Support information

Interfacial Growth of Free-Standing PANI Films: Toward High-Performance All-Polymer Supercapacitors

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1. Materials and analytical methods

1.1 Materials

Benzenamine, aniline, *p*-toluenesulfonic acid, tetra-*n*-butylammonium tribromide, sodium thiosulfate, sodium hydroxide, 4-dimethlyaminopyridine, di-*tert*-butyl dicarbonate, hydroxylamine hydrochloride, sodium acetate, triethylamine, $Pd_2(dba)_3$ (dba = dibenzylideneacetone), bidentate and monodentate phosphine ligands, hydrochloric acid, concentrated sulfuric acid, black carbon, linear polyaniline (PANI, M_w = 20000 Da), poly(vinylidene fluoride) (PVDF, M_n = 71000 Da), polyvinyl alcohol (PVA, M_n = 78400 Da), tetrabutylammoniun bromide (TBAB), *N,N,N*-trimethyl-1-dodecanaminium brominde (DTAB), polyethylene glycol (PEG, M_n = 600 Da), toluene, anisole, 1-methyl-2-pyrrolidinone (NMP), methanol, tetrahydrofunan (THF), dichoromethane (DCM), *N,N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich, Adamas or TCI. NMP and DCM were freshly distilled from CaH_2 before use. THF was freshly distilled from sodium before use. Other reagents were used without further purification. *N*-(tert-butoxycarbonyl)-*N*-(4-bromophenyl)-1,4-peneylenediamine was synthesized according to literature.[1]

1.2 Analytical methods

Fourier transform infrared (FT-IR) spectra were obtained from a Thermo Scientific Nicolet 6700 FT-IR instrument. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris I instrument at a heat rate of 10 °C/min under nitrogen atmosphere. The UV-visible absorption spectra of polymers were obtained using a Perkin-Elmer Lambda 750 UV-visible spectrophotometer. Nuclear magnetic resonance (NMR) was recorded using an Advance III 400 MHz Bruker spectrometer at 25 °C. ^1H NMR signals were measured relative to the signal for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$) or residual dimethyl sulfoxide (2.54 ppm) in hexadeutero-dimethyl sulfoxide (DMSO-*d6*), were reported in δ units, parts per million (ppm). Scanning electron microscope (SEM) measurements were performed on a VEGA 3 XMU TESCAN instrument. Energy dispersive X-ray (EDX) spectra were obtained from the same SEM microscopy equipped with Quantax 200 XFlash 6 analyzer. Cyclic voltammetry (CV) and other electrochemical experiments were performed on an electrochemical analyzer/workstation (Bio-logic VMP-300-based instrument and CHI 660E). The repeated charge and discharge tests were performed on a LAND battery test system CT2001A.

1.3 Calculation method for supercapacitor devices

The single-electrode capacitance, C_m (F/g), was calculated from their constant current charge/discharge curves according to Equation S1.

$$C_m = \frac{C_{cell}}{m} = \frac{2 \times I \times \Delta t}{\Delta V \times m}$$ **Equation S1**

Where I (A) is the applied current, Δt (s) is the discharging time, m (g) is the mass loading of the two electrodes, ΔV (V) is the voltage window of the discharging curve.

The device energy density E (Wh/g) and power density P (W/g) were calculated from their constant current charge-discharge curves according to Equations S2 and S3.

Power density:

$$P = \frac{(\Delta V)^2}{4 \times ESR \times m}$$ **Equation S2**

Where ΔV (V) is the voltage window of the discharging curve, ESR (Ω) is the internal resistance of device, m (g) is the mass loading of the two electrodes.

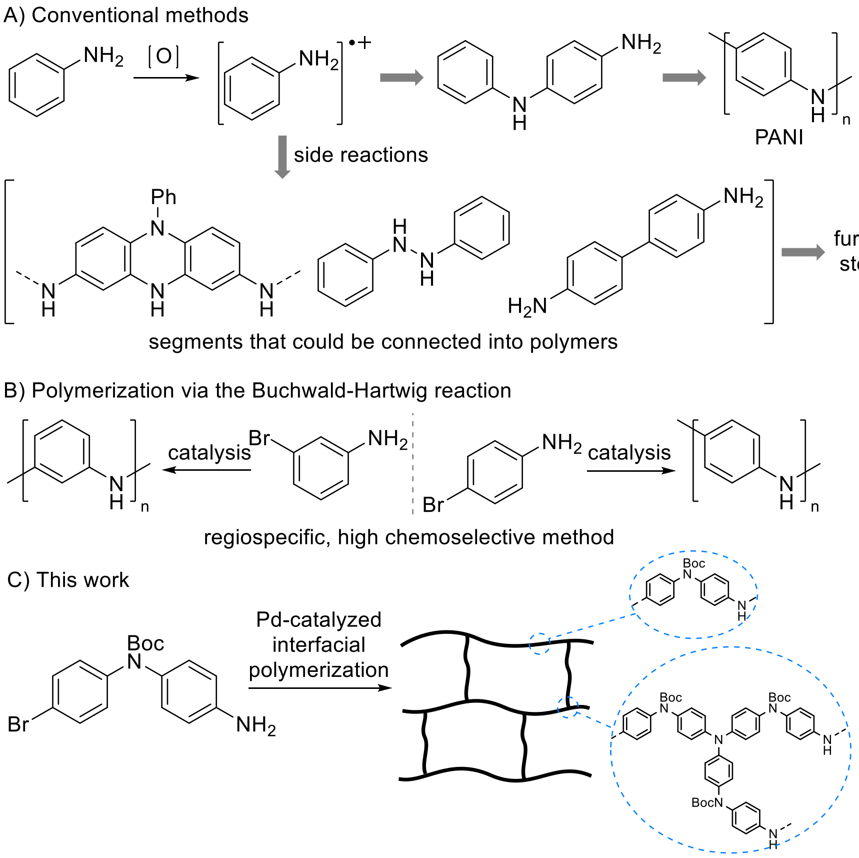
Energy density:

$$E = \frac{1}{2} \times C_m \times (\Delta V)^2$$ **Equation S3**

Where C_m (F/g) is the device capacitance calculated from the constant current charge-discharge curves. ΔV (V) is the voltage window of the discharging curve.

2. Synthesis and characterizations of monomer

Scheme S1. Synthetic Methods Toward PANI Backbone



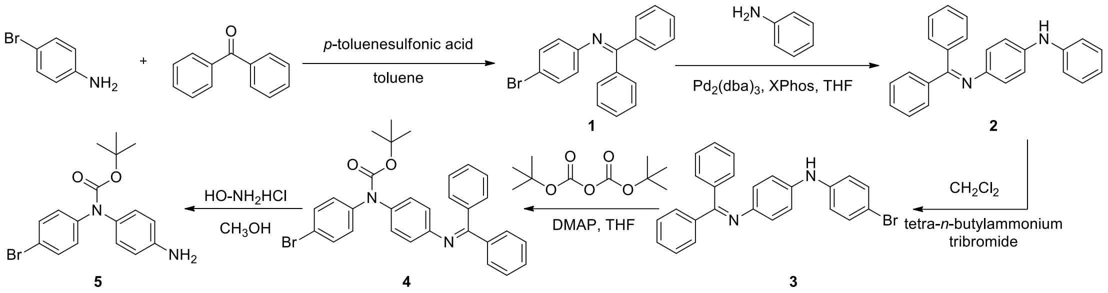


Figure S1. Synthetic route of compound **5**.

N-(diphenylmethylene)-4-bromoaniline (compound **1**) was synthesized according to literature.[2] After recrystallization from methanol, yellow solid was obtained (10.97 g, 81% yield). ^{1}H NMR (400 MHz, DMSO-*d₆*, Figure S2) *δ*: 7.67 (d, *J* = 8.0, 2H), 7.56- 7.45 (m, 3H), 7.36- 7.29 (m, 5H), 7.17-7.14 (m, 2H), 6.67 (dt, *J* = 8.4, 2.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-*d6*, Figure S3) *δ*: 168.8, 150.9, 138.9, 135.9, 131.7, 131.6, 129.3, 129.2, 128.9, 128.6, 123.0, 115.6 ppm.

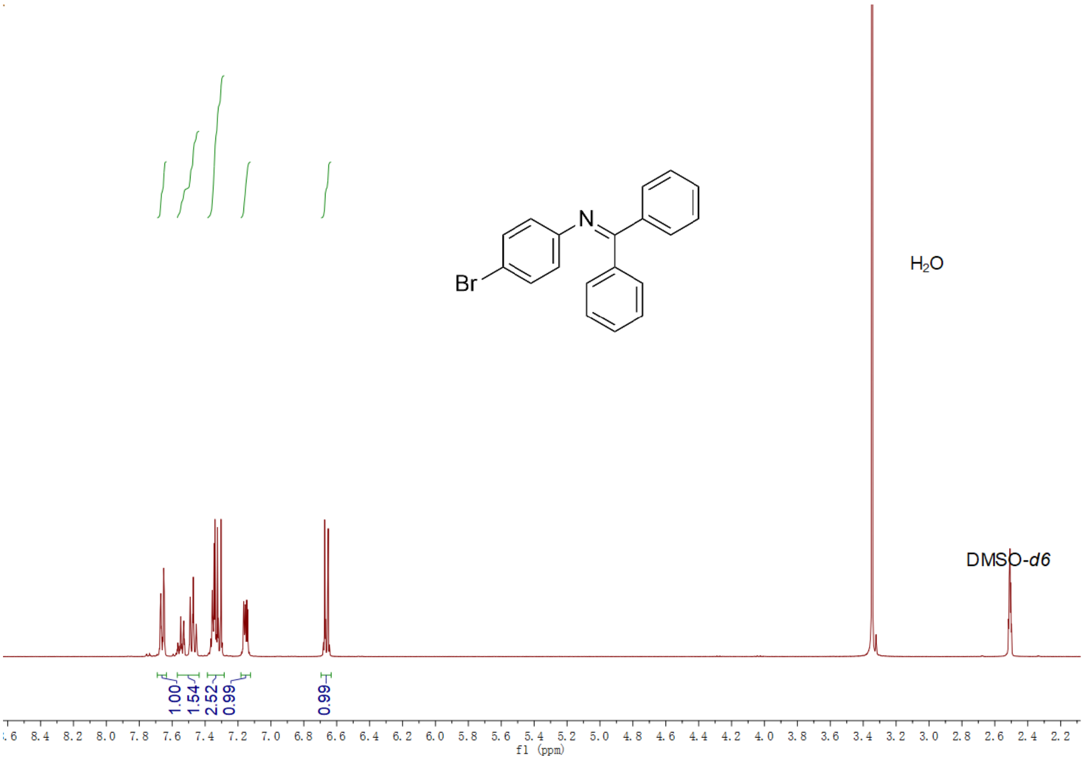


Figure S2. ^{1}H NMR of compound **1**.

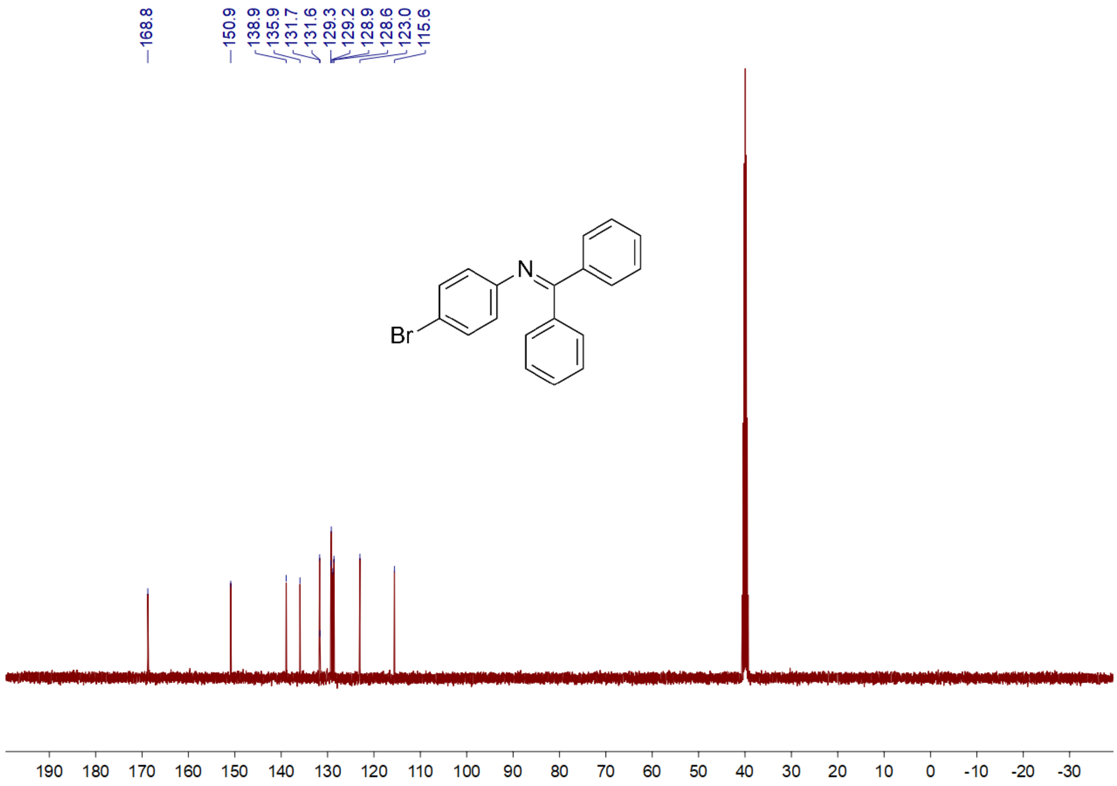


Figure S3. ^{13}C NMR of compound **1**.

A dry Schlenk flask equipped with a stir bar was charged with *N*-(diphenylmethylene)-4-bromoaniline (3.36 g, 10 mmol), aniline (1.00 mL, 11 mmol), $Pd_2(dba)_3$ (22.8 mg, 0.025 mmol) and XPhos (35.6 mg, 0.075 mmol). The flask was sealed with a rubber septum and deoxygenated with three vaccum-backfilled cycles under nitrogen atmosphere. Then, 40 mL tetrahydrofuran (THF) was added via a syringe to dissolve all solids in the flask. The reaction mixture was stirred at 80 °C for 12 h, and monitored by thin-layer chromatography (TLC) to ensure a complete consumption of compound **1**. After reaction, the obtained mixture was extracted with ethyl acetate (20 mL) and washed with aqueous solution of NaOH (2 M, 50 mL) and brine (50 mL). The organic phase was collected and dried by anhydrous Na_2SO_4. After filtration, the obtained solution was concentrated under vacuum to give crude product of compound **2**. Obtained crude product of compound **2** and tetra-*n*-butylammonium tribromide (5.78 g, 12 mmol) were dissolved by CH_2Cl_2 in a dry flask with a stir bar. The reaction mixture was stirred at room temperature for 1 h followed by adding 40 mL saturated sodium thiosulfate. After being stirred for another 30 min, the organic phase was washed with NaOH (2 M, 40 mL) and brine (50 mL) before drying over anhydrous Na_2SO_4. The obtained solution was concentrated under vacuum to give crude product of compound **3**.

The obtained crude product of compound **3** was added into an oven-dried flask charged with 4-dimethlyaminopyridine (0.13 g, 1.1 mmol) and di-*tert*-butyl dicarbonate (3.27 g, 15 mmol). The mixture was dissolved by THF and stirred at room temperature for 12 h. After reaction, the obtained solution was concentrated under vacuum. Compound **4** was recrystallized from methanol as a yellow solid (4.32 g, 82% yield). ^{1}H NMR (400 MHz, DMSO-d_6, Figure S4) δ: 7.66 (d, J = 7.2 Hz, 2H), 7.55- 7.45 (m, 5H), 7.33- 7.31 (m, 3H), 7.15- 7.12 (m, 2H), 7.08 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 1.31 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, Figure S5) δ: 168.9, 153.5, 149.5, 142.3, 139.4, 137.7, 136.1, 131.5, 130.9, 129.5, 129.3, 128.7, 128.2, 127.9, 127.6, 127.4, 121.5, 118.2, 81.3, 28.2 ppm.

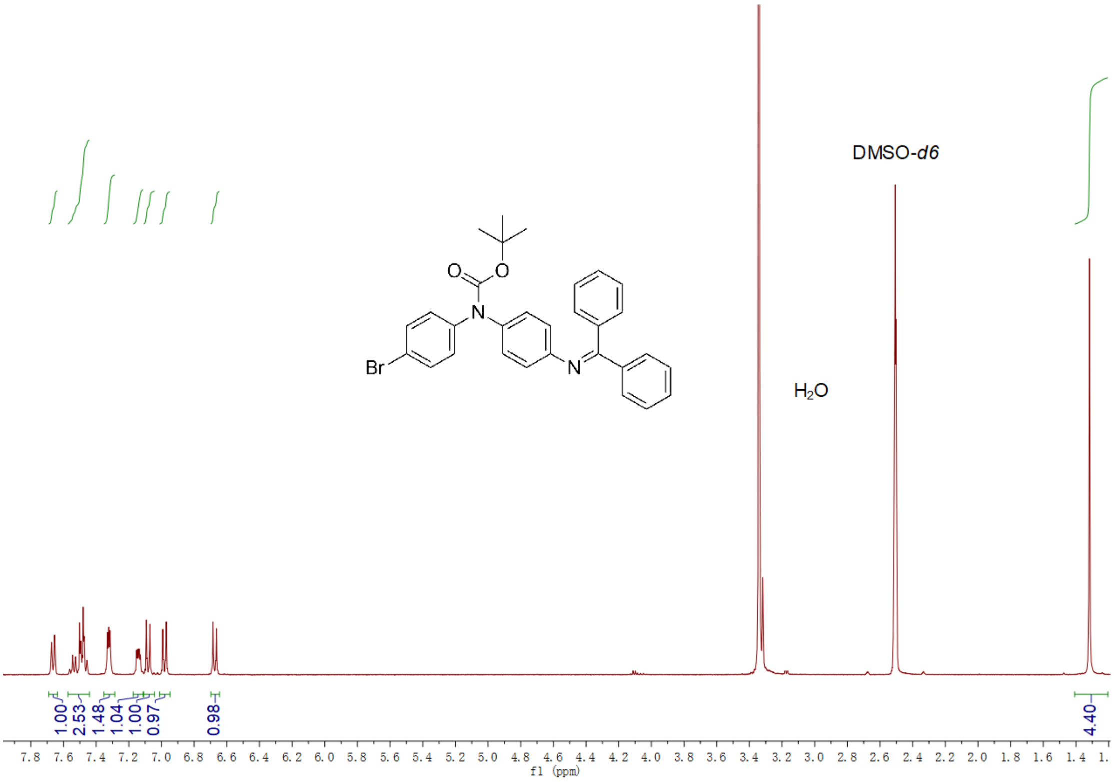


Figure S4. ^{1}H NMR of compound **4**.

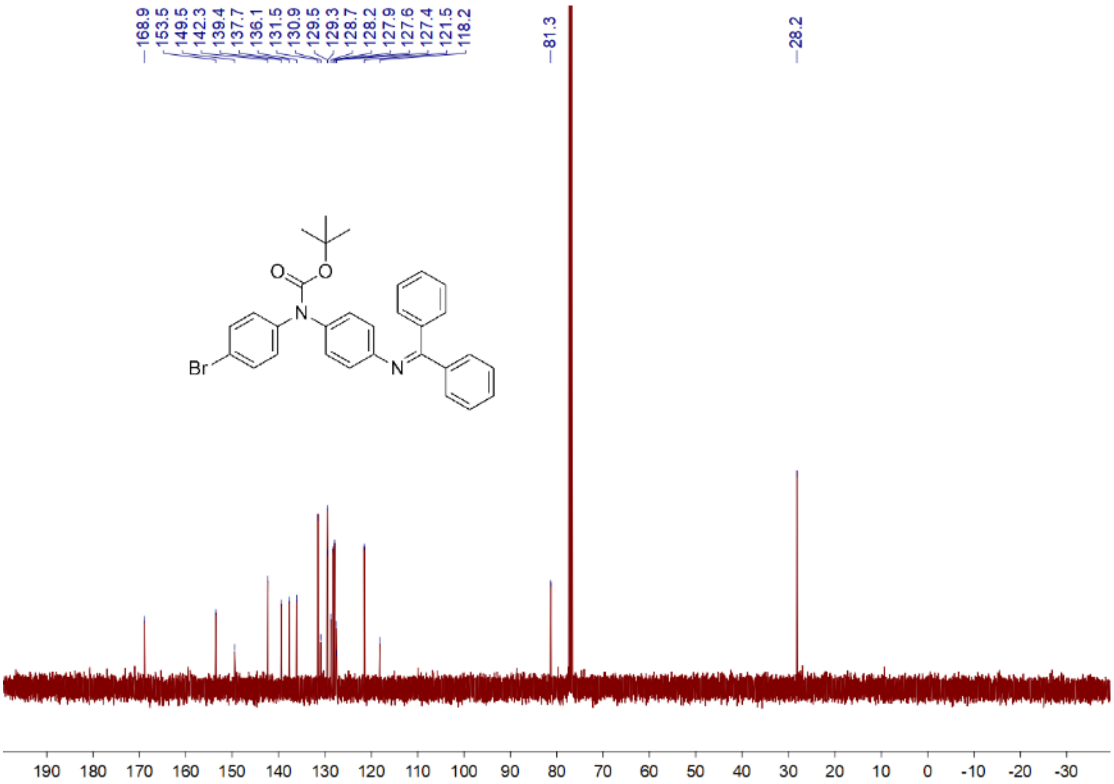


Figure S5. ^{13}C NMR of compound **4**.

A dry flask equipped with a stir bar was charged with compound **4** (4.32 g, 8.2mmol), sodium acetate (1.64 g, 20 mmol), hydroxylamine hydrochloride (1.03 g, 15 mmol). All solids were dissolved by 25 mL methanol and the mixture was stirred at room temperature for 5 h. Then, triethylamine (2.8 mL, 20 mmol) was added into the flask and the mixture continued stirring for 6 h. The mixture was concentrated under vacuum and treated with CH_2Cl_2. The organic layer was washed with water, dried over sodium sulfate, concentrated in vacuo. Compound **5** was recrystallized from isopropanol as a white powder (2.39 g, 80% yield). ^{1}H NMR (400 MHz, DMSO-d_6, Figure S6) δ: 7.47 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.8Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 5.13 (s, 2H), 1.35 (s, 9H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6, Figure S7) δ: 153.7, 147.7, 143.5, 131.7, 131.2, 128.8, 128.4, 117.5, 114.4, 80.6, 28.3 ppm.

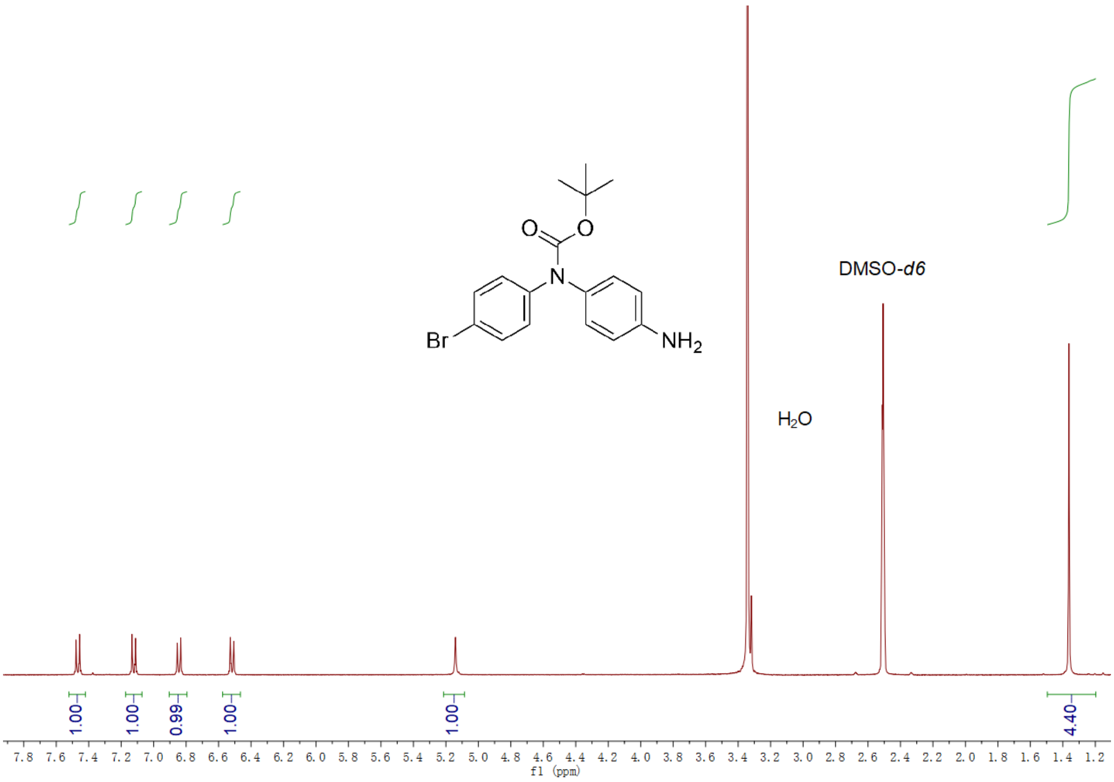


Figure S6. ^{1}H NMR of compound **5**.

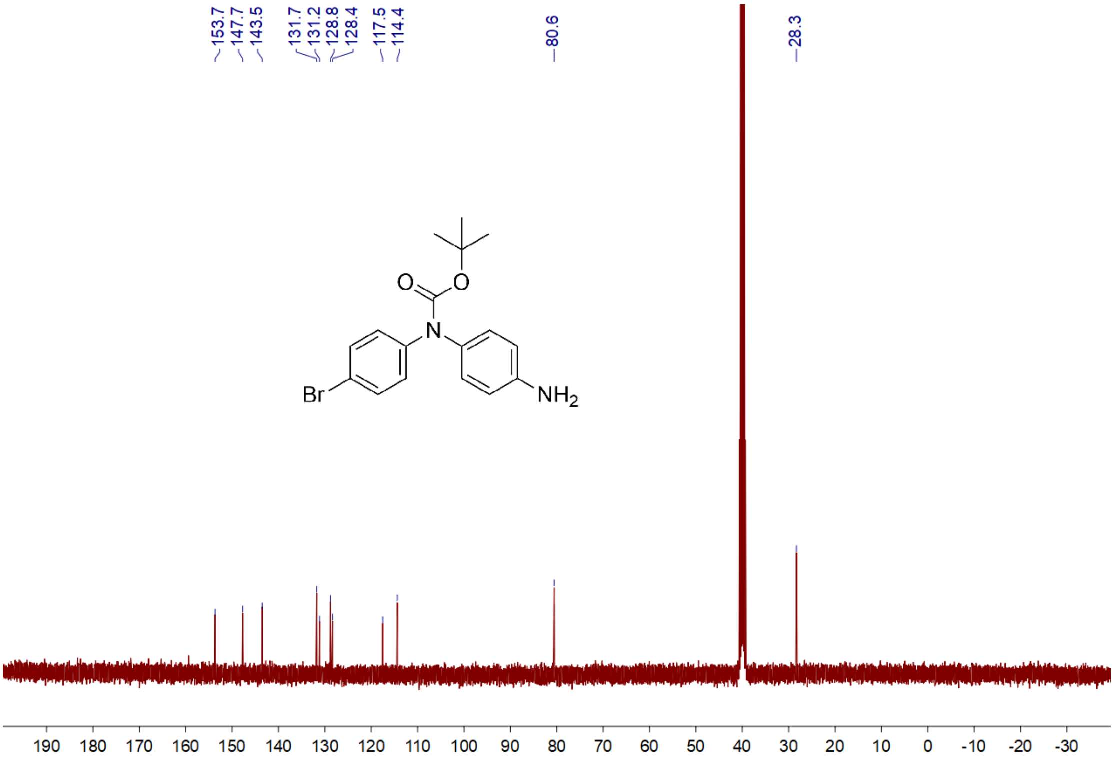


Figure 7. ^{13}C NMR of compound **5**.

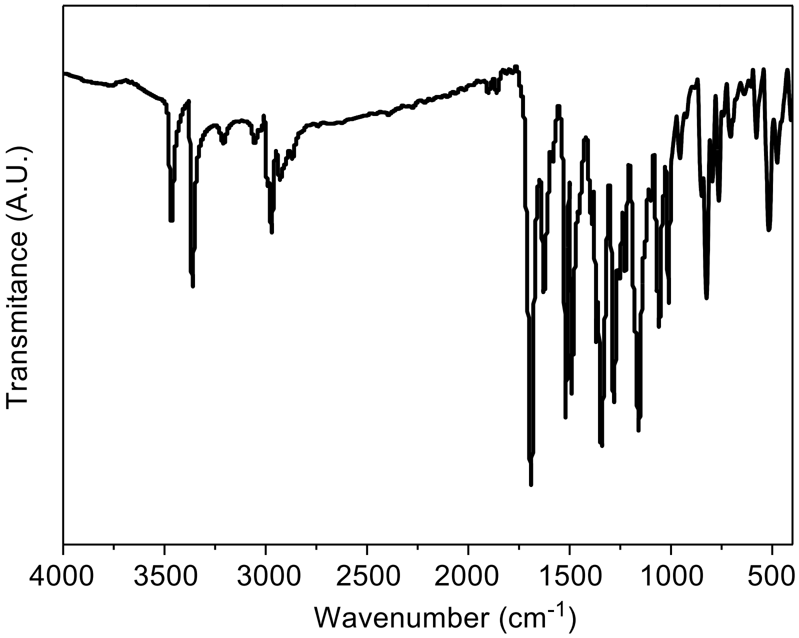


Figure S8. FT-IR spectrum of compound **5**.

3. Experimental details and results for Figure 1

3.1 Synthesis of BOC-PANI film in Figure 1

General procedure:

Details of all reagents, catalysts, ligands, solvents and reaction conditions were summarized in Table S1.

A dry 25 mL Schlenk bottle was charged with compound **5**, $Pd_2(dba)_3$ and corresponding ligand. The bottle was sealed with a rubber stopper and deoxygenated with vacuum and back filled with N_2 for three times. Toluene was injected into the bottle via a syringe to dissolve all solids. Subsequently, an aqueous solution containing NaOH and tetrabutylammoniun bromide (TBAB) was injected into the bottle. The mixture was heated at corresponding temperature without stirring. After reaction, when the BOC-PANI film was formed at the interface of two solvents, the material was directly taken out from the bottle, and washed with DMF, deionized water and methanol for three times in sequence, and subsequently dried under vacuum to give the BOC-PANI film. Because the obtained film is a cross-linked polymer network, which could not be dissolved in any solvent, SEC and NMR characterizations have not been conducted. The BOC-PANI film was analyzed by

SEM/EDX to provide elemental analysis. To give monomer conversion, the toluene phase collected from the top layer of the reaction mixture was analyzed by ^{1}H NMR.

Table S1. Condition optimization of synthesizing BOC-PANI film via the interfacial polymerization.[a]

Entry	Ligand	$V_{toluene}/V_{water}$	Temp (°C)	Time (h)	Conv. (%)[b]	Yeild (%)[c]	Cross-link (Y/N)[d]	Thickness (μm)
1	BINAP	2/5	110	16	95	6	N	—
2	BrettPhos	2/5	110	16	100	6	N	—
3	RuPhos	2/5	110	16	100	16	N	—
4	*t*BuXPhos	2/5	110	16	92	3	N	—
5	XPhos	1/5	90	12	100	84	Y	4
6	XPhos	2/5	90	12	100	85	Y	8
7	XPhos	4/5	90	12	100	82	Y	20

[a]Compound **5** (0.05 M) in toluene, [**5**]/[$Pd_2(dba)_3$]/[ligand] = 1/0.01/0.03, 5 mL aqueous solution containing NaOH (1 M) and phase transfer catalyst (PTC = TBAB), [base]/[TBAB] = 200/1. [b]Conversion was determined by ^{1}H NMR. [c]Isolated yield of solid material formed at the interface. [d]Y (yes) and N (no) represent whether the reaction is suitable to generate cross-linked PANI films.

Table S2. Other information for condition optimization of synthesizing BOC-PANI films via the interfacial polymerization.[a]

Entry	Solvent	PTC[b]	Base	[Base]/[PCT]	Temp (°C)	Time (h)	Conv. (%)[c]	Cross-link (Y/N)[d]	Complete film (Y/N)[e]
1	Toluene	TBAB	NaOH	200/1	90	12	>99	Y	Y
2	Toluene	DTAB	NaOH	200/1	90	12	>99	Y	Y
3	Toluene	PEG	NaOH	200/1	90	12	90	N	N
4	Anisole	TBAB	NaOH	200/1	90	12	>99	Y	N
5	Anisole	TBAB	NaOH	200/1	110	16	>99	Y	N

6	Anisole	DTAB	NaOH	200/1	110	16	>99	Y	N
7	Toluene/ Anisole (1:1)	TBAB	NaOH	200/1	90	12	>99	Y	N
8	Toluene	TBAB	K_3PO_4	200/1	90	12	80	N	N
9	Toluene	TBAB	NaOH	100/1	90	12	>99	Y	N
10	Toluene	TBAB	NaOH	200/1	90	12	>99	Y	Y
11	Toluene	TBAB	NaOH	400/1	90	12	>99	Y	Y

[a]Compound **5** (0.05 M), $Pd_2(dba)_3$ and XPhos in 2 mL toluene, [**5**]/[$Pd_2(dba)_3$]/[ligand] = 1/0.01/0.03, 5 mL aqueous solution containing NaOH and PTC (0.005 M). [b]TBAB: tetrabutylammoniun bromide, DTAB: *N,N,N*-trimethyl-1-dodecanaminium brominde, PEG: polyethylene glycol. [c]Conversion was determined by ^{1}H NMR. [d]Y (yes) and N (no) represent whether the reaction have generated cross-linked PANI films. [e]Y (yes) and N (no) represent whether cross-linked films were broken or not during reaction.

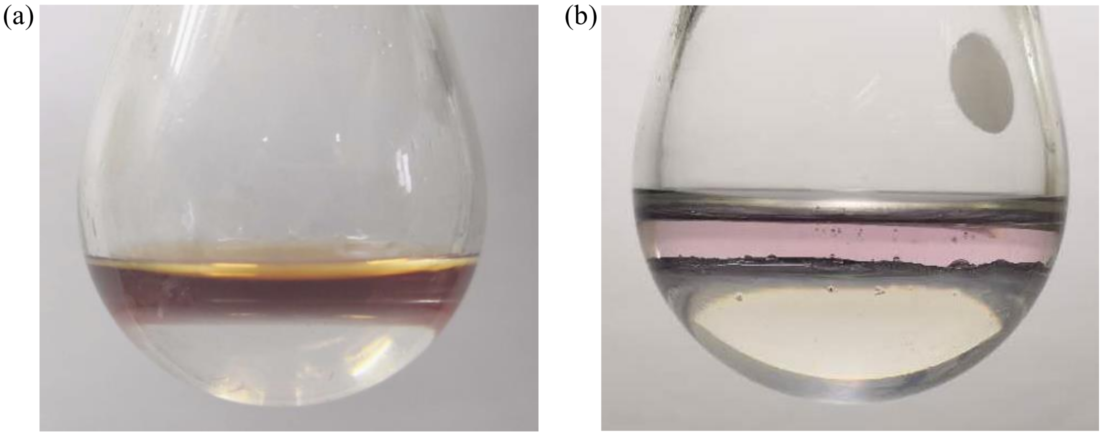


Figure S9. Images of the interfacial polymerization, (a) before and (b) after reactions.

3.2 Analyzing of the cross-linking density of BOC-PANI films

The cross-linking density (CLD) of BOC-PANI film was calculated by Equation S4. n_{tri} (mmol) is the amount of triphenylamine in the BOC-PANI film, n_{total} (mmol) is the amount of monomer unit in the BOC-PANI film.

$$\mathrm{CLD} = \frac{n_{\mathrm{tri}}}{n_{\mathrm{tatol}}} \times 100\%$$ **Equation S4**

n_{tatol} (mmol) was calculated according to Equation S5. Where m (mg) is the mass of PANI film, M_{unit} is the molar mass of the monomer unit (M_{unit} = 282 g/mol).

$$n_{\mathrm{total}} = \frac{m}{M_{\mathrm{unit}}}$$ **Equation S5**

During the polymerization of compound **5**, the formation of each C-N bond consumes a C-Br bond and a N-H bond. When a tertiary amine is formed by the C-N bond formation, a C-Br bond and a secondary amine was consumed, resulting in the left of a primary amine. Therefore, the number of generated triphenyl amines (n_{tri}) is equal to the number of primary amines contained in the polymer network. According to literature, while aniline could be quantitively consumed by reaction with *p*-tolylisocyanate (Figure S10a), diphenyl amine would be left intact.[3] The remaining extra *p*-tolylisocyanate could be titrated by dibutylamine and analyzed by ^{1}H NMR in the presence of an internal standard.[4]

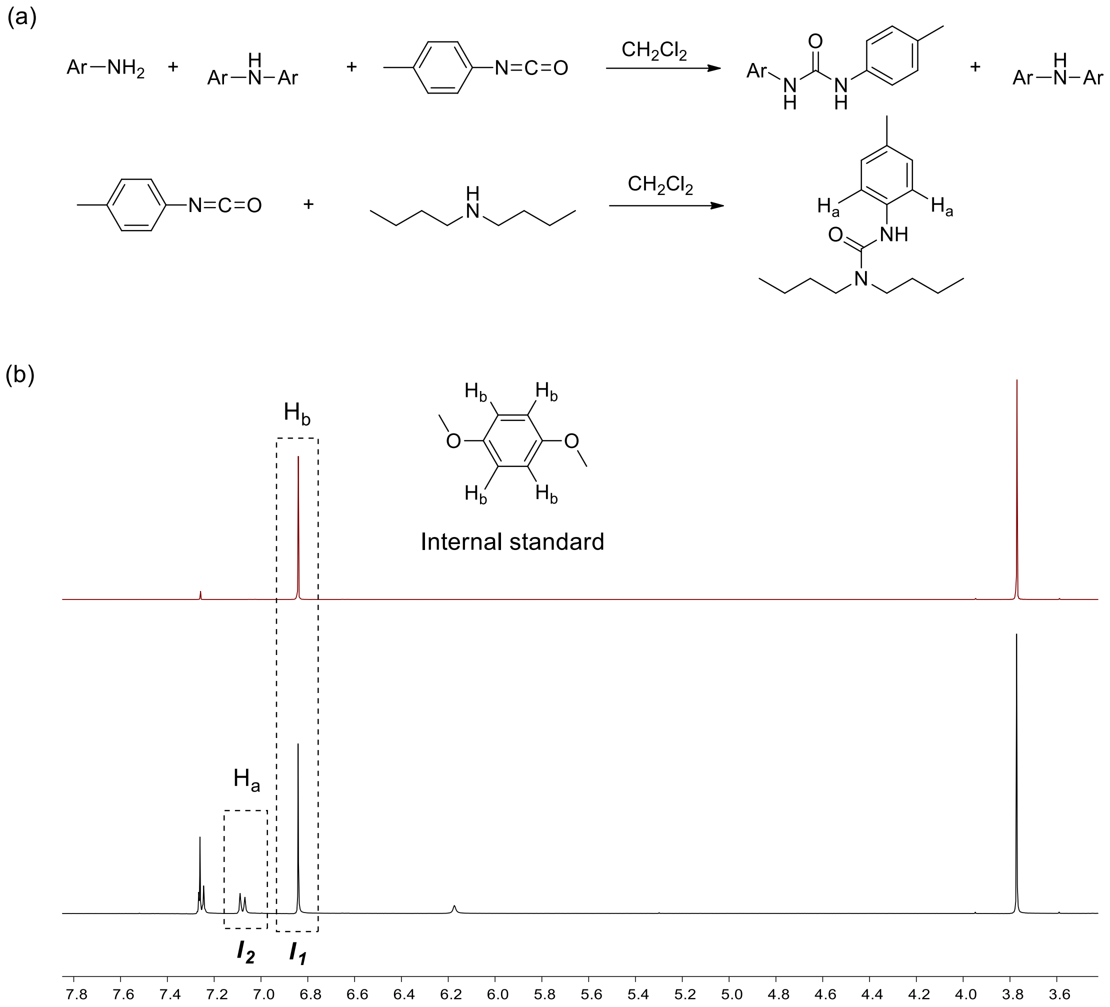


Figure S10. (a) Chemical reactions used to determine the amount of primary amine. (b) ^{1}H NMR spectra of internal standard (up) and reaction mixture after titrating by dibutylamine (down).

General procedure:

A solution of *p*-tolylisocyanate (0.02 M in DCM, V_1 in Table S3) and a solution of 1,4-dimethoxybenzene (0.04 M in DCM, V_2 in Table S3) were added into an oven-dried vial equipped with a stir bar. After stirring for 2 h, dibutylamine (5 equivalent of *p*-tolylisocyanate) was added into the vial to consume extra *p*-tolylisocyanate (n_2). 2 h later, the mixture was concentrated under vacuum, and extracted with $CDCl_3$. The organic layer was characterized by ^{1}H NMR to give the amount of extra *p*-tolylisocyanate (n_2) according to Equation S6. I_1 and I_2 represent the integration areas of protons H_b and H_a in Figure S10b.

$$n_2 = 2 \times \frac{I_2}{I_1} \times 0.04 \times V_2 \qquad \textbf{Equation S6}$$

The amount of triphenyl amine (n_{tri}) could be calculated by Equation S7.

$$n_{tri} = n_1 - n_2 \qquad \textbf{Equation S7}$$

Table S3. Results of determining the cross-link density.[a]

Thickness (μm)	m (mg)	V_1 (mL)	n_1 (mmol)	V_2 (mL)	n_2 (mmol)	CLD (%)
4	15.3	0.375	0.0075	0.625	0.0064	2.03
8	17.19	0.250	0.005	0.300	0.0037	2.10
20	14.1	0.375	0.0075	0.625	0.0063	2.41

[a]Note: for film of each thickness, related experiments have been conducted for 3 times to give the CLD result.

3.3 SEM/EDX results for BOC-PANI film

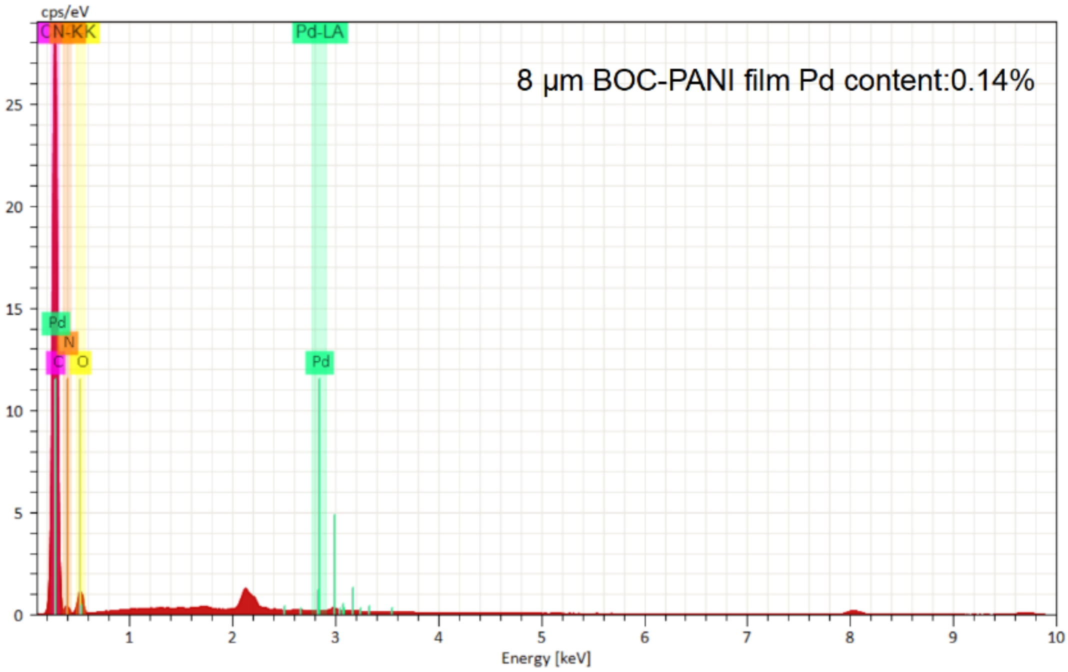


Figure S11. SEM/EDX spectrum of BOC-PANI film (entry 6, Figure 1A). Inset value indicates the palladium (Pd) content obtained by area elemental analysis.

Table S4. Pd residues in BOC-PANI films of three different thicknesses determined by SEM/EDX analysis.

Thickness (μm)	Carbon (wt%)	Nitrogen (wt%)	Oxygen (wt%)	Palladium (wt%)
4	67.86	15.61	16.22	0.30
8	67.29	15.21	17.37	0.14
20	66.17	14.78	18.88	0.18

3.4 Synthesis of BOC-PANI with triphenylamine unit

According to our hypothesis, the C-N bond formation using inappropriate combinations of catalyst and ligand would lead to linear BOC-PANI, which only contains diphenyl amine in the polymer backbone. In contrast, in order to generate the target cross-linked network of BOC-PANI, triphenylamine unit should be formed during the C-N bond formation. In order to confirm the presence of triphenylamine in our BOC-PANI film, a polymer containing triphenylamine unit was prepared according to Figure S12 to compare with our target cross-linked material.

Experimental procedure to prepare triphenylamine contained BOC-PANI:

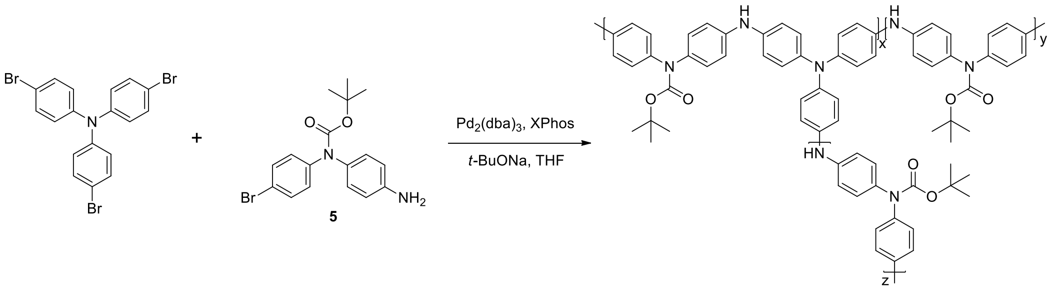


Figure S12. Copolymerization of compound **5** and tris(4-bromophenyl)amine. Interfacial polymerization with above starting materials of triphenyl amine and compound **5** has also been investigated. However, instead of PANI film, solid precipitate of cross-linked PANI was obtained.

A dry 10 mL Schlenk tube equipped with stir bar was charged with compound **5** (36.4 mg, 0.1 mmol), tris(4-bromophenyl)amine (9.6 mg, 0.02 mmol), potassium *tert*-butoxide (22.4 mg, 0.2 mmol), $Pd_2(dba)_3$ (0.9 mg, 0.001 mmol) and XPhos (1.6 mg, 0.003 mmol). After sealing the tube with a rubber stopper, the tube was vacuumed and recharged with N_2 for three times. Then, 2 mL THF was injected into the bottle via a syringe to dissolve all solids. The mixture was stirred at 80 °C for 12 h. After reaction, the reaction mixture was washed with deionized water, and concentrated under vacuum at 40 °C before further characterization. The obtained cross-linked PANI powder was analyzed by FT-IR.

Experimental procedure to prepare liner BOC-PANI：

An oven-dried 25 mL Schlenk bottle was charged with compound **5** (36.4 mg, 0.1 mmol), $Pd_2(dba)_3$ (0.9 mg, 0.001 mmol) and BrettPhos (1.5 mg, 0.003 mmol). Then, the Schlenk bottle was sealed with a rubber stopper and deoxygenated by vacuumed and recharged with N_2 for three times. After the bottle was filled with N_2, 2 mL toluene was injected into the bottle using a syringe to dissolve all solids. Then, 5 mL aqueous solution which contains tetrabutylammoniun bromide (8.0 mg) and NaOH (0.20 g) was injected into the bottle under N_2. The mixture was heated at 90 ºC for 20 h. The toluene phase was washed with DMF and deionized water for three times and concentrated under vacuum. Before analyzed by FT-IR, the obtained liner BOC-PANI was dried under vacuum at 60 ºC overnight.

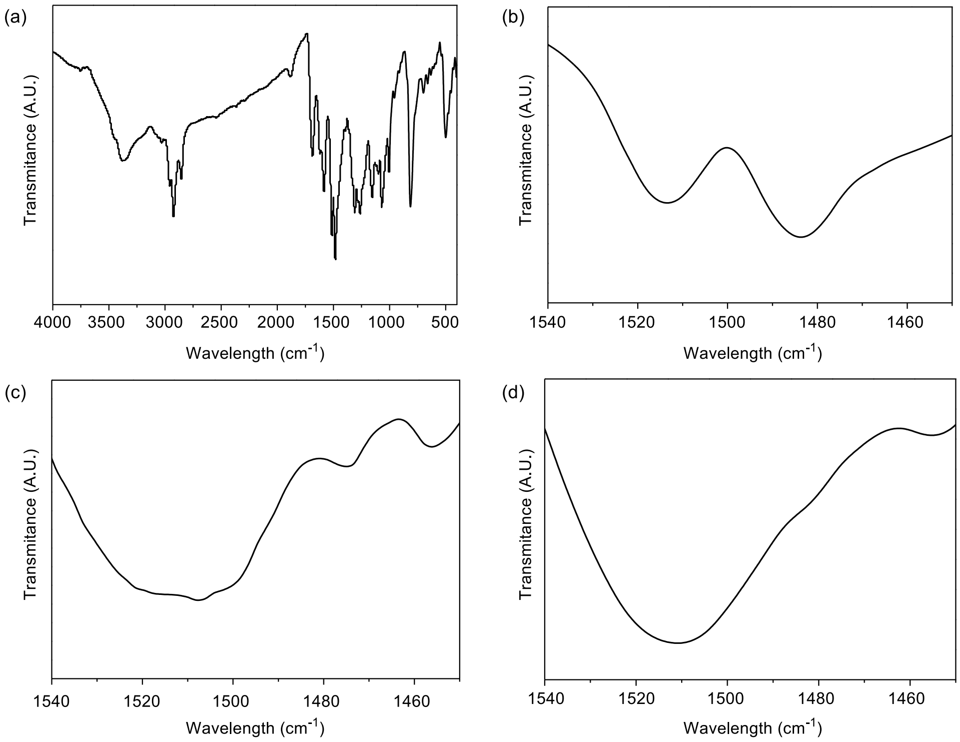


Figure S13. FT-IR spectra for copolymer prepared according to Figure S12. (a) FT-IR spectrum. (b) Magnified FT-IR spectrum of (a). (c) Magnified FT-IR spectrum of BOC-PANI film in Figure 1D. (d) Magnified FT-IR spectrum of linear BOC-PANI in Figure 1D.

As shown in Figures S13a and S13b, the FT-IR spectra of copolymer prepared according to Figure S12 exhibit two absorption peaks around 1500 cm^{-1}, which belong to ring quadrant stretch vibration of diphenylamine (1510 cm^{-1}) and triphenylamine (1483 cm^{-1}), respectively. Similarly, the FT-IR spectrum of BOC-PANI (Figure S13c) shows two absorption peaks around 1500 cm^{-1}, which belong to ring quadrant stretch vibration of diphenylamine (1510 cm^{-1}) and triphenylamine (1475 cm^{-1}), respectively, in sharp contrast to Figure S13d.

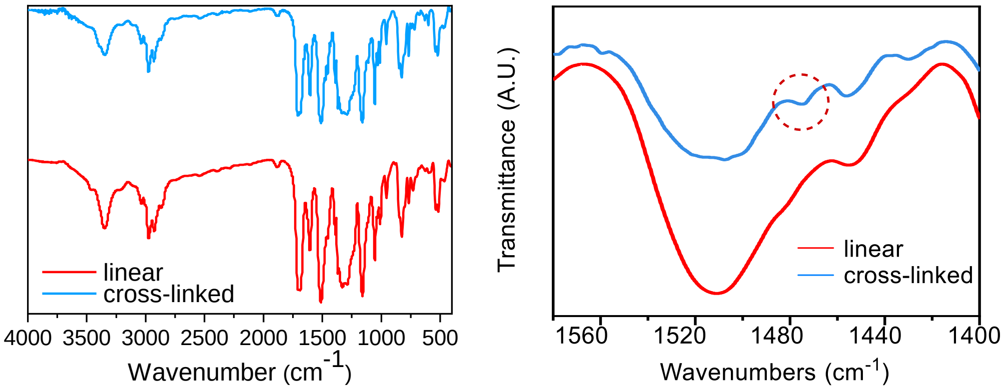


Figure S14. (left) Full FTIR spectrum of linear PANI vs. crosslinked PANI. (right) Enlarged area to highlight the difference between linear (synthesized with BrettPhos) and cross-linked PANI (synthesized with XPhos).

4. Experiment details and results for Figure 2 and Figure 3

4.1 Procedure of deprotection

The BOC-PANI film (diameter = 1 cm) was placed in a vial, and swollen by minimal amount of THF (~0.8 mL). Then, 3 mL concentrated hydrochloric acid was added into the vial dropwise at room temperature. After deprotection via acid doping under air, the PANI film turned to green immediately, and the generation of carbon dioxide was clearly observed. After 5 h, the obtained porous cross-linked PANI film (PCL-PANI) was washed with deionized water for 5 times and dried in oven at 60 °C under vacuum for 24 h before further characterization. The final mass loading of the PCL-PANI was kept to be ~ 1.0 mg/cm^2.

4.2 Other results for Figure 2

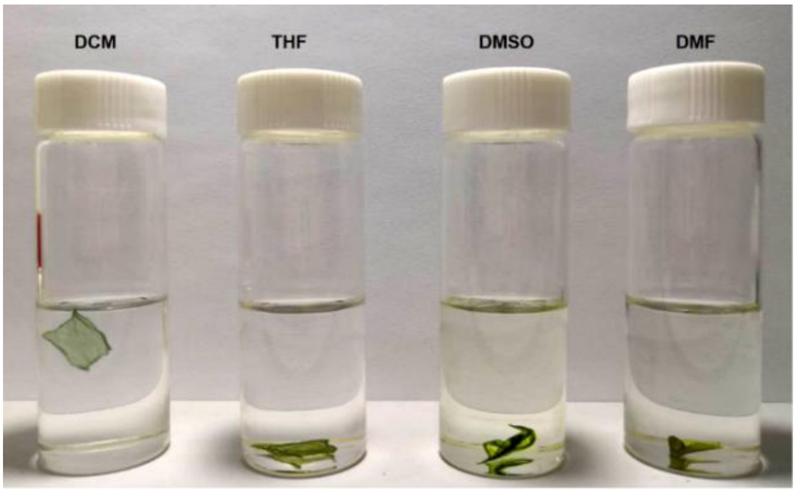


Figure S15. Optical images of PCL-PANI films treated with a variety of organic solvents. After immersing the PCL-PANI films in organic solvents for above 10 days, these films maintained the integrity without broken, indicating the mechanical stability of PCL-PANI films.

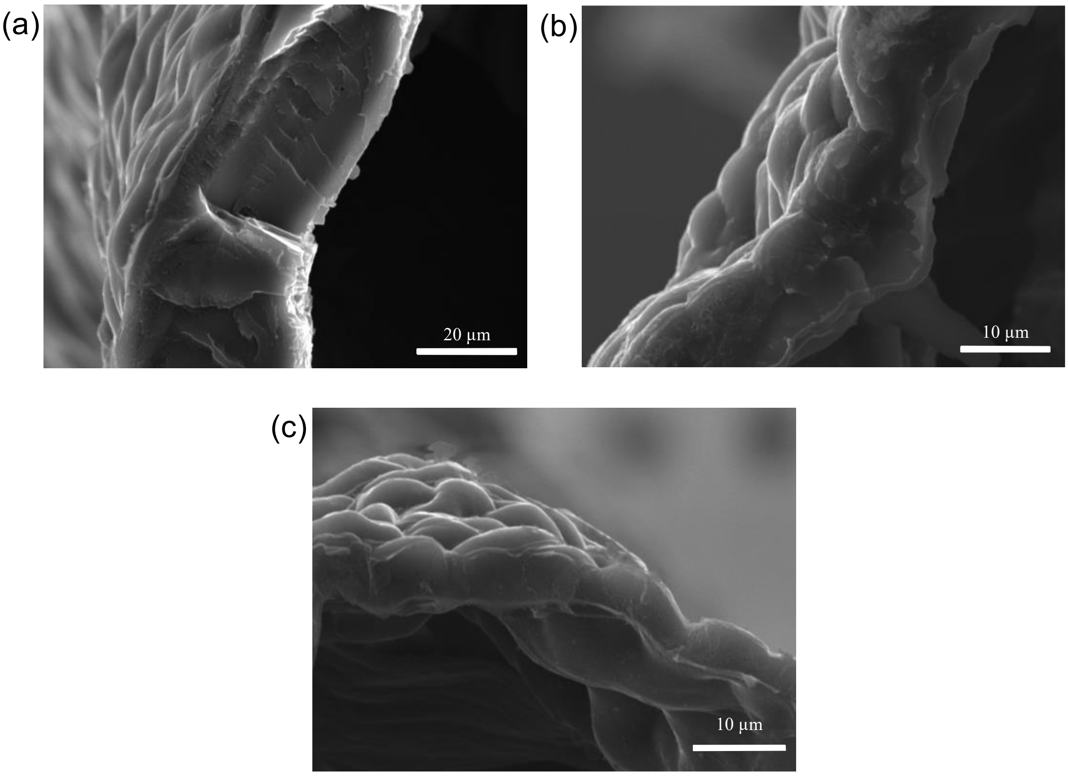


Figure S16. SEM images of BOC-PANI films of different thicknesses. (a) 20 µm, (b) 8 µm, (c) 4 µm.

4.3 Characterization and results for the conductivity of PCL-PANI

The four-point probe method was used to measure the conductivity of PCL-PANI films. Square resistance was obtained directly from the ST2263 double electric measuring digital four-probe tester. The resistivity and conductivity of PCL-PANI films were calculated using Equations S8 and S9.

$$\rho = R_s \times W \qquad \textbf{Equation S8}$$

$$\sigma = \frac{1}{\rho} \qquad \textbf{Equation S9}$$

Where R_s is the square resistance (Ω/☐), W is the thickness (cm) of PANI film, ρ is the resistivity (Ω•cm) of PANI film, σ is the conductivity (S/cm) of PANI film.

Table S5. The conductivity of PCL-PANI film[a]

Thickness (μm)	Square resistance (Ω/☐)	Resistivity (Ω•cm)	Conductivity (S/cm)
20	392.5	0.785	1.27
8	540.5	0.432	2.31
4	985.9	0.046	21.78

[a]The PANI film was oxidized by oxygen during deprotection, the oxidation state of PANI film transformed from leucoemeraldine base to emeraldine.

5. Experimental details and results for Figure 4 and Figure 5

5.1 General procedure of making supercapacitors with PCL-PANI films

A PANI film (mass loading = ~1 mg/cm^2) was placed on the FTO glass. H_2SO_4/PVA gel was used as the electrolyte and applied onto the PANI electrode as follows: H_2SO_4 (2.00 g, 98 wt%), 10 mL deionized water and PVA (1.00 g) were mixed together and heated at 80 °C for 12 h with stirring. A filter paper (pore size:

30-50 μm, thickness: 0.35 mm, cellulose paper) was placed as the separator and the PANI electrode and separator were soaked within the H_2SO_4/PVA mixture for 12 h and make them solidified at room temperature for about 3 h. Subsequently, another piece of PANI film (mass loading = ~1 mg/cm^2) treated FTO glass was placed on top to form a sandwich structure (Figure S17) to afford a supercapacitor. The device was hermetically sealed with hot-melt adhesive. The prepared device was rested at room temperature for 24 h before electrochemical measurement.

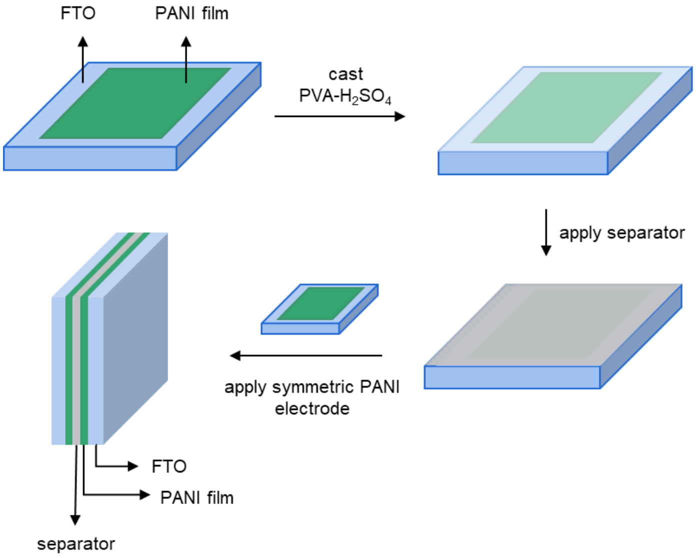


Figure S17. The assembly process of supercapacitors with PCL-PANI films and commercial PANI.

5.3 Experimental results for supercapacitor made of PCL-PANI-2 and PCL-PANI-3 electrodes

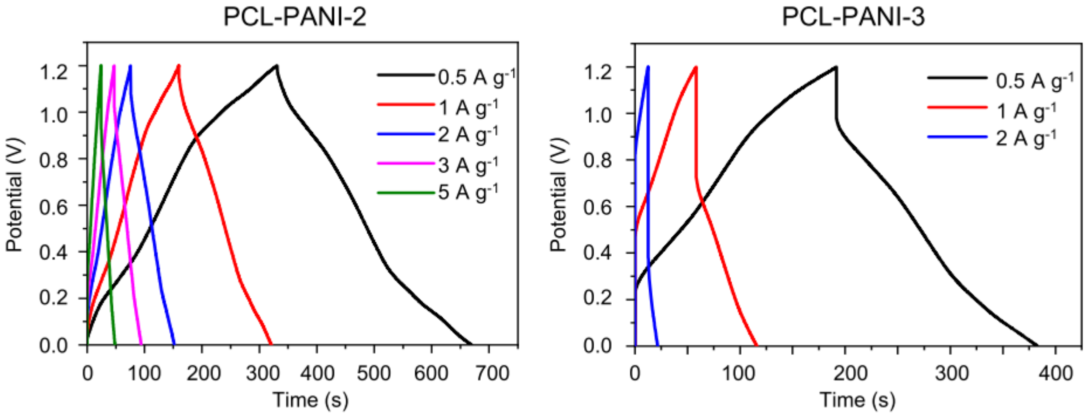


Figure S18. Galvanostatic charge and discharge for PCL-PANI-2 and PCL-PANI-3 at varied current densities.

The capacitance reduces significantly as the thickness increases. Specifically, the capacitance for PCL-PANI-2 and PCL-PANI-3 was 279 F g^{-1} and 160 F g^{-1}, when charged and discharged at 0.5 A g^{-1}.

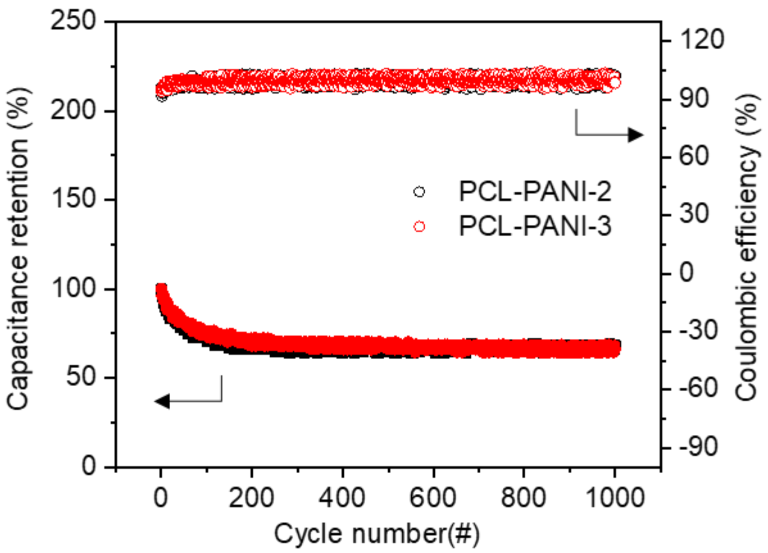


Figure S19. Cycling stability of PCL-PANI-2 and PCL-PANI-3 at 1 A g^{-1}.

Both PCL-PANI-2 and PCL-PANI-3 have shown good cycling stability and stable coulombic efficiency during the time period tested. Since PCL-PANI-2 and PCL-PANI-3 were not our lead material for their much lower conductivities and capacitances, only 1000 cycles were carried out for these materials.

5.3 General procedure of making a linear PANI-based supercapacitor

The commercial PANI was dried under vacuum at 60 °C for 24 h before use. 20 mg Poly(vinylidene fluoride) (PVDF), black carbon (20.0 mg), PANI (0.16 g) and 5 mL 1-methyl-2-pyrrolidinone (NMP) were added into an oven-dried bottle equipped with a stir bar. The mixture was stirred at room temperature for 12 h. After mixing, the obtained mixture was coated on FTO conducting glasses using a doctor blade and dried under vacuum at 60 °C for 24 h. The mass loading of the linear PANI electrode was ~ 1.1 mg/cm^2. Then, two pieces of FTO glasses coated with PANI powder and a separator were assembled into a sandwich-like structure as shown in Figure S16. The device was sealed with hot-melt adhesive before electrochemical analysis.

5.4 Experimental results for supercapacitor made of linear PANI electrodes

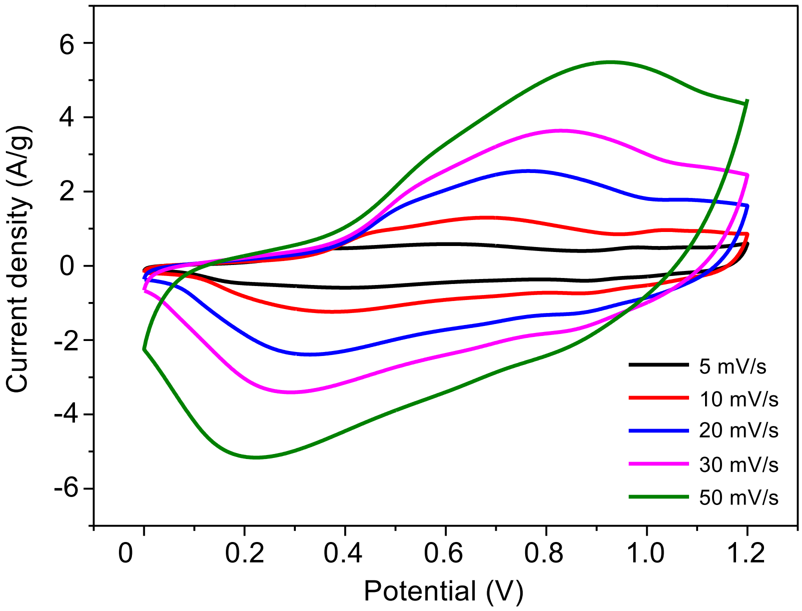


Figure S20. CV spectra of supercapacitor made of linear PANI electrodes.

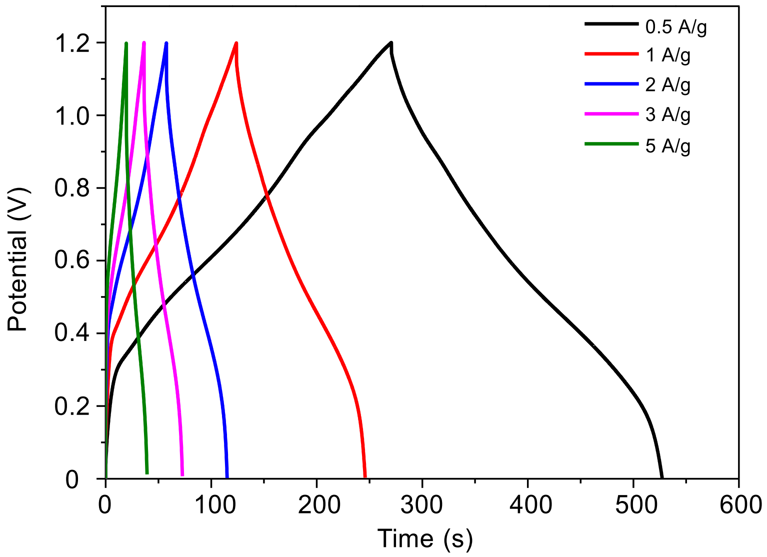


Figure S21. CP spectra of supercapacitor made of linear PANI electrodes.

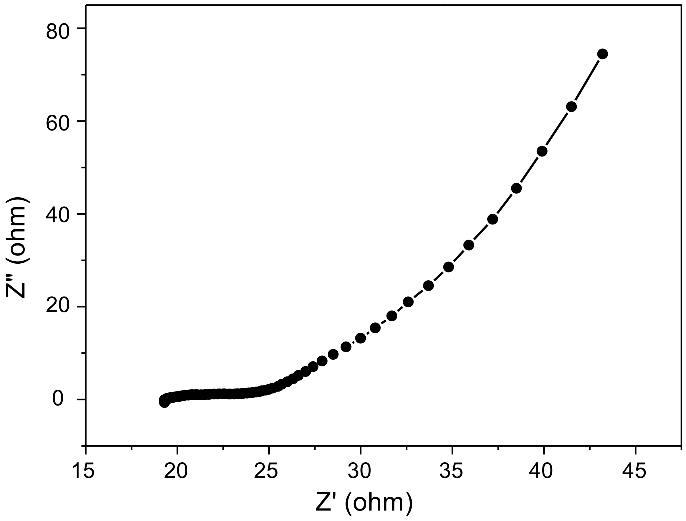


Figure S22. AC impedance profile of supercapacitor made of linear PANI electrodes.

5.5 Experimental procedures for floating test

Symmetric supercapacitor consisting of 2 pieces of 4 μm PCL-PANI electrodes and H_2SO_4/PVA gel as the electrolyte was assembled to conduct the floating test. The supercapacitor was charged at a constant potential at 1.2 V for 110 h. Temperature was maintained at 25 ºC. Subsequently, periodic sampling was performed by carrying out AC impedance test and charge-discharge (at a current density of 0.5A g^{-1}) every 12 h to keep track of resistance and capacitance change of the system, respectively.

Author contributions

F.Z., X.L. and M.C. conceived the idea. F.Z., M.M. and Z.Z. performed the synthesis and characterization experiments. F.Z., X.L. and M.C. analyzed the data and wrote the manuscript.

Reference

[1] Xiao-Xiang Zhang, Joseph P. Sadighi, Thomas W. Mackewitz and Stephen L. Buchwald. *J. Am. Chem. Soc*. 2000, 122, 7606-7607.

[2] Joseph P. Sadighi, Robert A. Singer, and Stephen L. Buchwald. *J. Am. Chem. Soc*. 1998, 120, 4960-4976.

[3] Vern G. DeVries, Jonathan D. Bloom, Minu D. Dutia, Andrew S. Katocs, Jr., and Elwood E. Largis. *J. Med. Chem.* 1989, 32, 2318-2325.

[4] Xin Liu, Fengxiang Chen, Yuanjia Cheng, Yongmin Wu, Weilin Xu. A method for determining primary amine content in natural protein fiber by titration. CN 103336002, Oct 2, 2013.