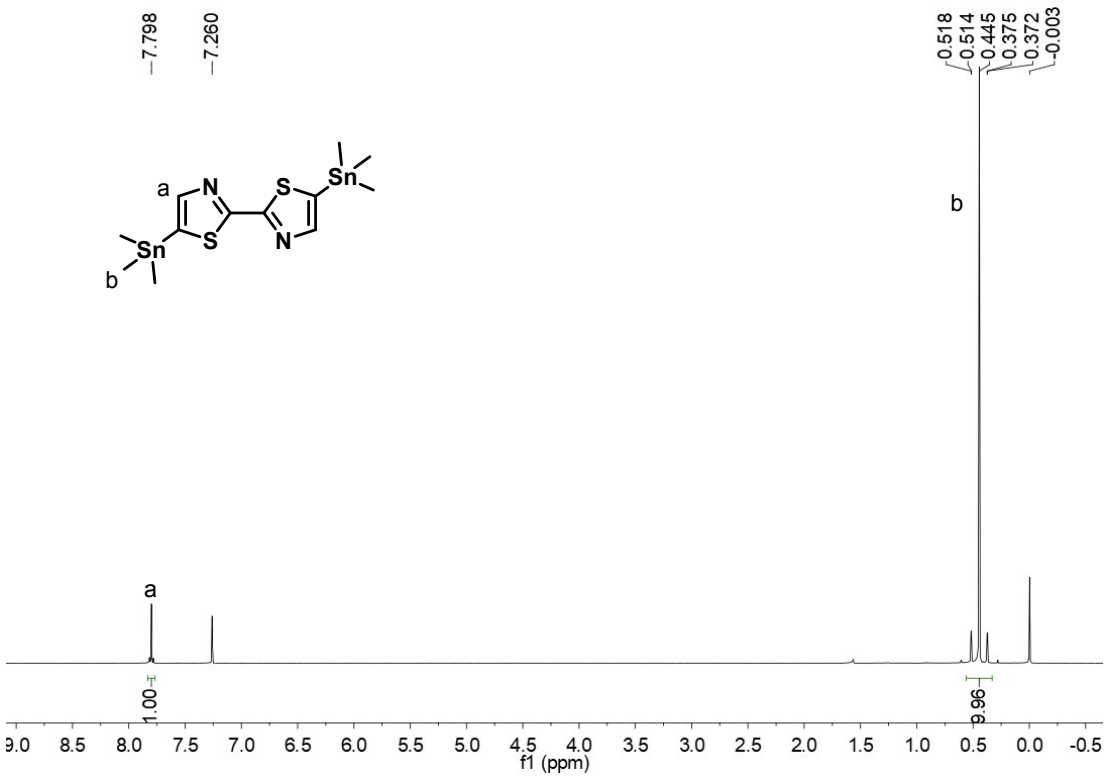


Figure S7. ^{1}H NMR spectrum of Sn-2Tz in $CDCl_3$

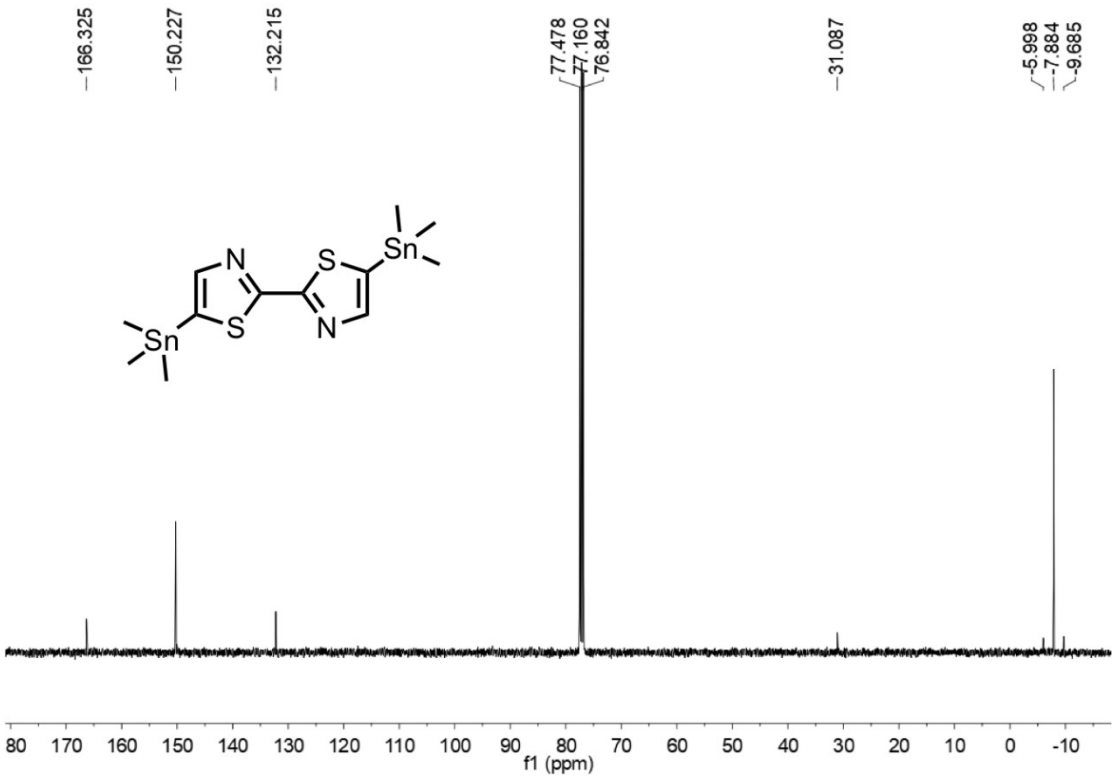


Figure S8. ^{13}C NMR spectrum of Sn-2Tz in $CDCl_3$

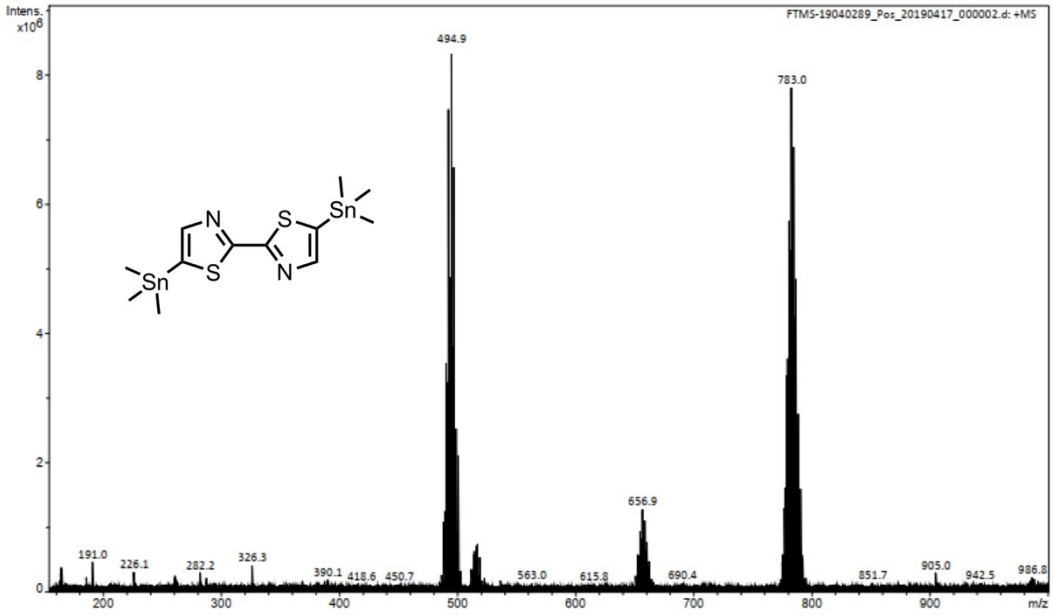


Figure S9. Mass spectrum of Sn-2Tz

Cirrus GPC Sample Peak Report

Generated by: dell 2021年3月22日 15:56
Workbook: D:\Cirrus Workbooks\luyang\luyang.plw

Sample Details

Sample Name: 8
Acquired: 2019-5-8 3:30:09 By Analyst: dell
Batch Name: 2019-5-8
Filename: D:\Cirrus Workbooks\luyang\2019-5-8-0004.cgrm
Concentration: 0.10 mg/ml K of Sample: 14.1000
Injection Volume: 200.0 ul Alpha of Sample: 0.7000
LIMS ID: Bottle ID:

Workbook Details

Eluent: TCB Flow Rate: 1.00 ml/min
Column Set: Column Set Length: 0 mm
Detector: RI Temperature: 150

Analysis Using Method: luyang-2017

Comments:

Results File: D:\Cirrus Workbooks\luyang\2019-5-8-0004-Repeat (02).rst

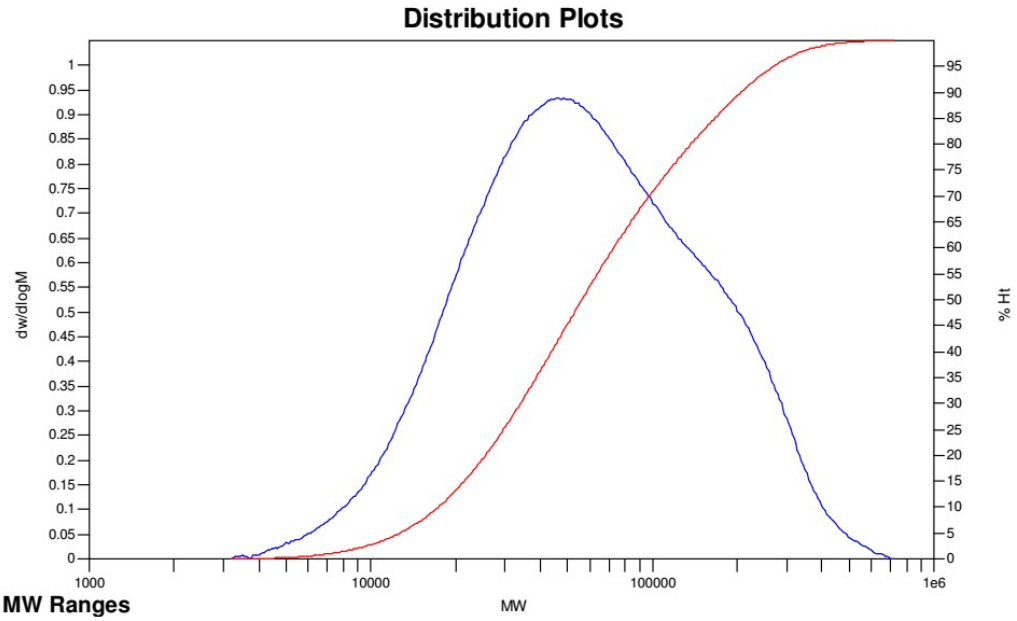
Calibration Used: 2017-12-7 19:19:32

Calibration Type: Narrow Standard Curve Fit Used: 1
Calibration Curve: y = 12.627022 - 0.389278x^1

High Limit MW RT: 17.37 mins Low Limit MW RT: 23.40 mins
High Limit MW: 735470 Low Limit MW: 3295
K: 14.1000 FRM Name:
Alpha: 0.7000 Flow Marker RT: 0.00 mins
FRCF: 1.0000

MW Averages

Mp: 46375	Mn: 37467	Mv: 77198	Mw: 86992
Mz: 171243	Mz+1: 258568	PD: 2.3218	



MW Ranges

Figure S10. Molecular weights and polydispersity index (PDI) of P(PyDPP2OD-2T) measured by high-temperature GPC at 150 °C.

Cirrus GPC Sample Peak Report

Generated by: dell 2021年3月22日 15:59
Workbook: D:\Cirrus Workbooks\luyang\luyang.plw

Sample Details

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Acquired: 2019-5-8 4:23:01 By Analyst: dell
Batch Name: 2019-5-8
Filename: D:\Cirrus Workbooks\luyang\2019-5-8-0005.cgrm
Concentration: 0.10 mg/ml K of Sample: 14.1000
Injection Volume: 200.0 ul Alpha of Sample: 0.7000
LIMS ID: Bottle ID:

Workbook Details

Eluent: TCB Flow Rate: 1.00 ml/min
Column Set: Column Set Length: 0 mm
Detector: RI Temperature: 150

Analysis Using Method: luyang-2017

Comments:

Results File: D:\Cirrus Workbooks\luyang\2019-5-8-0005-Repeat (01).rst

Calibration Used: 2017-12-7 19:19:32

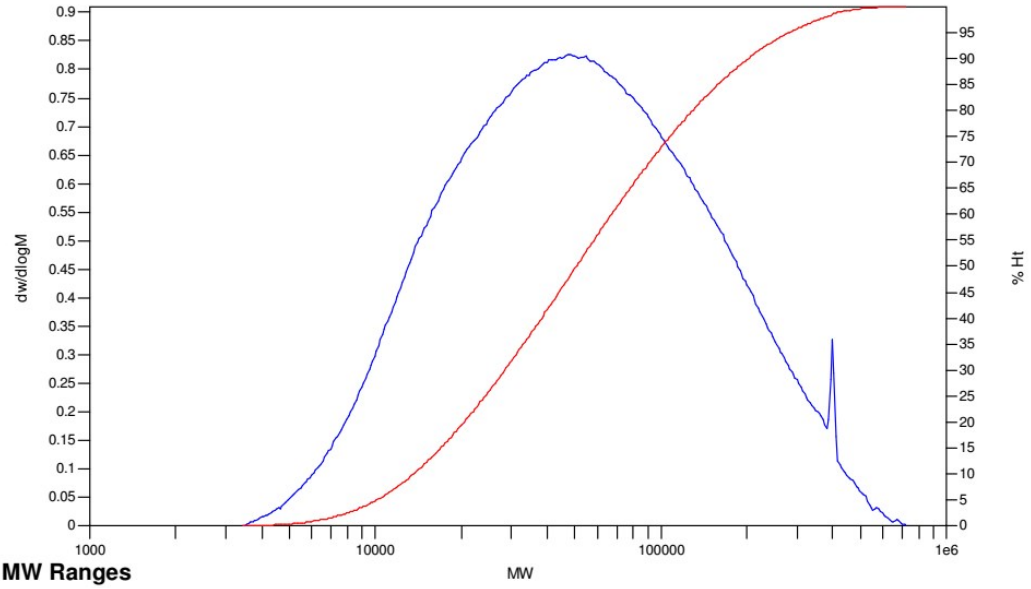
Calibration Type: Narrow Standard Curve Fit Used: 1
Calibration Curve: y = 12.627022 - 0.389278x^1

High Limit MW RT: 17.37 mins Low Limit MW RT: 23.40 mins
High Limit MW: 735470 Low Limit MW: 3295
K: 14.1000 FRM Name:
Alpha: 0.7000 Flow Marker RT: 0.00 mins
FRCF: 1.0000

MW Averages

Mp: 47073	Mn: 31654	Mv: 72480	Mw: 83340
Mz: 180789	Mz+1: 279648	PD: 2.6328	

Distribution Plots



MW Ranges

Figure S11. Molecular weights and PDI of P(PyDPP2OD-2Tz) measured by high-temperature GPC at 150 °C.