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Supporting information

Aza-substitution on naphthalene diimide-based conjugated polymers for *n*-type bottom gate/top contact polymer transistors in ambient conditions

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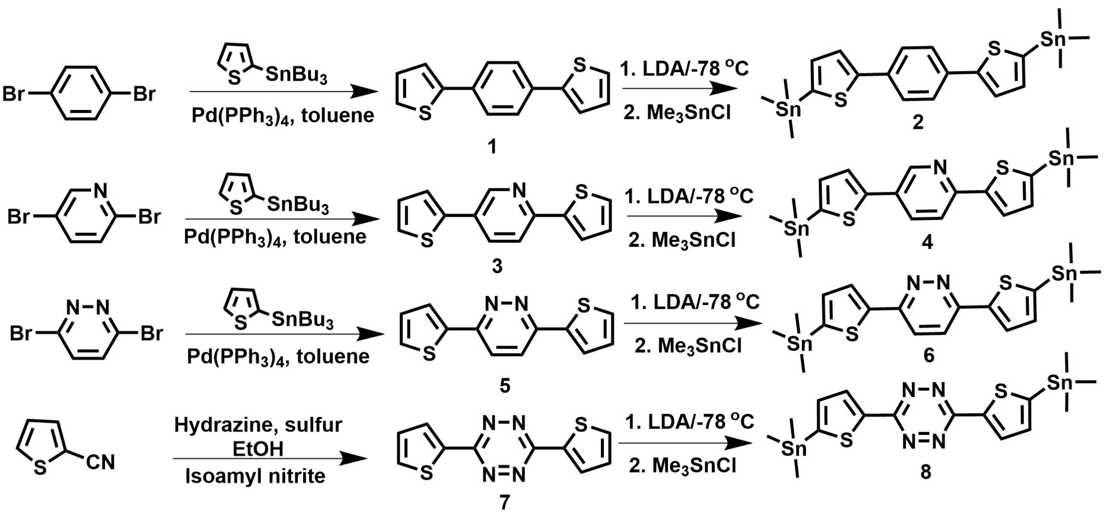

Scheme S1. Synthetic route for the monomers.

Experimental section

All the regents were used as received without further purification. Tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$), (tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), tri(*o*-tolyl)phosphine ($P(o\text{-tol})_3$), and other chemicals were purchased from Sigma-Aldrich Chemical Company, Alfa Aeasar Chemical Company, J&K, and Sinopharm Chemical Reagent Co. Ltd., China. Compound **7** was synthesized according to our previous procedure.[1]

Synthesis of compound 1. 1,4-Dibromobenzene (2.0 g, 8.5 mmol), 2-(tributylstannyl)thiophene (6.9 g, 18.6 mmol) was dissolved in toluene (50 mL). The mixture was then degassed under N_2 for about 20 min. $Pd(PPh_3)_4$ (10 mg) was added to the reaction solution. The reaction mixture was heated to 110 °C and stirred for about 24 h. After cooling to room temperature, the mixture was poured into water and then extracted with chloroform. The collected organic layer was dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from hexane to give the title compound (1.81 g, 87%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 7.62 (s, 4H), 7.34 (dd, 2H), 7.29(dd, 2H), 7.10 (m, 2H).

Synthesis of monomer 2. Diisopropylamine (1.5 g, 14.9 mmol) was dissolved in THF (30 mL). A solution of *n*-butyllithium (5.2 mL, 2.4 M) was added slowly to the solution at -78 °C. The mixture was stirred at room temperature for 1 h and then cooled to -78 °C again. The solution of compound **1** (1.0 g, 4.1 mmol, 60 mL THF) was added and the mixture was stirred at -78 °C for 90 min. Trimethyltin chloride solution (13 mL, 1M in hexane) was added to the mixture. The mixture was warm to room temperature and stirred overnight. The reaction was quenched with water and was extracted with dichloromethane. The collected organic layer was dried with Na_2SO4. Solvent was removed under reduced pressure and the residue was recrystallized in methanol to give the title compound (1.5 g, 64%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 7.62 (s, 4H), 7.45 (d, 2H), 7.18(d, 2H), 0.48 (t, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ= 149.72, 137.75, 136.24, 133.35, 126.24, 124.23, -8.15. Elemental Analysis: calcd for $C_{20}H_{26}S_2Sn_2$ (%): C, 42.29, H, 4.61, found (%) C, 42.75, H, 4.42.

Synthesis of compound 3. Use the same procedure as compound **1**. Reagent used were 2-(tributylstannyl)thiophene (6.9 g, 18.6 mmol), 2,5-dibromopyridine (2.0 g, 8.44 mmol), $Pd(PPh_3)_4$ (10 mg), and toluene (50 mL). After workup, the product was yellow powder (1.8 g, 88.%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 8.85 (d, 1H), 7.88 (d, 1H), 7.68(d, 1H), 7.66 (d, 1H), 7.38(d, 2H), 7.35 (m, 2H), 7.13 (t, 2H).

Synthesis of monomer 4. Use the same procedure as monomer **2**. Reagent used were diisopropylamine (2.24 g, 22.2 mmol), *n*-butyllithium (7.7 mL, 2.4 M), compound **3** (1.5 g, 6.2 mmol, THF 60 mL), trimethyltin chloride solution (22.8 mL, 1 M), and THF (30 mL). After workup, the product pale solid (1.4 g, 40%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 8.85 (d, 1H), 7.88 (d, 1H), 7.66 (d, 1H), 7.35 (m, 2H), 7.13 (t, 2H), 0.49(t, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ= 151.08, 149.93, 146.60, 146.14, 141.18, 139.06, 136.37, 136.15, 133.52, 128.45, 125.53, 124.96, 118.76, -8.15. Elemental Analysis: calcd for $C_{19}H_{25}NS_2Sn_2$ (%): C, 40.11, H, 4.43, N, 2.46, found (%) C, 39.85 H, 4.55, N, 2,17.

Synthesis of compound 5. Used the same procedure as compound **1**. Reagent used were 3,6-dibromopyridazine (2.0 g, 8.4 mmol), 2-(tributylstannyl)thiophene (6.9 g, 18.6 mmol), $Pd(PPh_3)_4$ (10 mg), and toluene (50 mL). After workup, the product was yellow powder (1.6 g, 78%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 7.76 (s, 2H), 7.68 (d, 2H), 7.50(d, 2H), 7.17-7.15 (m, 2H).

Synthesis of monomer 6. Use the same procedure as monomer **2**. Reagent used were diisopropylamine (2.2 g, 21.7 mmol), *n*-butyllithium (7.6 mL, 2.4 M), compound **5**

(1.5 g, 6.1 mmol, THF 60 mL), trimethyltin chloride solution (22.5 mL, 1 M), and THF (30 mL). After workup, the product was yellow needle crystal (1.2 g, 34%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 7.78 (s, 2H), 7.71 (d, 2H), 7.25(d, 2H), 0.49 (t, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ= 153.05, 146.14, 143.00, 136.08, 126.95, 122.68, -8.5. Elemental Analysis: calcd for $C_{18}H_{24}N_2S_2Sn_2$ (%): C, 37.93, H, 4.24, N, 4.92, found (%) C, 37.65, H, 4.47, N, 4.76.

Synthesis of monomer 8. Use the same procedure as monomer **2**. Reagent used were diisopropylamine (2.5 g, 24.8 mmol), *n*-butyllithium (8.6 mL, 2.4 M), compound **7** (1.5 g, 6.9 mmol, THF 30 mL), trimethyltin chloride solution (25.5 mL, 1 M), and THF (30 mL). After workup, the product was red powder (0.4 g, 12%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 8.31 (d, 2H), 7.33 (d, 2H), 0.49 (t, 18H). ^{13}C NMR (150 MHz, $CDCl_3$): δ= 161.05, 148.01, 141.25, 136.73, 131.35, -8.5. Elemental Analysis: calcd for $C_{16}H_{22}N_4S_2Sn_2$ (%): C, 33.60, H, 3.88, N, 9.80, found (%) C, 33.14, H, 4.02, N, 9.73.

Synthesis of PNDI-TPhT. Dibrominated NDI (0.12 g, 0,11 mmol), monomer **2** (0.062 g, 0.11 mmol), and anhydrous chlorobenznen (8 mL) were added to a Schlenck tube (100 mL). The tube was charged with liquid nitrogen through a freeze-pump-thaw cycle for three times. Then $Pd_2(dba)_3$ (4 mg) and $P(o\text{-}tol)_3$ (5 mg) were added quickly in one portion. After charged with liquid nitrogen for another two times, the mixture was stirred at 130 °C for three days. Finally, the reaction mixture was poured into 80 mL of methanol. The precipitation was collected by filtration, and purified by Soxhlet extrarion using methanol, hexane, and chloroform. A purple solid was obtained after removing the solvent (90 mg, 69%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 8.82 (br, 2H), 7.70 (br, 4H), 7.45 (br, 2H), 7.38 (br, 2H), 4.10 (br, 4H), 1.97 (br, 2H), 1,20-1.40 (br, 80H), 0.83-0.90 (br, 12H).

Synthesis of **PNDI-TPdT**. Use the same procedure as **PNDI-TPhT**. The used reagent and monomers were dibrominated NDI (0.12 g, 0,11 mmol), monomer **4** (0.062 g, 0.11 mmol), and anhydrous chlorobenznen (8 mL). A purple solid was collected after removing the solvent (95 mg, 73%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 9.04 (br, 1H), 8.81 (br, 2h), 8.30 (br, 1H), 7.56 (br, 1H), 7.40 (br, 2H), 7.38 (br, 2H), 4.08 (br, 4H), 1.95 (br, 2H), 1.15-1.55 (br, 80H), 0.84-0.86 (br, 12H).

Synthesis of **PNDI-TPaT**. Use the same procedure as **PNDI-TPhT**. The used reagent and monomers were dibrominated NDI (0.10 g, 0.091 mmol), monomer **6** (0.052 g, 0.091 mmol), and anhydrous chlorobenznen (8 mL). A solid was collected after removing the solvent (82 mg, 76%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 8.81 (br, 2H), 7.86 (br, 2H), 7.30-7.45 (br, 4H), 4.08 (br, 4H), 1.97 (br, 2H), 1.15-1.35 (br, 80H), 0.82-0.88 (br, 12H).

Synthesis of **PNDI-TTzT**. Use the same procedure as **PNDI-TPhT**. The used reagent and monomers were dibrominated NDI (0.10 g, 0.091 mmol), monomer **8** (0.052 g, 0.091 mmol), and anhydrous chlorobenznen (8 mL). A solid were obtained after removing the solvent (86 mg, 80%). ^{1}HNMR (600 MHz, $CDCl_3$): δ= 8.81 (br, 2H), 7.20-7.30 (br, 2H), 7.10-7.20 (br, 2H), 4.10 (br, 4H), 1.98 (br, 2H), 1.16-1.32 (br, 80H), 0.81-0.87 (br, 12H).

Measurements and Characterizations

NMR spectroscopy wad performed on an Agilent VNMRS600 machine using $CDCl_3$ as the solvent. Thermogravimetric analysis (TGA) were conducted with a STA449F5 at a heating rate of 10°C/min under nitrogen flow. Differential scanning calorimetry (DSC) measurements were performed using TA Q2000 machine under nitrogen atmosphere with heating and cooling rate of 10 ^{o}C/min. UV-Vis-NIR absorption spectra were measured in chloroform solutions and films cast from onto quartz glass using Agilent Cary 5000 model spectrophotometer. Electrochemical cyclic voltammetry (CV) characterization was carried out in anhydrous acetonitrile solution (0.1 M tetra-n-butylammonium hexafluorophosphate) using a CHI 660D electrochemical workstation. The platinum (Pt) electrodes were used as both the working and auxiliary electrode. The Ag/Ag^+ electrode was used as the reference electrode. The gel permeation chromatography (GPC) measurements were carried out using a Waters Series 1525 binary HPLC pump and polystyrene and trichlorobenzene as the standard. Grazing-incidence-X-ray diffraction (GIXD) measurements were performed using 3C beeline at the Pohang Accelerator Laboratory (PAL) in Korea. The fabrication of sample for GIXD measurements was same as the devices. The atomic force microscopy (AFM) images of the thin films were obtained on a SPA300HV instrument in tapping mode.

OFET device fabrication

Bottom-gate/top-contact (BG/TC) OFETs devices were fabricated on a gate of *n*-doped Si with a 300 nm thick SiO_2 dielectric layer. A chloroform solution (~ 6 mg/mL) was dropped onto the octadecyltri-chlorosilane (OTS)-treated Si/SiO_2 and spin-coated at 3500 rpm for 40 s. The film thickness was about 80 nm. The polymer films were annealed in glove box. The Au source-drain electrodes were prepared by thermal evaporation. The OFET devices had a channel length (L) of 130 μm and a channel wide (W) of 760 μm. The devices were both characterized under vacuum and air conditions using a Keithley 4200 semiconductor parametric analyzer. Mobility (μ) was obtained using the following equation in the saturation regime: $I_d = (W/2L)Ci\mu(V_g\text{-}V_{th})$, where I_d is the drain current, C_i is the capacitance of the gate dielectric, V_g is the gate-source voltage and V_{th} is the threshold voltage.

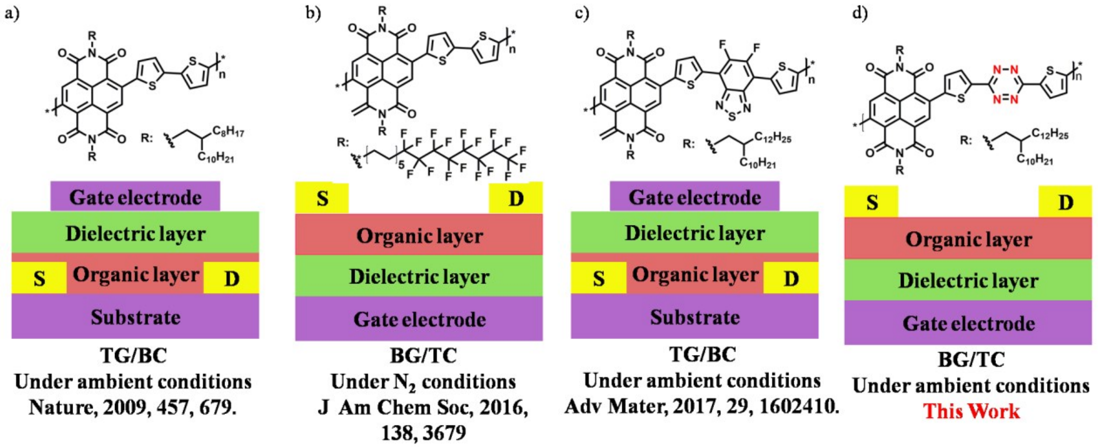

Fig. S1. The NDI-based polymers and the OFET device configuration.

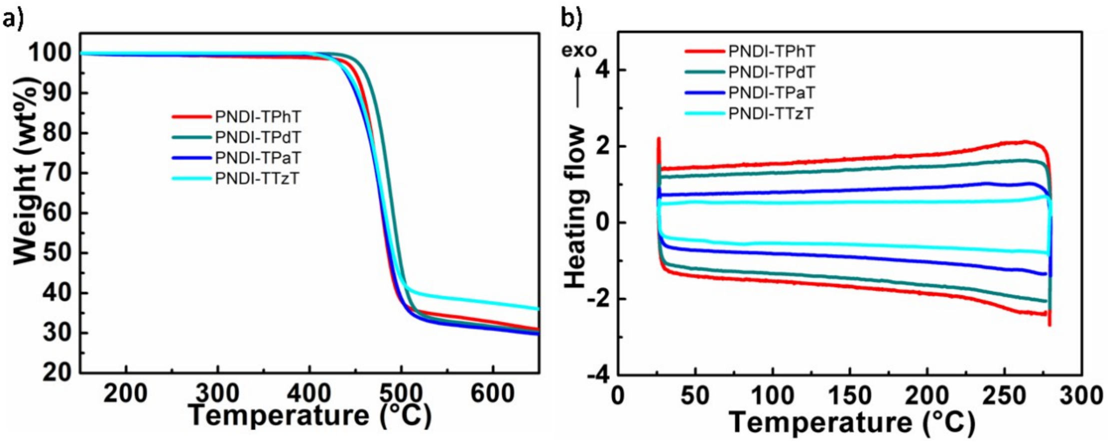

Fig. S2. Tg and DSC curves of NDI-based polymers.

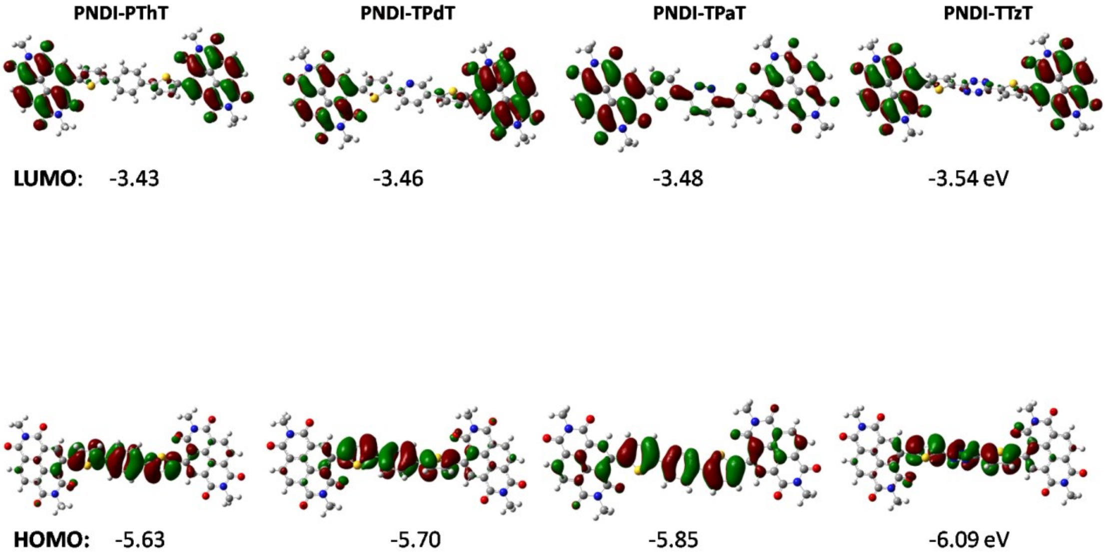

Fig. S3. The calculated energy levels using DFT calculations at the B3LYO/6-31G(d) level.

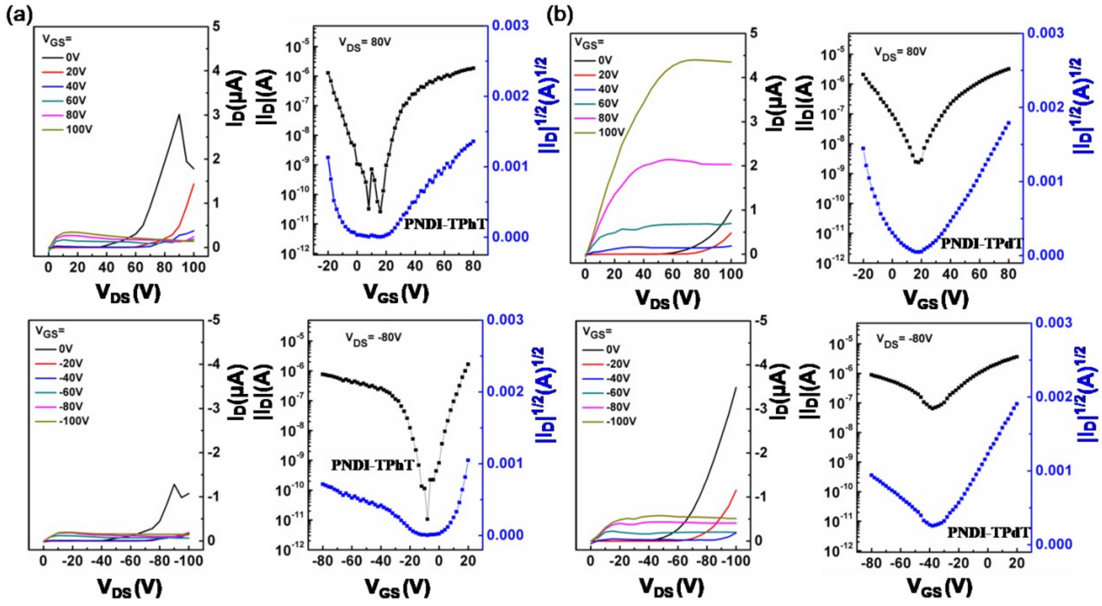

Fig. S4. The output and transfer curves of **PNDT-TPdT** and **PNDI-TPaT** based OFET devices. The devices were characterized in ambient conditions directly.

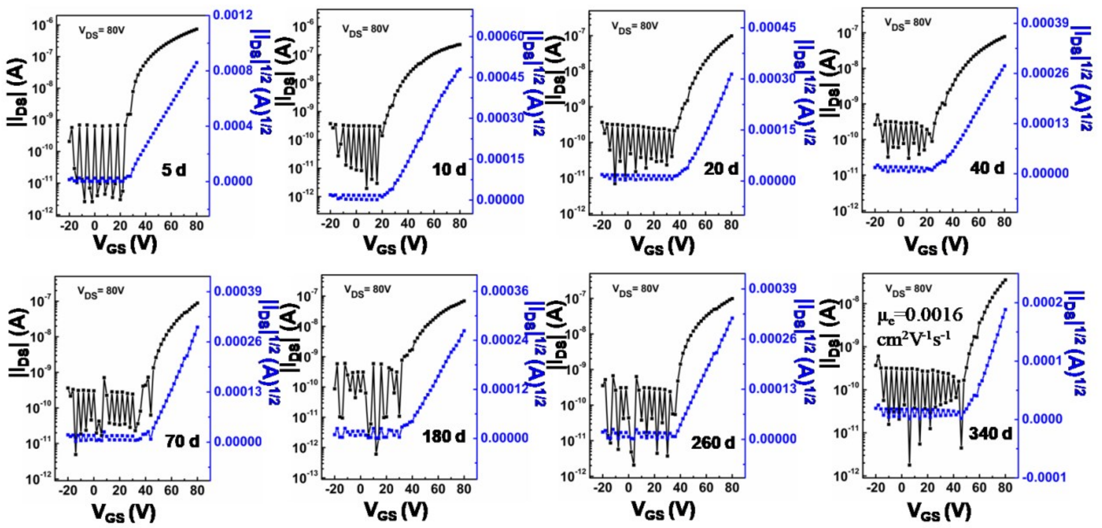

Fig. S5. The transfer curves of **PNDI-TTzT**-based devices under different days' of air exposure. The devices were characterized in ambient conditions directly.

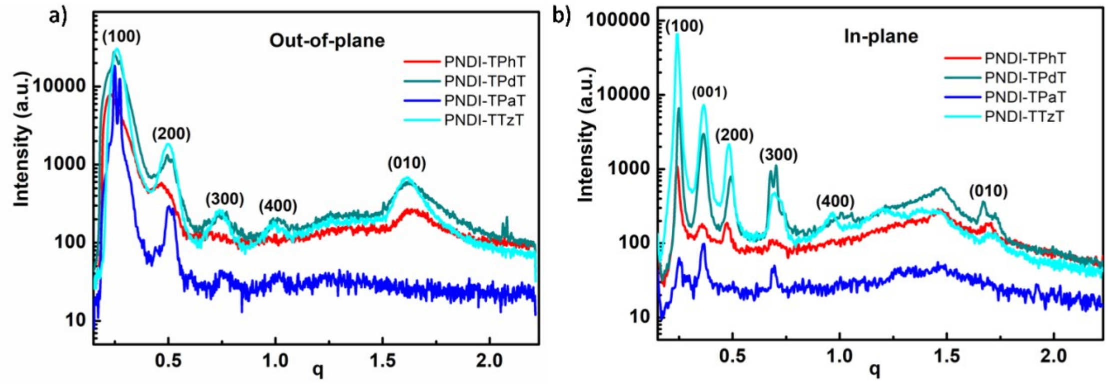

Fig. S6. Out-of-plane and in-plane line cuts of GIXD.

Table S1. The OFET performances of devices evaluated in vacuum conditions.

Polymer	Annealing temperature (°C)	*n*-channel			
		$\mu_{e,max}$ ($cm^2V^{-1}s^{-1}$)	$\mu_{e,avg}$ ($cm^2V^{-1}s^{-1}$)	V_{th} (V)	I_{on}/I_{off}
PNDI-TPhT	N/A	-	-	-	-
	180	0.026	0.024	15.00	4.55×10^5
	210	0.053	0.050	25.70	4.56×10^5
	240	0.027	0.025	18.60	2.36×10^5
PNDI-TPdT	N/A	0.014	0.013	5.91	1.48×10^5
	180	0.054	0.052	8.05	2.01×10^6
	210	0.059	0.057	9.53	2.13×10^6
	240	0.051	0.048	13.30	2.23×10^4
PNDI-TPaT	N/A	0.0018	0.0017	0.41	4.36×10^3
	180	0.0052	0.0045	1.77	3.81×10^4
	210	0.014	0.013	5.24	1.24×10^5
	240	0.0075	0.0071	3.97	1.33×10^5
PNDI-TTzT	N/A	0.073	0.066	5.67	7.71×10^4
	180	0.041	0.038	2.31	6.19×10^5
	210	0.058	0.052	9.17	1.04×10^5
	240	0.046	0.045	8.05	1.02×10^5

Table S2. The OFET performances of fresh devices characterized in air conditions.

Annealing temperature(^{o}C)	n-channel			p-channel		
	$\mu_{e,max}$ / $\mu_{e,avg}$ ($cm^2V^{-1}s^{-1}$)	V_{th}(V)	I_{on}/I_{off}	$\mu_{h,max}$ / $\mu_{h,avg}$ ($cm^2V^{-1}s^{-1}$)	V_{th}(V)	I_{on}/I_{off}
PNDI-TPhT						
N/A	-	-	-	-	-	-
180	0.0053 / 0.0048	33.60	4.24×10^3	0.0022 / 0.0018	-14.60	2.10×10^3
210	0.015 / 0.009	14.80	1.93×10^3	0.010 / 0.0083	-6.16	4.01×10^3
240	0.0050 / 0.0045	53.50	2.66×10^3	0.0035 / 0.0027	-20.60	1.29×10^3
PNDI-TPdT						
N/A	0.0060 / 0.0054	30.60	3.61×10^2	0.0042 / 0.0033	-25.90	2.68×10^2
180	0.012 / 0.009	26.30	5.08×10^2	0.0082 / 0.0078	-21.20	51.60
210	0.040 / 0.033	28.00	1.13×10^3	0.0094 / 0.0084	-21.00	13.70
240	0.0070 / 0.0060	18.80	5.71×10^2	0.0067 / 0.0059	-8.30	35.30
PNDI-TPaT						
N/A	0.0001 / 0.0001	24.40	7.57×10^2			
180	0.0021 / 0.0016	26.60	9.13×10^3			
210	0.0057 / 0.0050	38.40	2.46×10^4			
240	0.0049 / 0.0042	38.10	1.39×10^4			
PNDI-TTzT						
N/A	0.053 / 0.049	16.10	1.34×10^4			
180	0.020 / 0.016	13.20	2.36×10^5			
210	0.025 / 0.022	19.10	8.41×10^4			
240	0.021 / 0.014	13.10	9.52×10^4			

Table S3. Crystallographic parameters for polymer films.

Polymer	**Edge-on**				**Faced-on**			
	q^{100}	**d^{100}**	**q^{010}**	**d^{010}**	**q^{100}**	**d^{100}**	**q^{010}**	**d^{010}**
	$Å^{-1}$	**Å**	**$Å^{-1}$**	**Å**	**$Å^{-1}$**	**Å**	**$Å^{-1}$**	**Å**
PNDI-TPhT	0.236	26.61	1.631	3.85	0.240	26.17	1.695	3.70
PNDI-TPdT	0.246	25.53	1.623	3.87	0.249	25.22	1.673	3.75
PNDI-TPaT	0.249	25.22	-	-	0.251	25.02	-	-
PNDI-TTzT	0.258	24.34	1.620	3.88	0.242	25.95	1.699	3.70

NMR

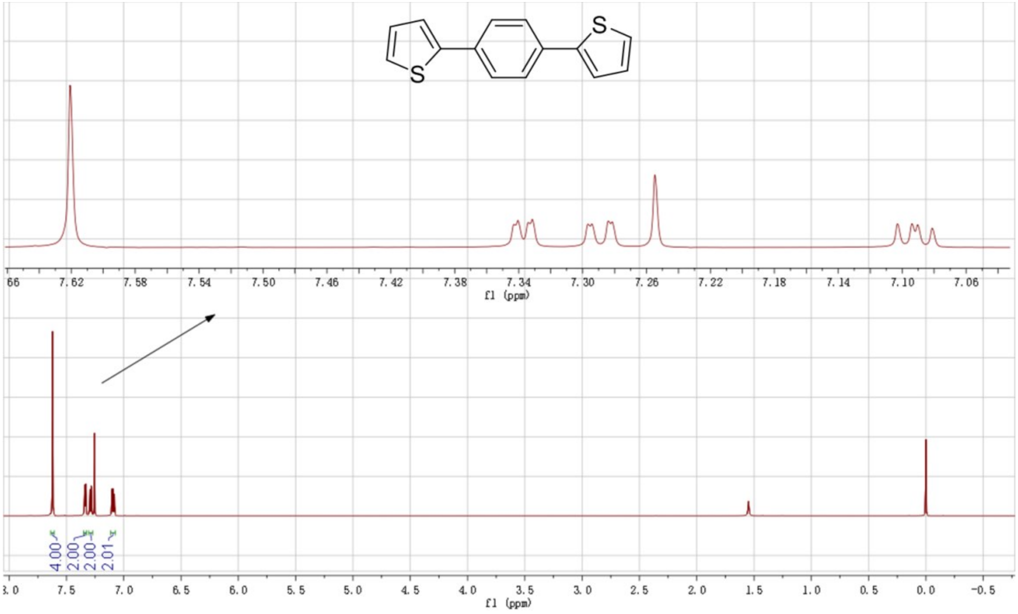

Fig. S7. The ^{1}H spectrum of compound **1** in $CDCl_3$.

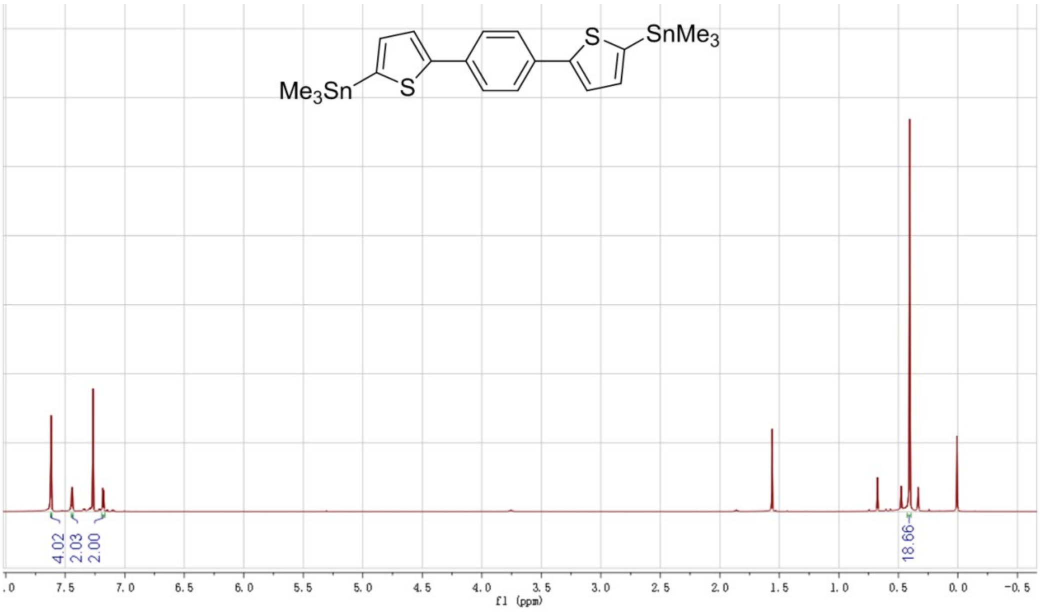

Fig. S8. The ^{1}H spectrum of monomer **2** in $CDCl_3$.

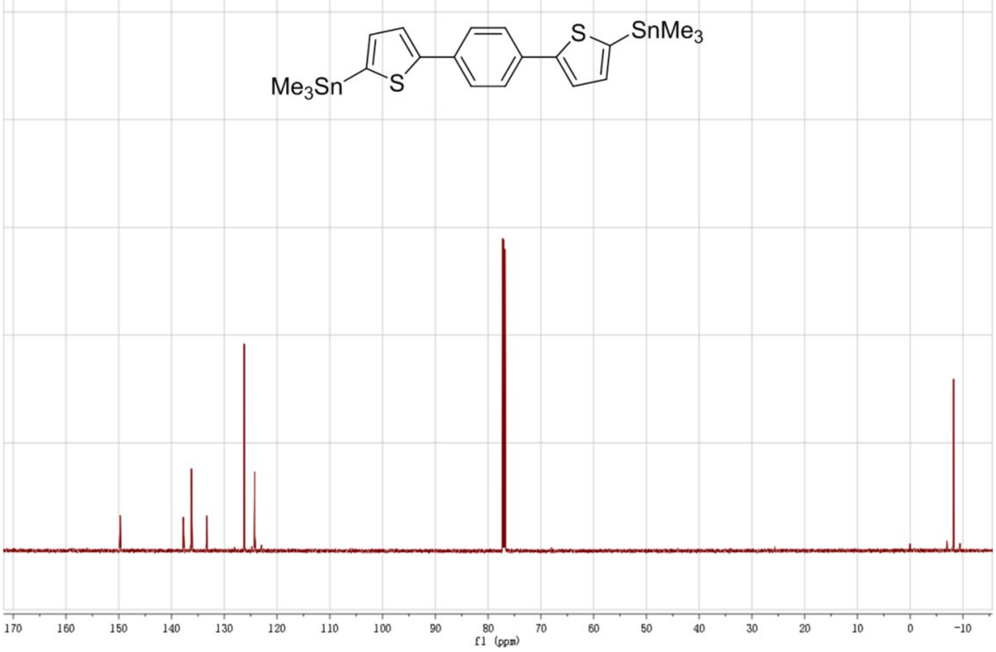

Fig. S9. The ^{13}C spectrum of monomer **2** in CDCl$_3$.

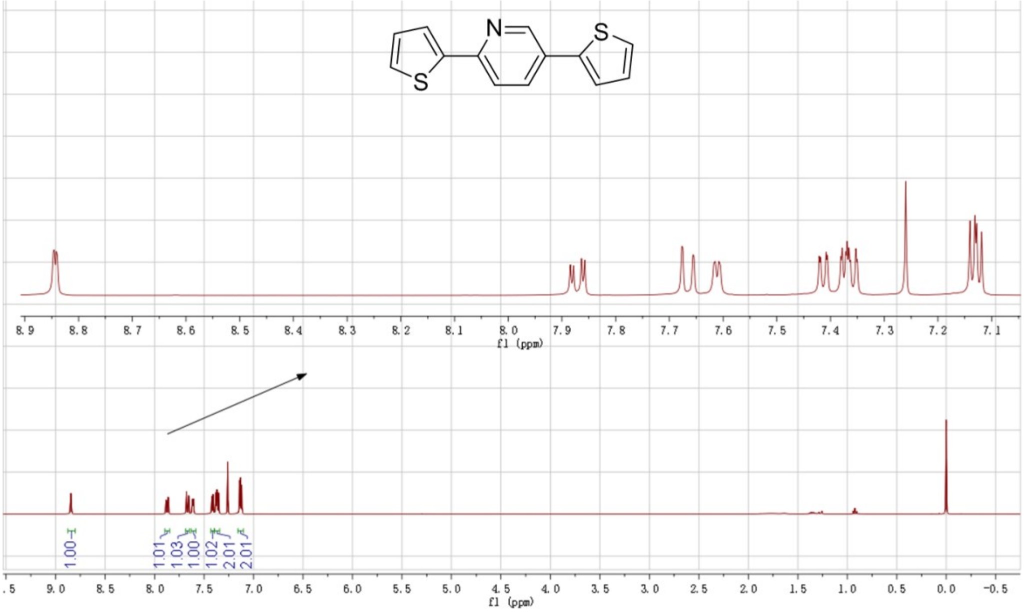

Fig. S10. The ^{1}H spectrum of compound **3** in CDCl$_3$.

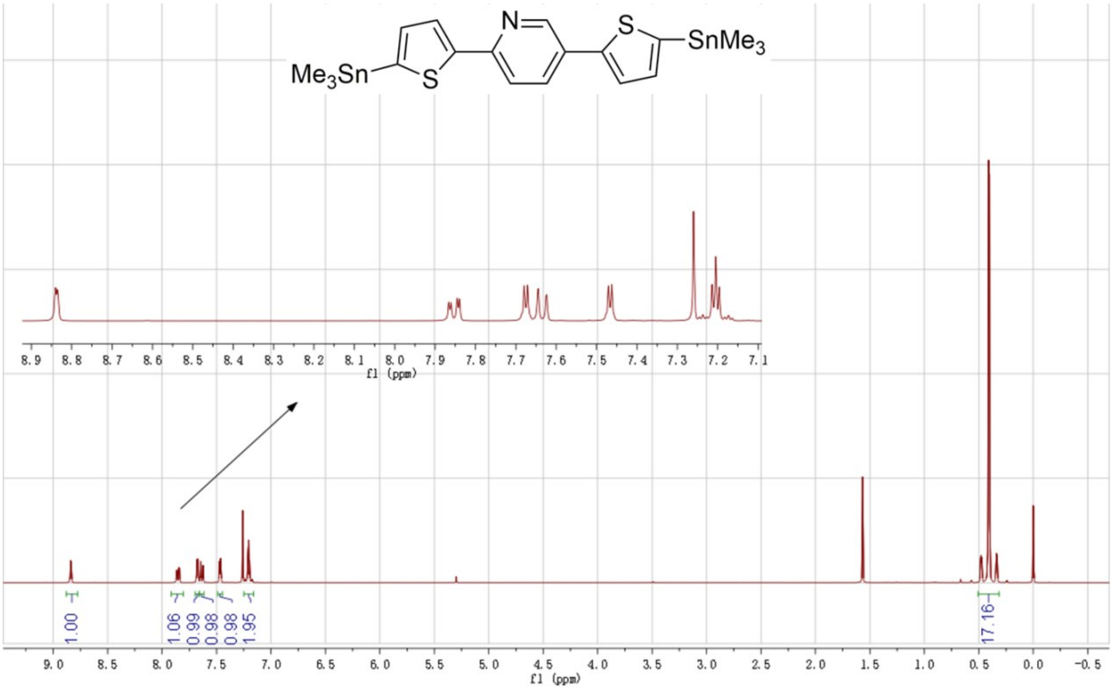

Fig. S11. The ^{1}H spectrum of monomer **4** in $CDCl_3$.

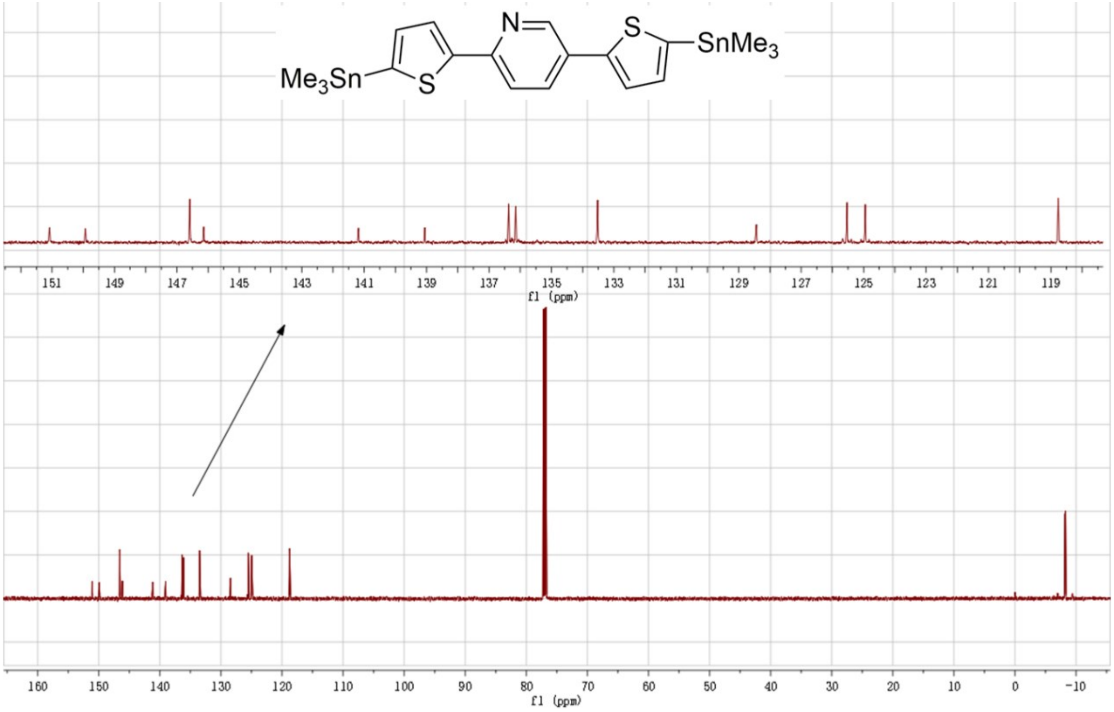

Fig. S12. The ^{13}C spectrum of monomer **4** in $CDCl_3$.

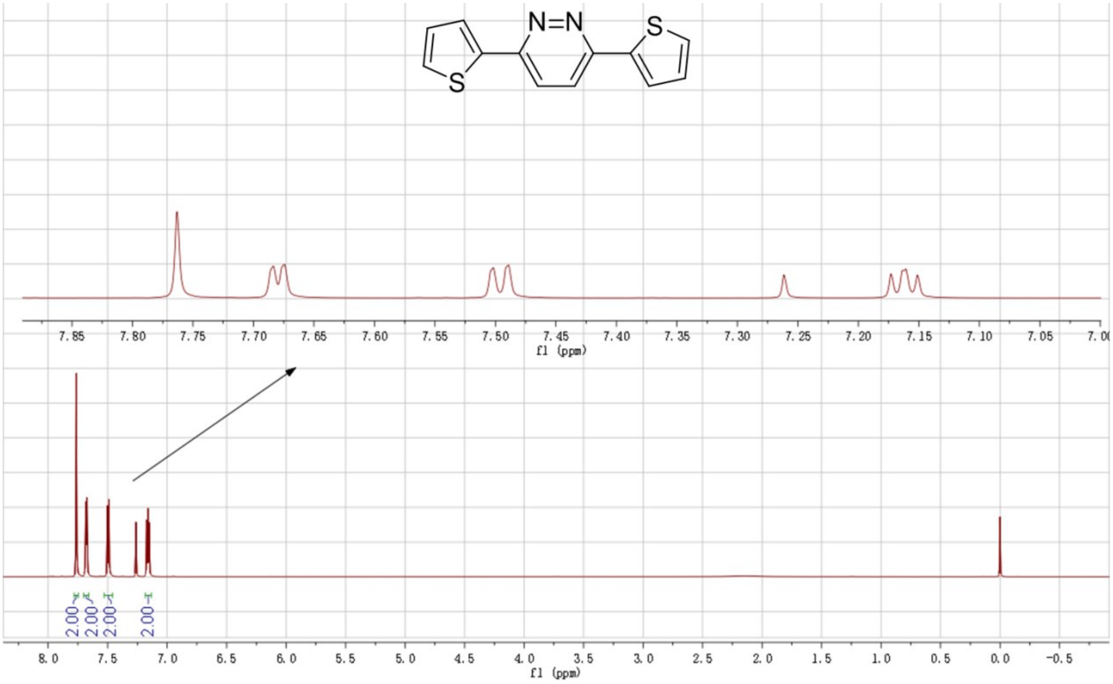

Fig. S13. The ^{1}H spectrum of compound **5** in $CDCl_3$.

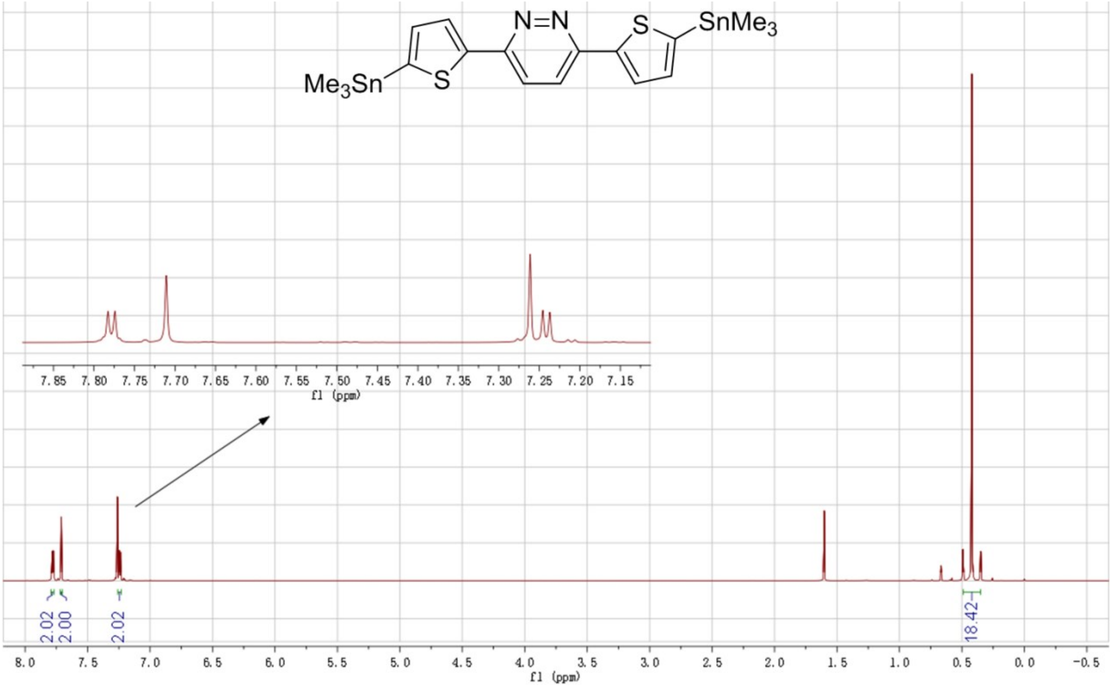

Fig. S14. The ^{1}H spectrum of monomer **6** in $CDCl_3$.

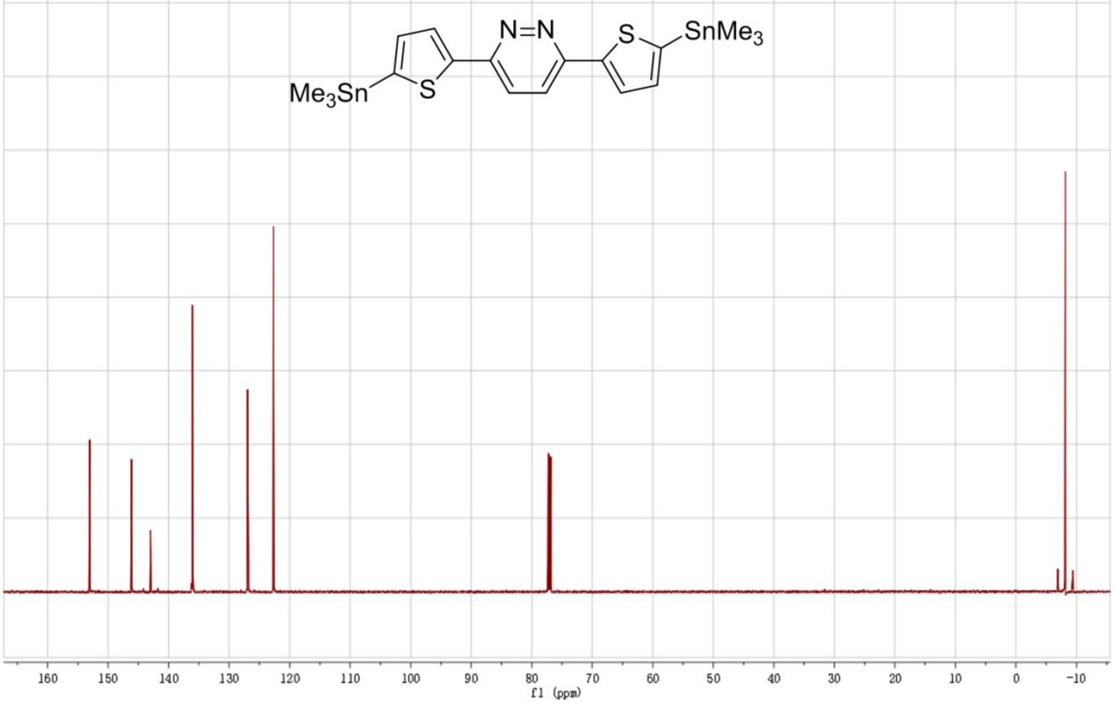

Fig. S15. The ^{13}C spectrum of monomer **6** in CDCl$_3$.

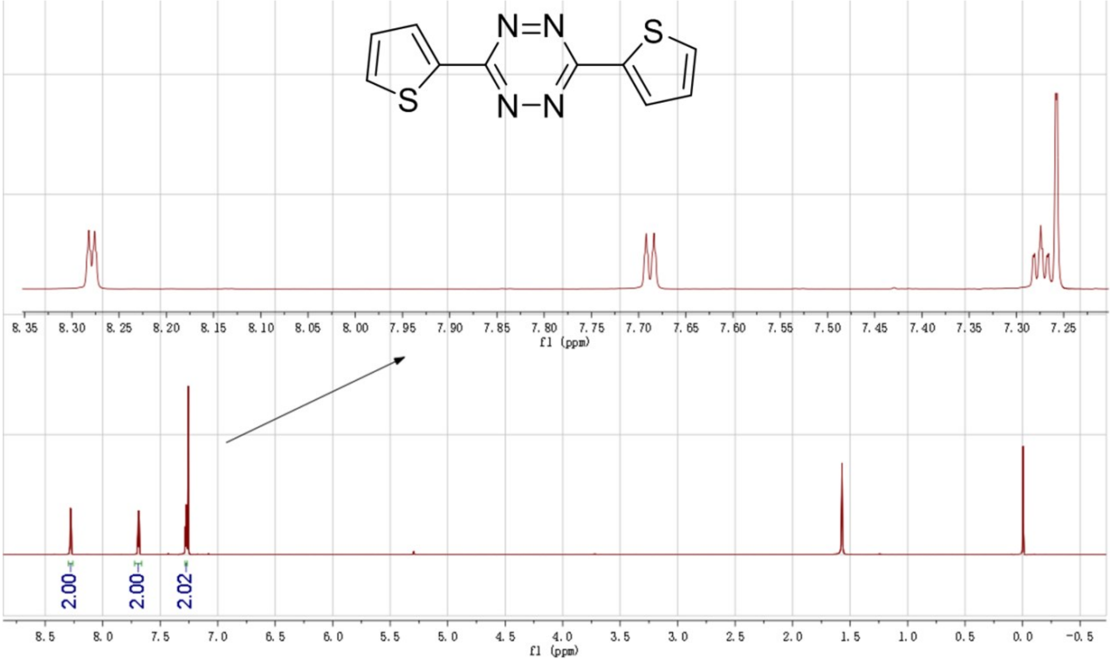

Fig. S16. The ^{1}H spectrum of compound **7** in CDCl$_3$.

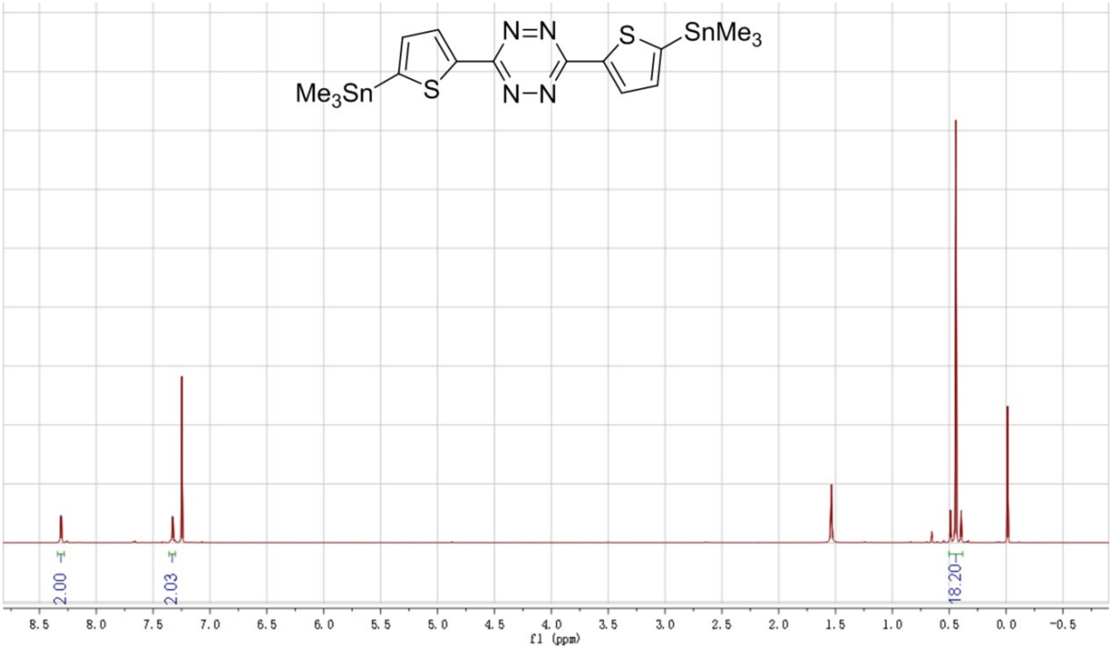

Fig. S17. The ^{1}H spectrum of monomer **8** in CDCl$_3$.

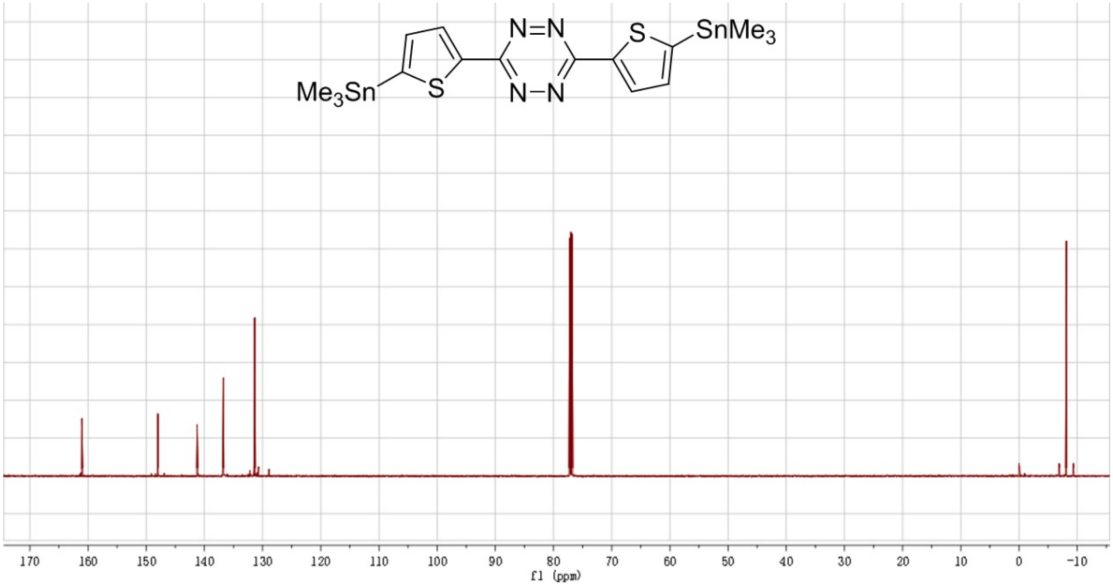

Fig. S18. The ^{13}C spectrum of monomer **8** in CDCl$_3$.

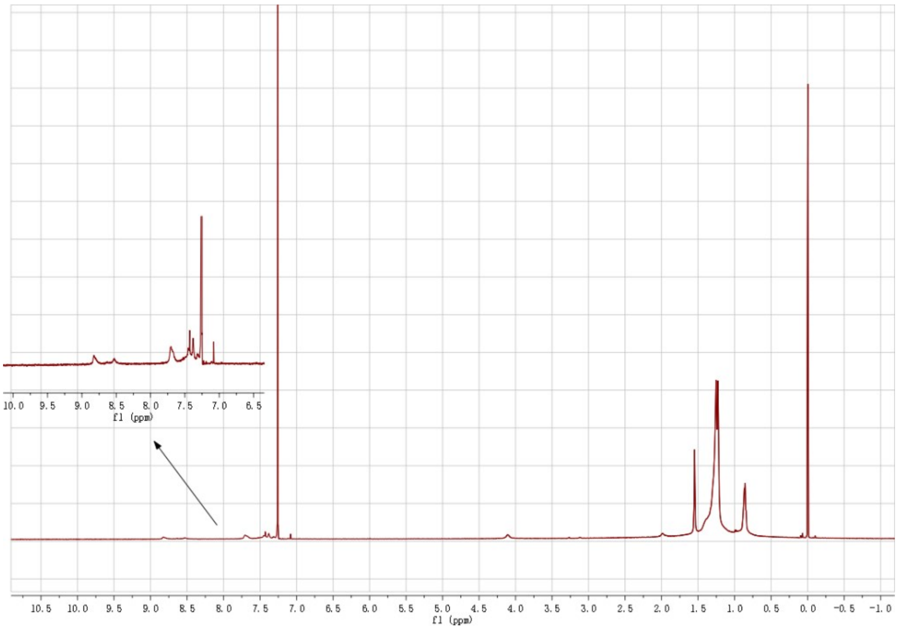

Fig. S19. The ^{1}H spectrum of **PNDI-TPhT** in $CDCl_3$.

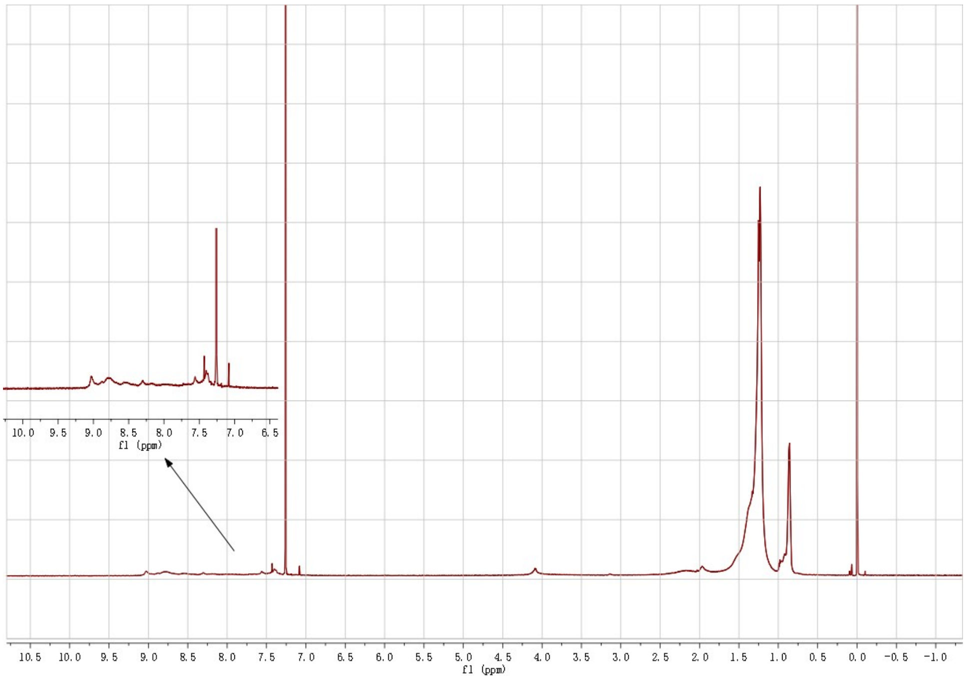

Fig. S20. The ^{1}H spectrum of **PNDI-PTdT** in $CDCl_3$.

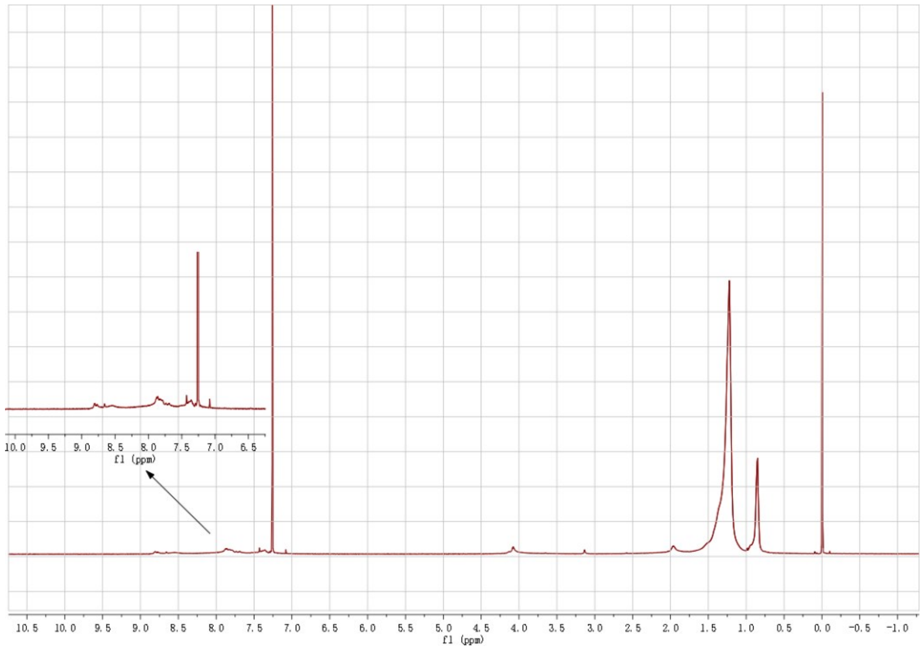

Fig. S21. The ^{1}H spectrum of **PNDI-TPaT** in $CDCl_3$.

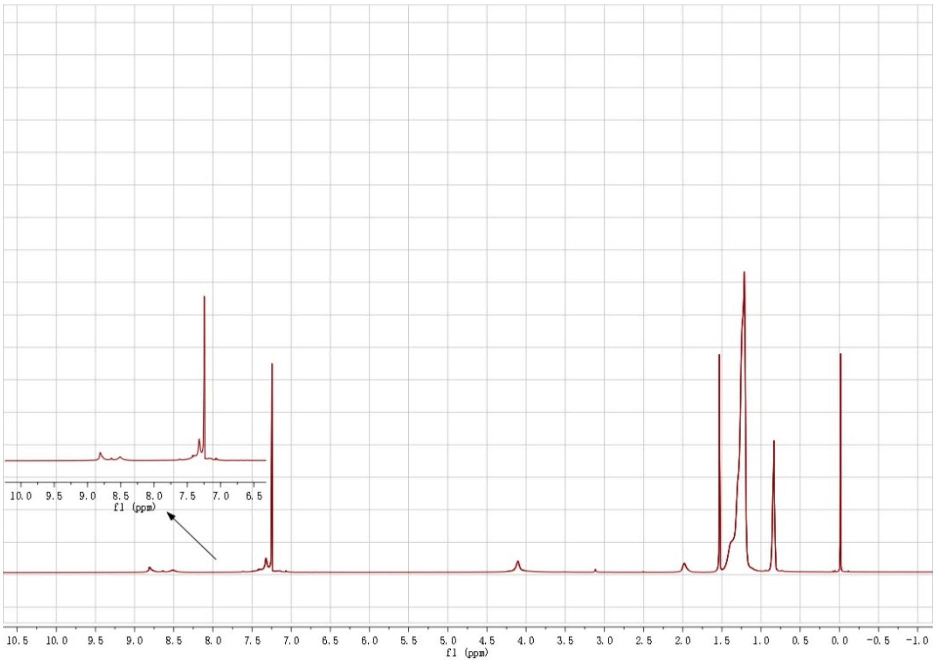

Fig. S22. The ^{1}H spectrum of **PNDI-TTzT** in $CDCl_3$.

S1. G. Zhang, J. Zhang, G. Ding, J. Guo, H. Lu, L. Qiu, W. Ma, Polymer, 2016, 93, 213-220.