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Supporting Information

Iptycene Substitution Enhances the Electrochemical Activity and Stability of Polyanilines

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General Methods

Gel Permeation Chromatography. GPC was performed on a Waters HPLC system consisting of two Shodex GPC columns (KF-805 and KF-803) arranged in series and a photodiode array (PDA) detector using N-methyl-2-pyrrolidone (NMP) with 0.1% w/v LiBr as the eluent at 50^{o}C with a flow rate of 0.5 mL/min. Molecular weight and polydispersity data are reported relative to polystyrene standards.

Elemental Analysis. Elemental analysis data were obtained on a elementar Vario EL cube type (for NCSH, German) instrument and a thermo Flash 2000 type (for NCHS, Italy) instrument. The amount of samples for analysis was ca. 2.5 mg. The three elements N, C, and H were determined for each polymer samples. Selected polymers (PANI and P-40) were also analyzed for the content of sulfur, which might result from residual APS oxidizing reagent or from sulfonation of the backbone,[1] and the results show that the component of S is negligible (< 0.8% for PANI and < 0.3% for P-40).

FT-IR Measurements. Fourier transform infrared (FT-IR) spectra were collected on a Thermo Scientific Nicolet iS5 FT-IR spectrometer by using a KBr pellet method. The concentration of the samples in KBr was about 1 to 2%.

NMR Measurement. Solution-phase 1D and 2D NMR spectra were recorded by Bruker AVIII-400 MHz or Bruker AVIII-500 MHz. Solid-state ^{13}C-NMR spectra were determined at a MAS rotation frequency of 20 - 23 kHz, employing around 100 mg of material by Bruker AVIII-600 MHz.

Electron Microscopy. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-7600F field emission scanning electron microscopy with INCA X-Max EDS, and transmission electron microscopy (TEM) images were taken with a EOL JEM-1200EX II transmission electron microscopy. The samples for SEM and TEM were dispersed in deionized water, and use drop-casting method onto a quartz glass and a Formvar/Carbon film on Copper 200 mesh grids, respectively.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed on a TA Instrument TGA2950 thermal analysis instrument in nitrogen atmosphere with a heating rate of 10^{o}C/min from 40^{o}C to 800^{o}C. The amount of samples for analysis was about 3 to 4 mg.

Conductivity Measurements. The conductivity of polymers was determined by a four-point probe method for a 13 mm diameter pellet obtained by pressing the materials with 7 tons of force.

Electrochemical Measurements. All the electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge-discharge cycling, and electrochemical impedance spectroscopy (EIS), were recorded on a CHI 6114A electrochemical instrument and carried out in a three-electrode system, consisting of a glassy carbon working electrode (GCE) with working area of 0.071 cm^2, a Ag/Ag^+ reference electrode, and a platinum wire counter electrode, in acetonitrile with 0.1 M $(NBu_4)BF_4$ and $HBF_4{\cdot}OEt_2$ as the electrolyte. The working electrodes were fabricated with 36 μg of samples by drop-casting method and use 1 μL of 0.5% Nafion® 117 solution in ethanol as binder. The potential range for the CV and galvanostatic charge-discharge experiments was -0.2−1.2 V and 0.2−1.0 V, respectively. EIS was tested in the frequency range from 10 MHz to 0.1 Hz at the open circuit potential.

DFT Optimization. DFT calculations were performed using *Gaussian 09*[2] program package by a density functional theory method with the B3LYP functional,[3] and 6-31G++ basis sets were employed. The vibration analyses were carried out for the optimized geometries at the same computational level to ensure that the obtained structures correspond to a minimum.

Materials and Synthesis

Materials. The synthesis of compound **1** has been reported.[4] All the solvents and reagents for synthesis were reagent grade and used as received unless otherwise stated. Aniline was distilled with zinc dust under reduced pressure and stored at 4°C in brown bottles in inert atmosphere before use.

Synthesis of 2. A mixture of **1** (166 mg 0.36 mmol), Pd_2dba_3 (65 mg, 0.07 mmol), tri-*tert*-butylphosphine (42 mg, 0.44 mmol), sodium *tert*-butoxide (42 mg, 0.44 mmol) and 1-bromo-4-nitrobenzene (23 mg, 1.16 mmol) were refluxed in 6 mL nitrogen-bubbled 1,4-dioxane for 16 h under a nitrogen atmosphere. The mixture was filtered through celite, diluted with CH_2Cl_2 and washed with water. The organic layer was concentrated and further purification was carried by column chromatography with CH_2Cl_2/hexane/ethyl acetate (2:4:1) as eluent to afford yellow solid of **2** with a yield of 51% (130 mg). mp >

300 ^{o}C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.46 (s, 4H), 6.17 (s, 2H), 6.54 (d, *J* = 8.6 Hz, 4H), 6.92-6.94 (m, 8H), 7.12-7.15 (m, 8H), 8.16 (d, *J* = 8.6 Hz, 4H); $^{13}C\{^{1}H\}$NMR (125 MHz, $CDCl_3$) δ: 49.6, 112.8, 123.9, 125.6, 126.6, 128.0, 139.8, 142.8, 144.2, 152.3; IR (KBr): 3443, 3387, 2546, 2967, 2921, 2850, 1636, 1598, 1513, 1497, 1478, 1458, 1323, 1307, 1266, 1112, 835, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{46}H_{30}N_4O_4$ ($[M]^+$): 702.2262, found: 702.2244.

Synthesis of PAT. To a stirred solution of compound **2** (90 mg, 0.13 mmol) in ethyl acetate (2.5 mL) were added tin(II) chloride dihydrate (87 mg, 0.384 mmol) and concentrated HCl (5 drops). The mixture was stirred at 90^{o}C under N_2 for 24 h. After cooling, excess ethyl acetate was added and precipitate formed. The residue was filtered and washed by 1 M HCl and dried under vacuum to afford pale yellow solid of **PAT** with a yield of 80% (66 mg). mp > 300^{o}C; ^{1}H-NMR, (400 MHz, CD_3OD) δ: 5.54 (s, 4H), 6.51 (d, *J* = 8.6 Hz, 4H), 6.85-6.88 (m, 8H), 7.09-7.11 (m, 8H), 7.13 (d, *J* = 8.6 Hz, 4H); $^{13}C\{^{1}H\}$NMR (125 MHz, CD_3OD) δ: 51.1, 115.5, 121.1, 124.6, 124.8, 126.0, 130.5, 143.3, 146.8, 150.5; IR (KBr) 3325, 2972, 2579, 1714, 1600, 1514, 1455, 1324, 1309, 1269, 111.6, 840, 753 cm^{-1}; FAB-HRMS calcd for $C_{46}H_{34}N_4$ ($[M\text{-}2HCl]^+$): 642.2778, found: 642.2763.

General synthesis of P-*n*. Take the synthesis of P-20 as example. The solution of compound PAT 0.0643 g (0.1 mmol) and aniline (0.186 g, 2 mmol) in 10 mL of 1 M HCl, THF, and methanol (v/v/v: 2/1/1) mixed solvents was prepared and placed in an ice-salt bath. The solution was added slowly (in a period of 5 min) with the solution of ammonium peroxydisulfate (APS, 0.513 g, 2.25 mmol) in 5 mL of 1 M HCl, THF, and methanol (v/v/v: 2/1/1) mixed solvents. Then, the ice-salt bath was removed and the mixed solution was stirred at room temperature for 24 h. The precipitates were filtered and washed sequentially by distilled water, methanol, and acetone to remove the unreacted reactants and oligomers and to afford the green pristine PANIs in the form of emeraldine salt. The polymer was dedoped with 1 M ammonia for 4 h and then filtered and washed with methanol and dichloromethane to form dark blue solid (emeraldine base) of P-20 with a yield of 61%. Redoping of the emeraldine base was carried out by stirring it in 1 M aqueous HCl for 5 h. The loadings of compound PAT for the synthesis of P-20, P-40 and P-80 are 0.0643 g (0.1 mol), 0.0321 g (0.05 mmol), and, 0.0161 g (0.025 mmol) respectively. The yields of P-20, P-40 and P-80 are 61%, 69% and 72%, respectively.

Synthesis of Pani. The solution of aniline (0.186 g, 2 mmol) in 5 mL of 1 M HCl, THF, and methanol (v/v/v: 2/1/1) mixed solvents was placed in an ice-salt bath and added slowly with the solution of ammonium peroxydisulfate (APS, 0.513 g, 2.25 mmol) in 5 mL of 1 M HCl, THF, and methanol (v/v/v: 2/1/1) mixed solvents. Then, the ice bath was removed and the mixture was stirred at room temperature for 24 h. The precipitated product was filtered and washed by distilled water, methanol, and acetone to afford the green polymer (emeraldine salt). The polymer was dedoped with 1 M ammonia for 4 h and then filtered and washed to form dark blue solid (emeraldine base) of PANI with a yield of 80%. mp > 350^{o}C; IR (KBr) 3286, 3027, 1591, 1496, 1379, 1305, 1165, 1008, 955, 830, 745, 698 cm^{-1}.

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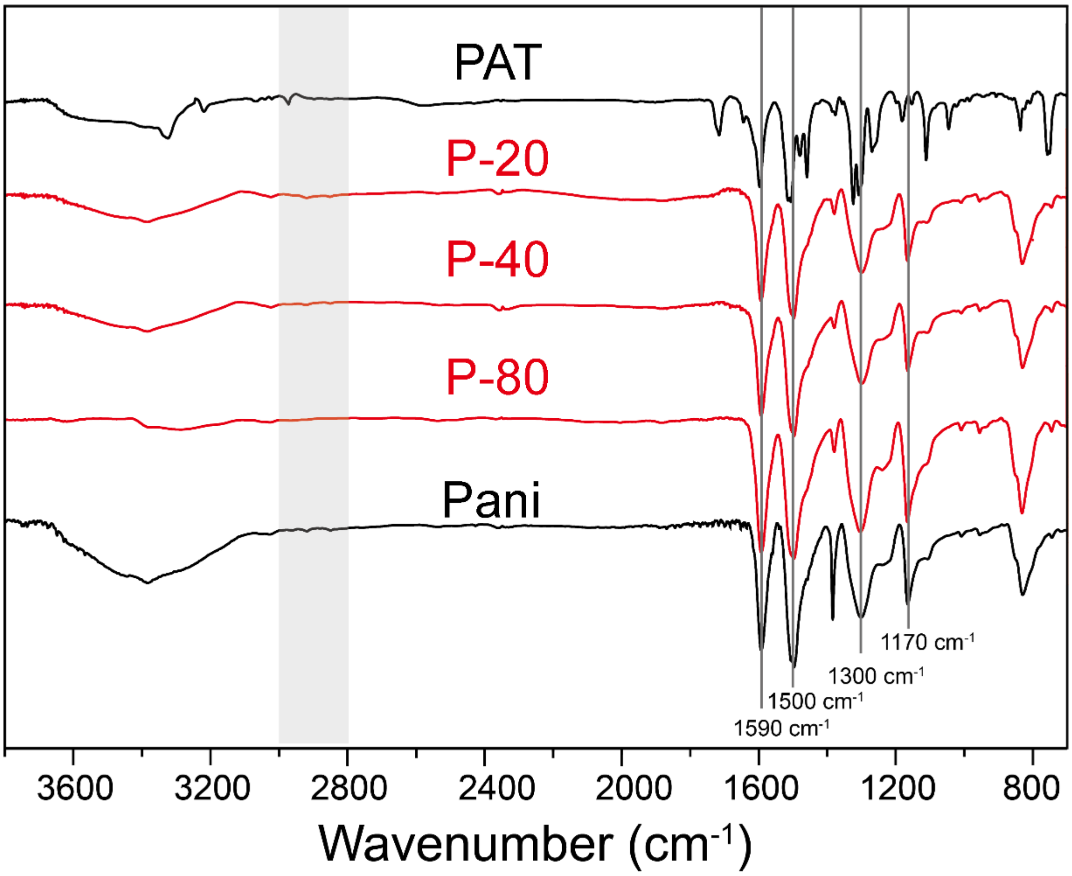
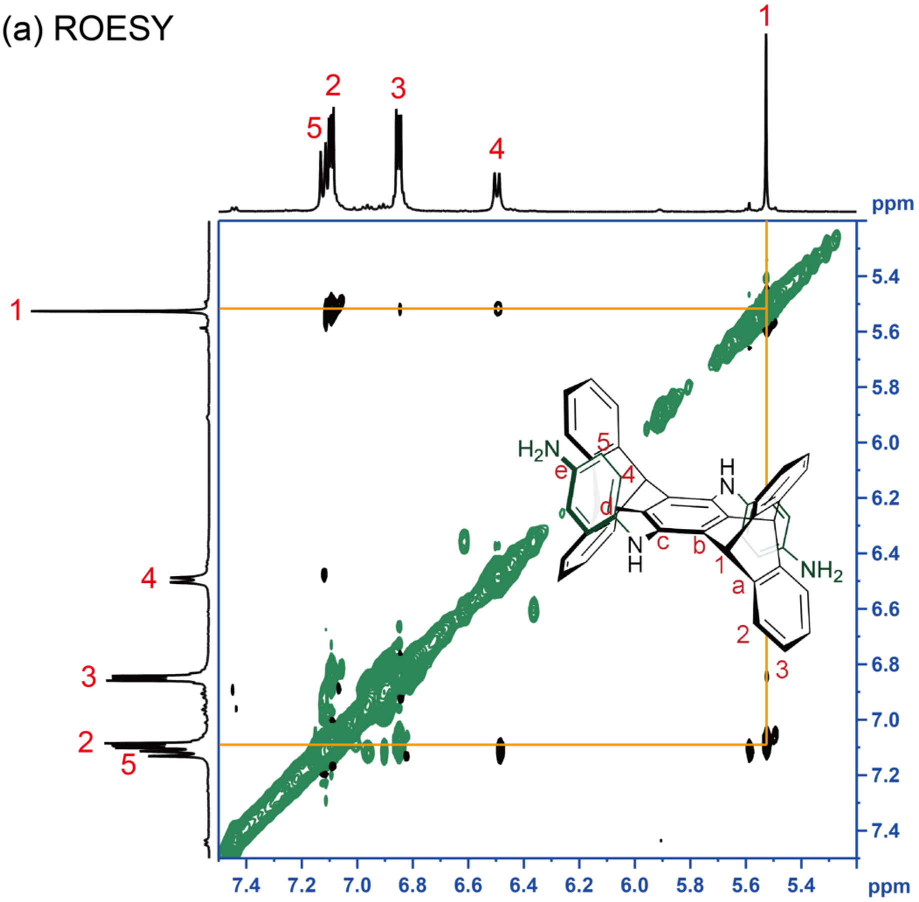
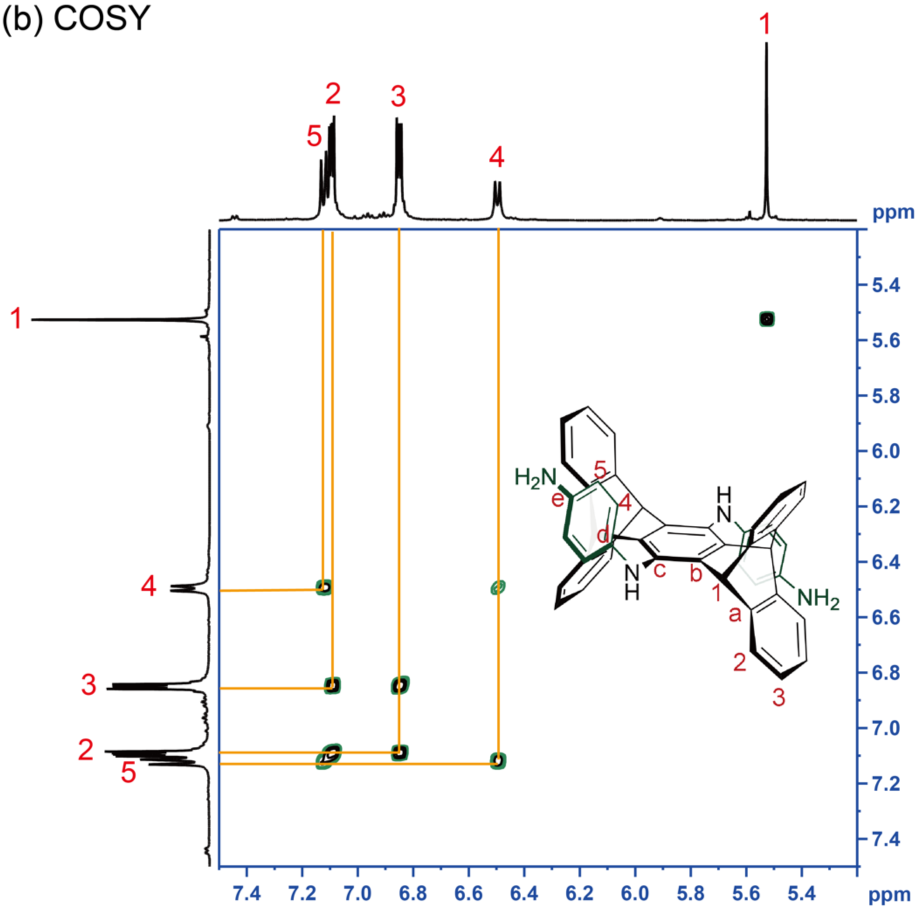


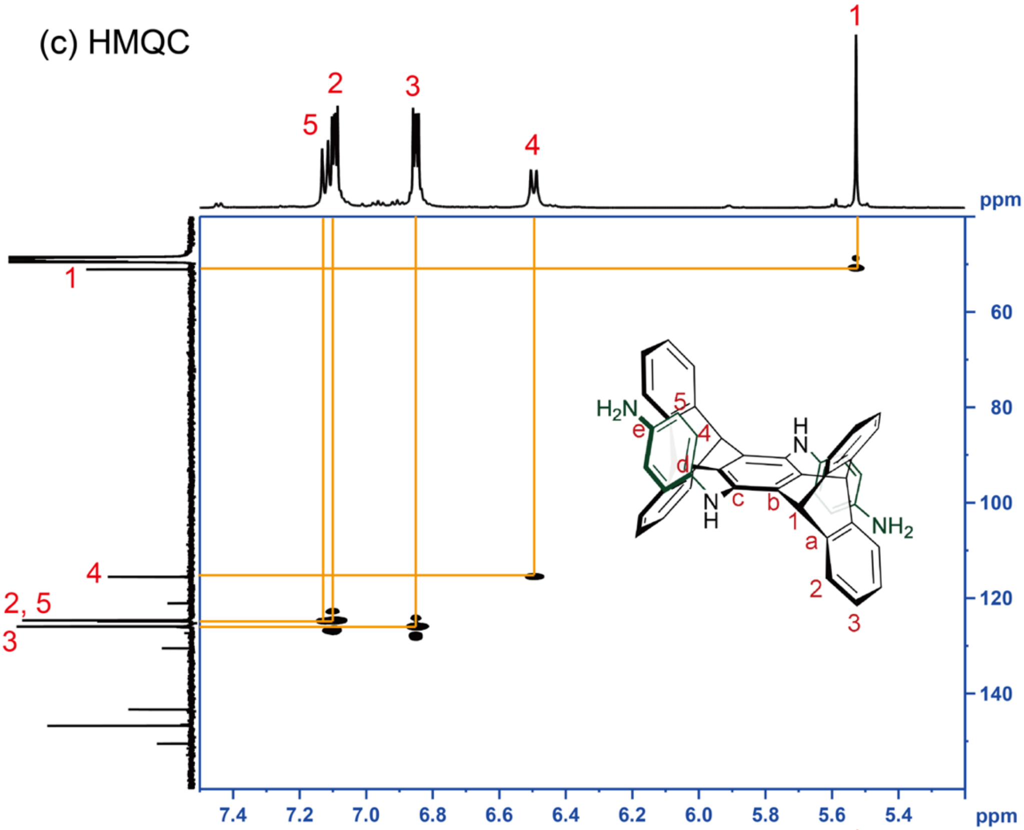
Fig. S1 IR spectra (KBr) for PAT, P-20, P-40, P-80 and Pani in same intensity scale. Polymers are in the dedoped form.

(a) ROESY



(b) COSY





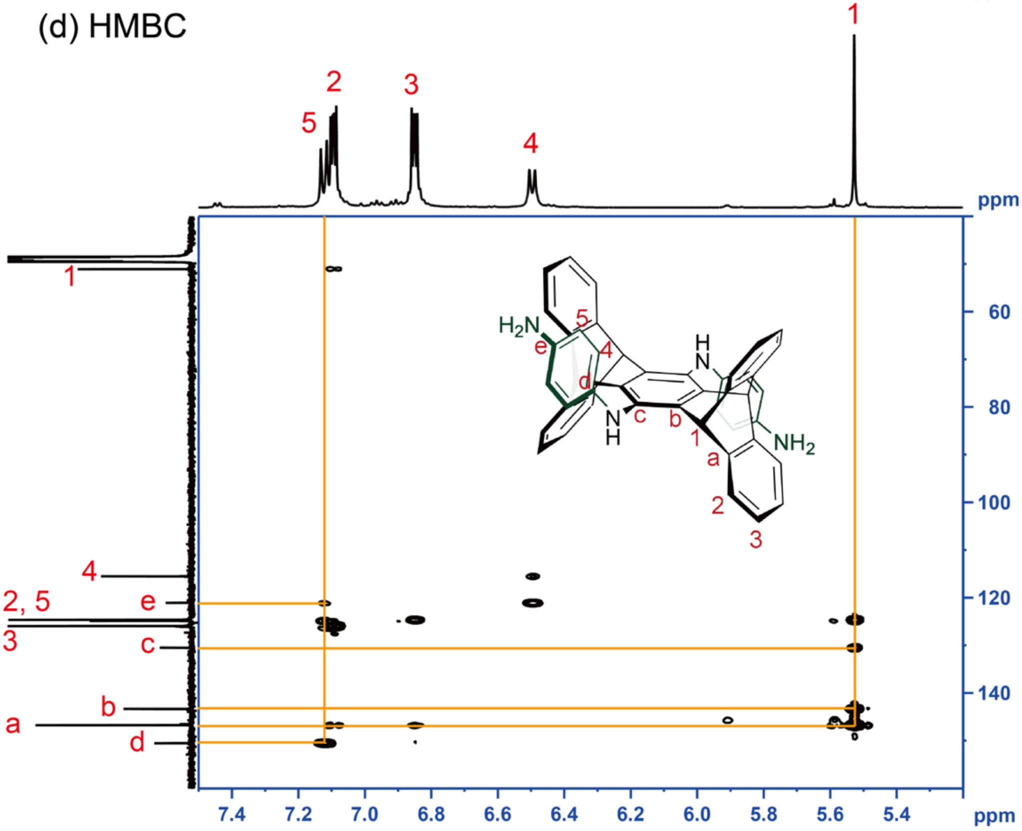


Fig. S2 (a) ROESY spectrum, (b) COSY spectrum, (c) HMQC spectrum, and (d) HMBC spectrum of compound PAT in CD_3OD.

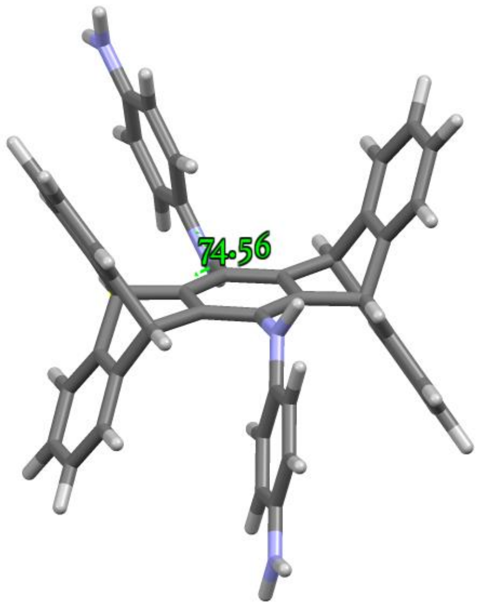


Fig. S3 DFT-optimized structure of compound PAT.

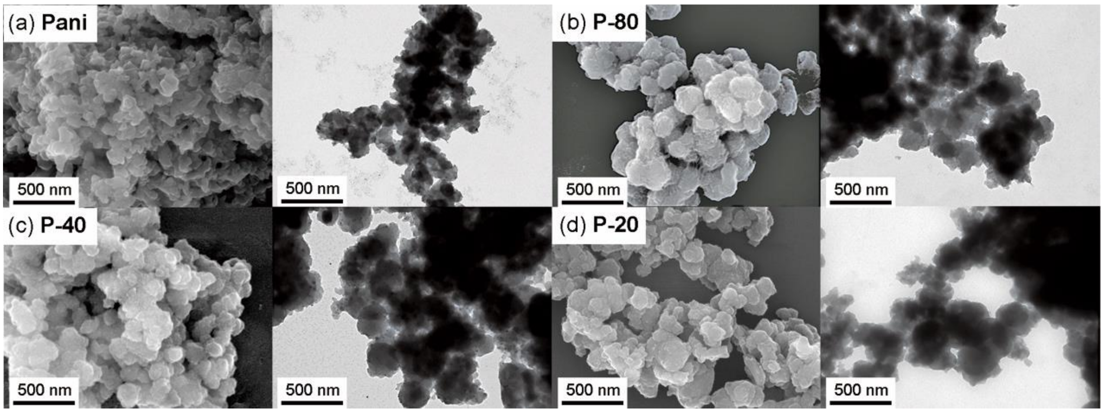


Fig. S4 SEM images (left) and TEM images (right) of Pani and P-*n*.

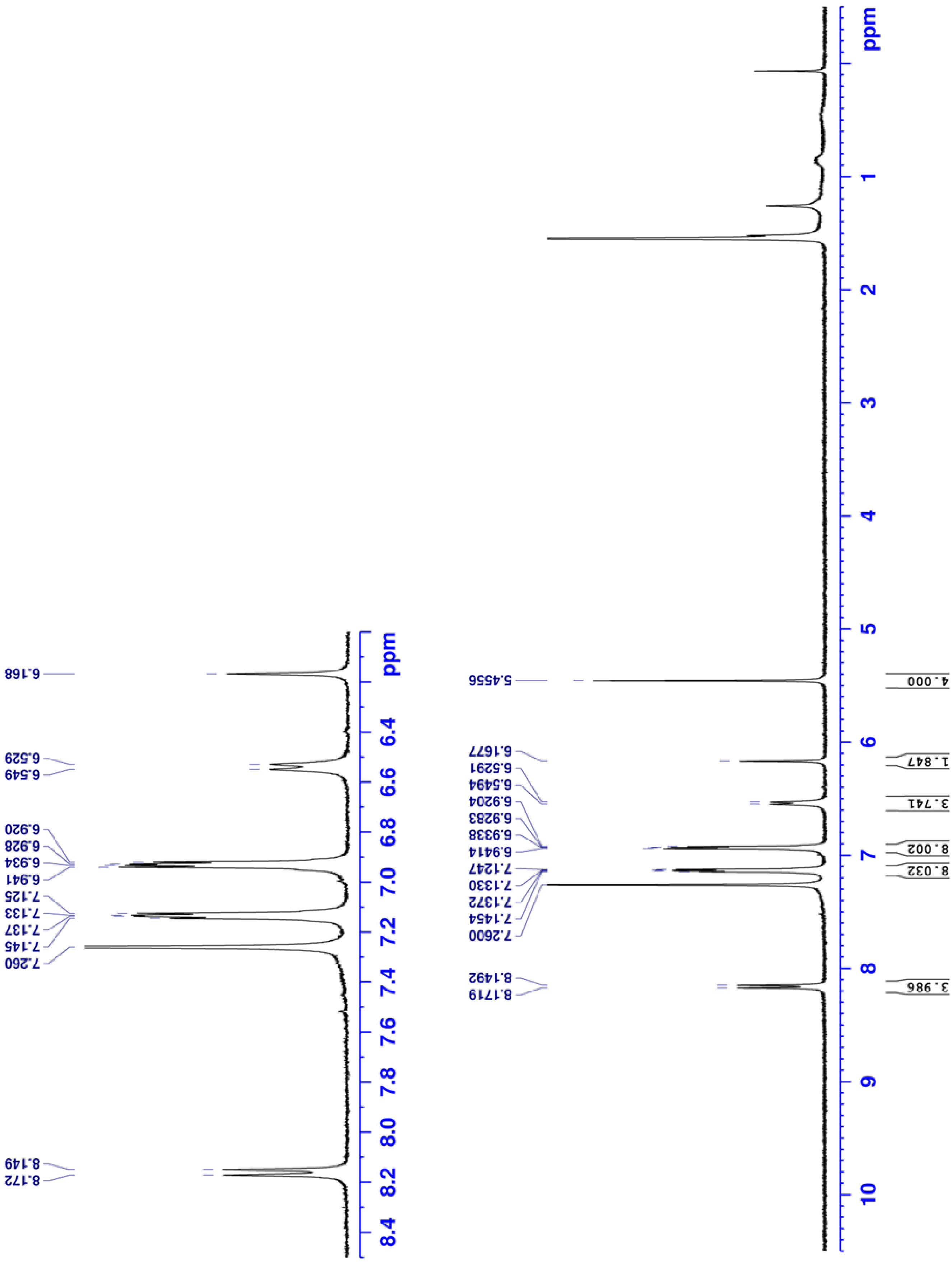


Fig. S5 ^{1}H NMR spectrum of **2** (400 MHz, CDCl$_3$).

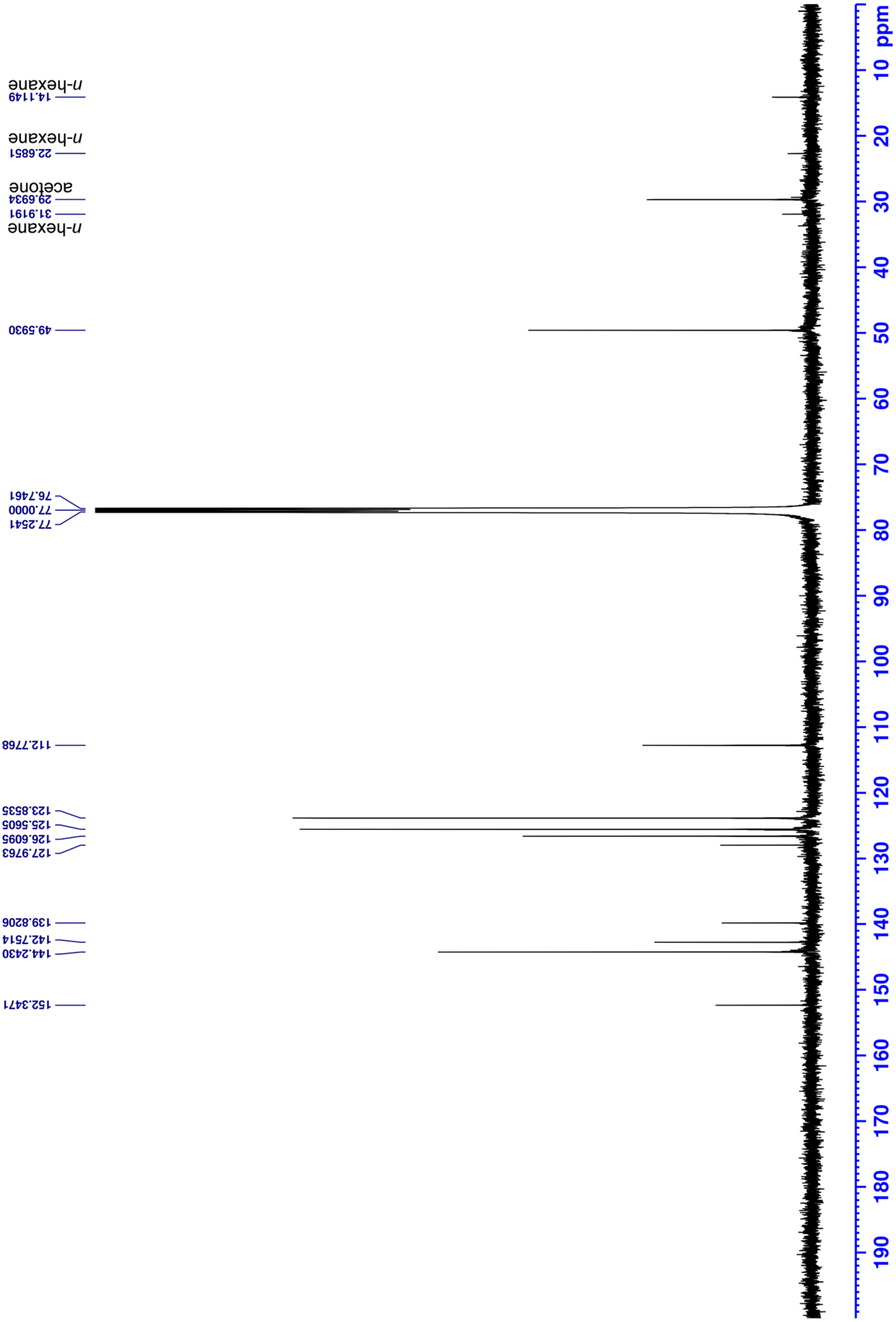


Fig. S6 ^{13}C NMR spectrum of **2** (100 MHz, CDCl$_3$).

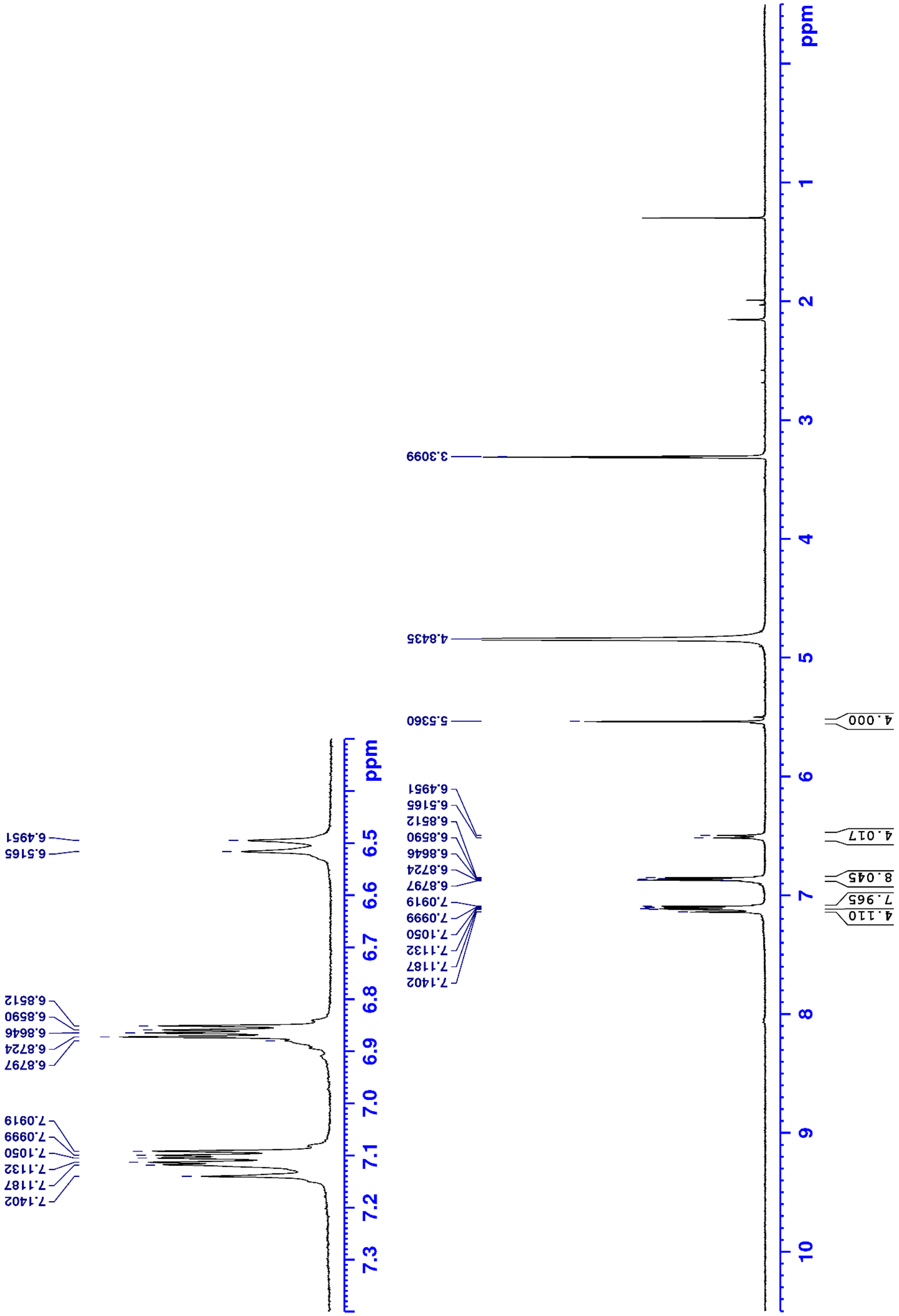


Fig. S7 ^{1}H NMR spectrum of PAT (400 MHz, CD$_3$OD).

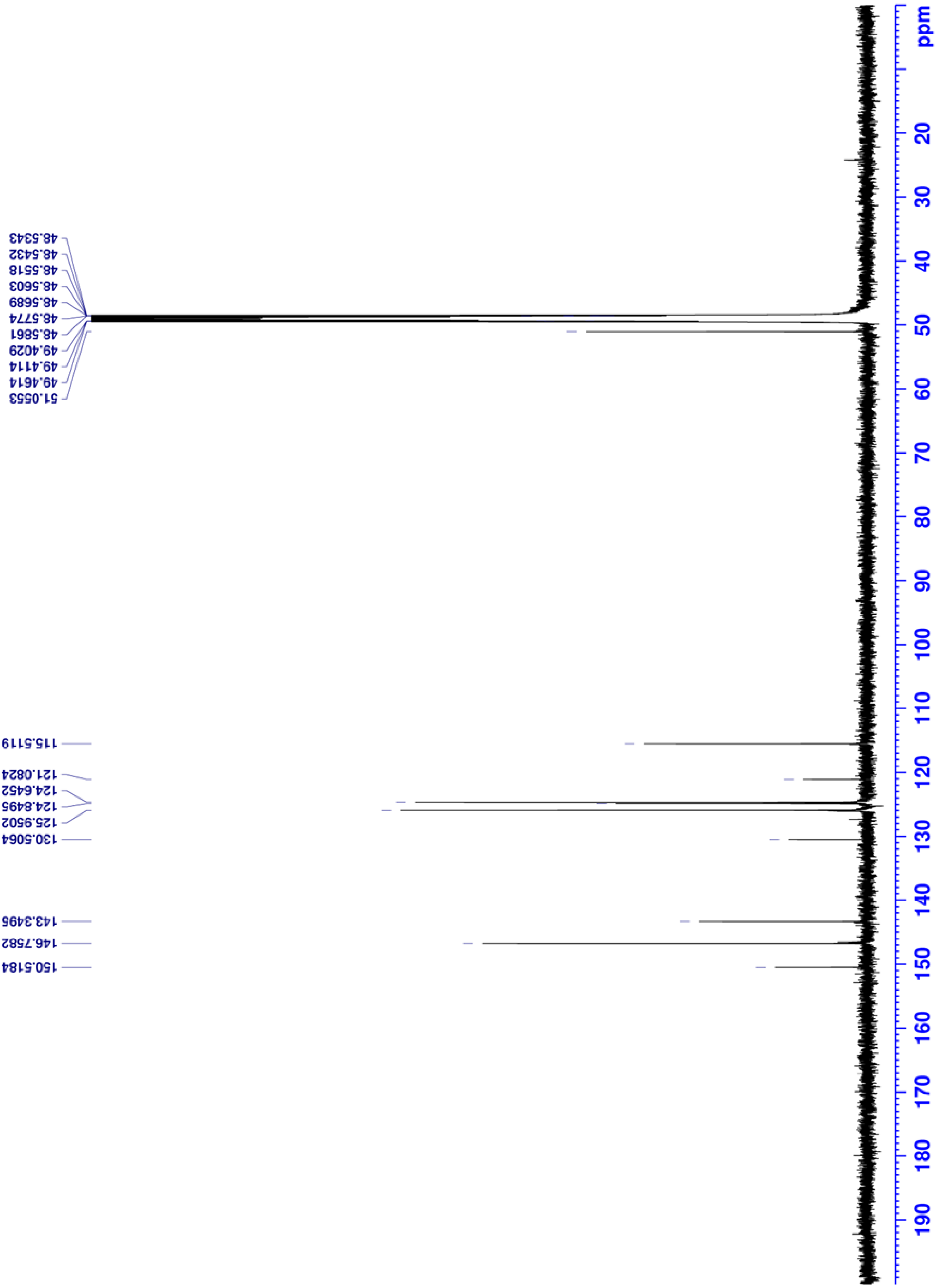


Fig. S8 ^{13}C NMR spectrum of PAT (125 MHz, CD_3OD).

Table S1 Equivalent series resistance (R_S), which is based on the following equivalent circuit model, and charge transfer resistance (R_{CT}) fitted from electrochemical impedance spectroscopy for Pani and P-*n*.

	R_S (Ω)	R_{CT} (Ω)
Pani	62.0	110.3
P-80	57.9	65.7
P-40	53.4	74.9
P-80	54.6	66.0

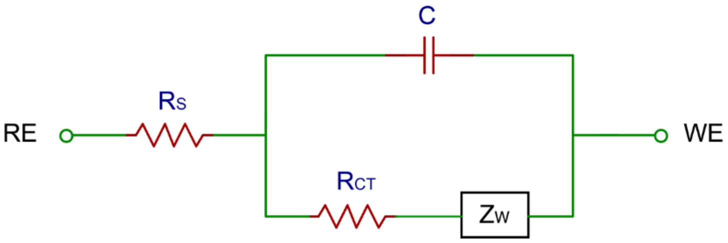


Table S2 Cartesian coordinate of the DPT-optimized structure of PAT

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.60057	1.42470	-0.36666
2	6	0	0.60063	1.42467	0.36666
3	6	0	1.20714	0.22305	0.77062
4	6	0	0.59037	-0.98105	0.38125
5	6	0	-0.59042	-0.98103	-0.38126
6	6	0	-1.20713	0.22311	-0.77063
7	6	0	-2.41574	-3.71183	1.13196
8	6	0	-1.25891	-3.10580	0.64362
9	6	0	-0.07560	-3.10393	1.41130
10	6	0	-0.04774	-3.70879	2.66737
11	6	0	-1.21426	-4.32114	3.16180
12	6	0	-2.38893	-4.32248	2.39953
13	6	0	1.25875	-3.10587	-0.64362
14	6	0	2.41554	-3.71197	-1.13195
15	6	0	2.38871	-4.32262	-2.39952
16	6	0	1.21404	-4.32122	-3.16179
17	6	0	0.04755	-3.70880	-2.66736
18	6	0	0.07544	-3.10394	-1.41129
19	6	0	-2.29400	4.74569	2.50672
20	6	0	-1.08622	4.75783	3.21473
21	6	0	0.06333	4.15754	2.66804
22	6	0	-0.01410	3.55205	1.41456
23	6	0	-1.23004	3.54420	0.69945
24	6	0	-2.36992	4.13676	1.24029
25	6	0	-0.06313	4.15755	-2.66804
26	6	0	1.08644	4.75778	-3.21473
27	6	0	2.29422	4.74559	-2.50672
28	6	0	2.37012	4.13665	-1.24030
29	6	0	1.23020	3.54414	-0.69945
30	6	0	0.01427	3.55205	-1.41456
31	6	0	-1.11864	2.84112	-0.66097
32	6	0	1.11878	2.84107	0.66097
33	6	0	-1.09123	-2.39606	-0.70836
34	6	0	1.09111	-2.39611	0.70836
35	1	0	-3.32921	-3.70633	0.54433
36	1	0	0.86491	-3.70908	3.25766
37	1	0	-1.20130	-4.79528	4.13881

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
38	1	0	-3.28587	-4.79671	2.78703
39	1	0	3.32902	-3.70651	-0.54432
40	1	0	3.28562	-4.79689	-2.78702
41	1	0	1.20105	-4.79536	-4.13880
42	1	0	-0.86510	-3.70905	-3.25765
43	1	0	-3.17804	5.20815	2.93535
44	1	0	-1.03456	5.23195	4.19033
45	1	0	1.00141	4.17002	3.21736
46	1	0	-3.30857	4.12571	0.69283
47	1	0	-1.00121	4.17008	-3.21736
48	1	0	1.03481	5.23190	-4.19033
49	1	0	3.17828	5.20801	-2.93535
50	1	0	3.30877	4.12555	-0.69283
51	1	0	-2.06214	2.83625	-1.20792
52	1	0	2.06227	2.83616	1.20792
53	1	0	-2.00402	-2.38773	-1.30299
54	1	0	2.00390	-2.38783	1.30300
55	7	0	-2.38717	0.22645	-1.57344
56	7	0	2.38718	0.22634	1.57344
57	6	0	-3.68218	-0.10173	-1.11813
58	1	0	-2.31670	0.62380	-2.49938
59	6	0	-4.74541	-0.19400	-2.03854
60	6	0	-6.04038	-0.50401	-1.61740
61	6	0	-6.32106	-0.74735	-0.25764
62	6	0	-5.25685	-0.65894	0.65945
63	6	0	-3.96195	-0.33558	0.24082
64	1	0	-6.83943	-0.56482	-2.35214
65	1	0	-4.55594	-0.02664	-3.09655
66	1	0	-5.44068	-0.83725	1.71608