Electronic supplementary information (ESI)

Facile synthesis of novel poly(α−aminonitrile) networks through one-pot Strecker reactions

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Experimental Section

Chemicals

All starting materials and various solvents, unless otherwise specified, were purchased from commercial sources (Toyko Chemical Industry or Kanto Chemical (reagent grade)) without purification before use. Trimethylsilyl cyanide (98%) was used as the cyanide source purchased from Aldrich. Tris(4-aminophenyl)methane was prepared by the reduction of pararosaniline hydrochloride salt in ethanol using sodium tetrahydroborate ($NaBH_4$). The usual workup of the solution gave the earth-yellow colored solid in 90% yield.[1]

General synthesis process for organic polymer neworks (OPNWs) through one-pot Strecker reaction:

A 30-mL Schlenk flask fitted with a water-cooled condenser and a magnetic stir bar was charged with amine (**A**), aldehyde (**B**, 1:1 ratio of aldehyde to amine functional groups) and dimethyl sulfoxide (DMSO). The molar concentration of amine functional groups was fixed at 0.48 M. After degassing by nitrogen, the mixture was heated to 180 ^{o}C for 5-60 min. Then the reaction temperature was decreased to room temperature, followed by the addition of TMSCN (2 equiv. of aldehyde functional group) as the cyanide source to the reaction system. The reaction mixture was further stirred at 120 ^{o}C under nitrogen atmosphere for another 1 h. After cooling down to room temperature, dichloromethane (30 mL) was added to the flask and the mixture was stirred for 10 min. The solid product was separated by filtration over a Büchner funnel and washed with dimethyl formamide (DMF, 3×30 mL), tetrahydrofuran (THF, 3×30 mL) and dichloromethane (DCM, 3×30 mL). The resulting earth yellow to brown powder was then dried in vacuum at room temperature for 0.5 h and then at 120 ^{o}C for 2 h.

OPNW-1 was prepared using **A1** (0.25 mmol), **B1** (0.375 mmol), Me_3SiCN (1.5 mmol) and DMSO (1.58 mL) according to the general synthesis process for **OPNWs**. Brown solid; 93% yield;

OPNW-2 was prepared using **A1** (0.25 mmol), **B2** (0.375 mmol), Me_3SiCN (1.5 mmol) and DMSO (1.58 mL) according to the general synthesis process for **OPNWs**. Earth yellow solid; 88% yield;

OPNW-3 was prepared using **A2** (0.25 mmol), **B1** (0.25 mmol), Me_3SiCN (1 mmol) and DMSO (1.05 mL) according to the general synthesis process for **OPNWs**. Brown solid; 90% yield;

OPNW-4 was prepared using **A2** (0.25 mmol), **B2** (0.25 mmol), Me_3SiCN (1 mmol) and DMSO (1.05 mL) according to the general synthesis process for **OPNWs**. Brown solid; 91% yield.

Synthesis of model compound (MC), 2-phenyl-2-(phenylamino)ethanenitrile through solvent-free and catalyst-free one-pot Strecker reaction:[2]

Benzaldehyde (0.103 mL, 1 mmol) and aniline (0.091 mL, 1 mmol) were added to a 30-mL flask at room temperature. The mixture was vigorously stirred for 10 min and then Me_3SiCN (0.160 mL, 1.2 mmol) was added to the mixture. The obtained white solid was further purified by rinsing with excess hexane,[3] followed by evaporation of the hexane to afford 2-phenyl-2-(phenylamino)ethanenitrile (206 mg, 99 %). ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.03$ (s, 1H), 5.43 (s, 1H), 6.77 (d, $J = 7.55$ Hz, 2H), 6.90 (t, $J = 7.35$ Hz, 1H), 7.20-7.30 (m, 2H), 7.37-7.50 (m, 3H), 7.60 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 144.7$, 133.9, 129.6, 129.6, 129.4, 127.3, 120.3, 118.1, 114.1, 50.2.

Synthesis of imine-linked polymer (ILP-1) from tris(4-aminophenyl)methane (A1) and terephthalaldehyde (B1):

A 30-mL Schlenk flask fitted with a water-cooled condenser and a magnetic stir bar was charged with **A1**, **B1** (1:1 ratio of aldehyde to amine functional groups) and dimethyl sulfoxide. The molar concentration of amine functional group was fixed at 0.48 M. After degassing by nitrogen, the mixture was heated to 180 ^{o}C for 0.5 h. The yellow product was separated by filtration over a Büchner funnel and washed with dimethyl formamide (DMF, 3×30 mL), tetrahydrofuran (THF, 3×30 mL) and dichloromethane (DCM, 3×30 mL). The resulting yellow material, which is imine-linked polymer (**ILP-1**), was then dried in vacuum at room temperature.

Material Characterization

Nitrogen sorption experiments of the organic networks were performed at -196 ^{o}C using an automatic adsorption system (BEL 28SA, BEL Japan). Samples were degassed at 120 ^{o}C for 2 h under vacuum (10^{-4} bar) before analysis.

Fourier transform infrared (FT-IR) spectra were measured using a JASCO IR-630 spectrophotometer (KBr pellets).

Liquid ^1H and ^{13}C nuclear magnetic resonance (NMR) were recorded using Bruker AV500 III NMR spectrometer with the samples in $CDCl_3$. ^1H NMR chemical shifts were determined relative to the internal tetramethylsilane at δ 0.0 ppm. ^{13}C NMR chemical shifts were determined relative to the internal tetramethylsilane at δ 0.0 ppm or to ^{13}C signal of $CDCl_3$ at δ 77.0 ppm. Coupling constants (J) are given in Hz.

Solid-state ^{13}C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were collected on a Bruker Avance 400WB solid-state NMR spectrometer (9.36 T) operating at Lamor frequency of 100.63 MHz for ^{13}C using a ZrO_2 rotor equipped with a Kel-F cap. The $\pi/2$ pulse length for ^1H was 3.4 μs. The acquisition time was 34 ms, using a sweep width of 30 kHz. The relaxation delay was adjusted to 5 s, the contact time to 2 ms, and the sample spinning rate to 15 kHz.

TGA measurements were conducted on a themogravimetric analysis instrument (TA Instruments) over the temperature range 30 to 600 °C, and the sample was scanned at a rate of 10 °C per minute in a nitrogen flow.

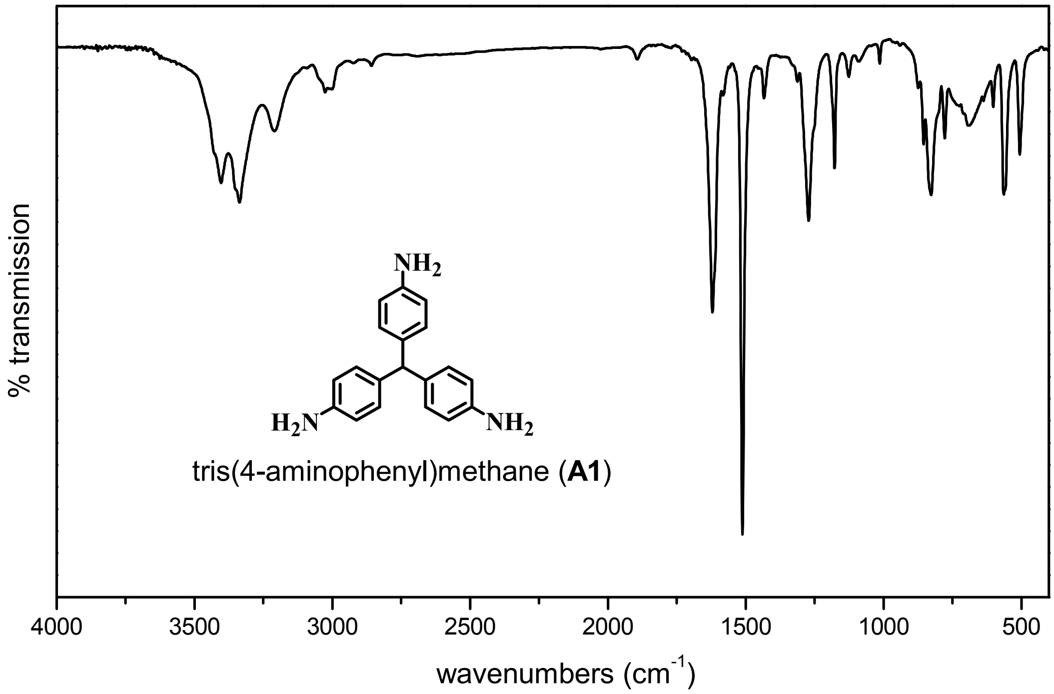


Figure S1. FT-IR spectrum of tris(4-aminophenyl)methane (**A1**).

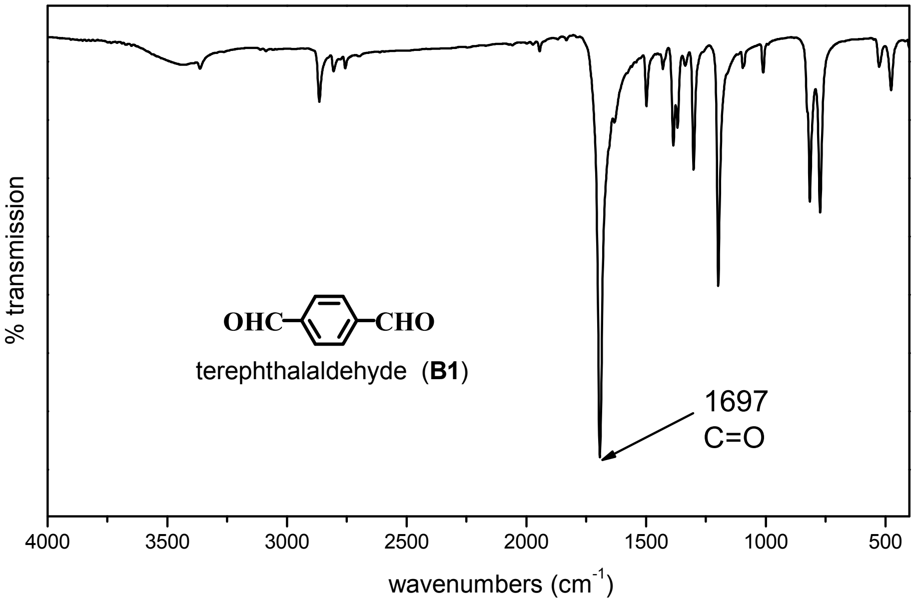


Figure S2. FT-IR spectrum of terephthaldehyde (**B1**).

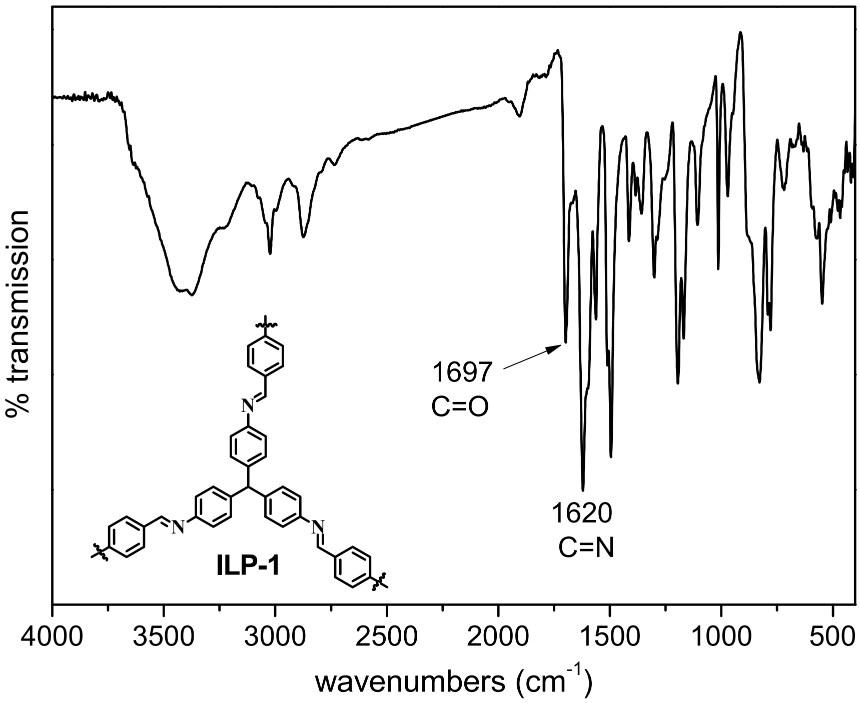


Figure S3. FT-IR spectrum of imine-linked polymer (ILP-1).

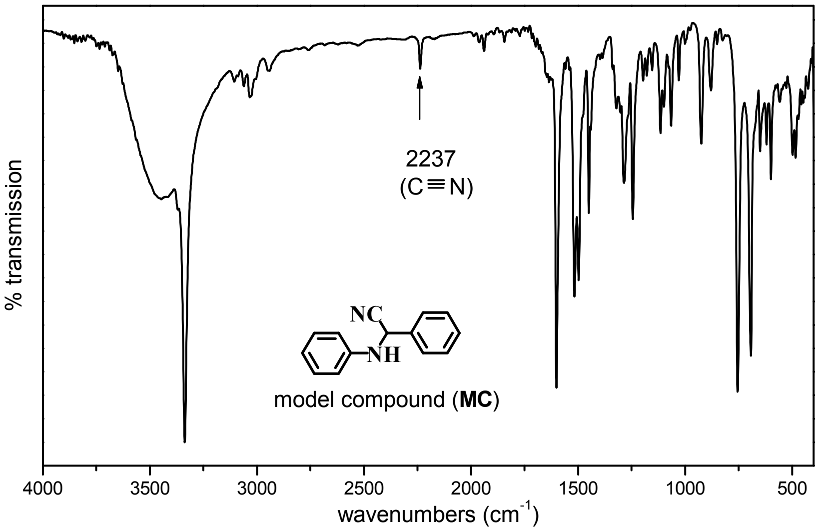


Figure S4. FT-IR spectrum of model compound (**MC**, 2-phenyl-2-(phenylamino)ethanenitrile).

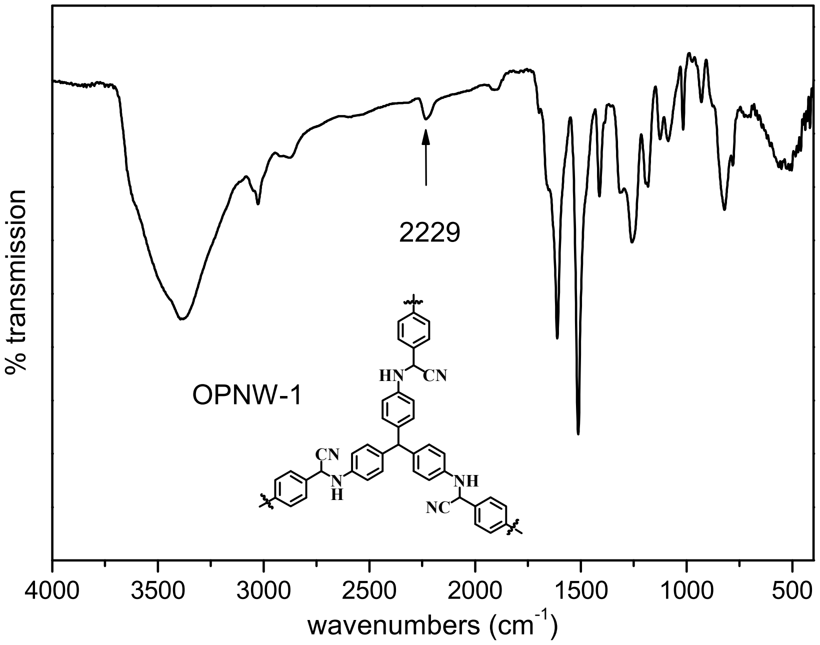


Figure S5. FT-IR spectrum of OPNW-1.

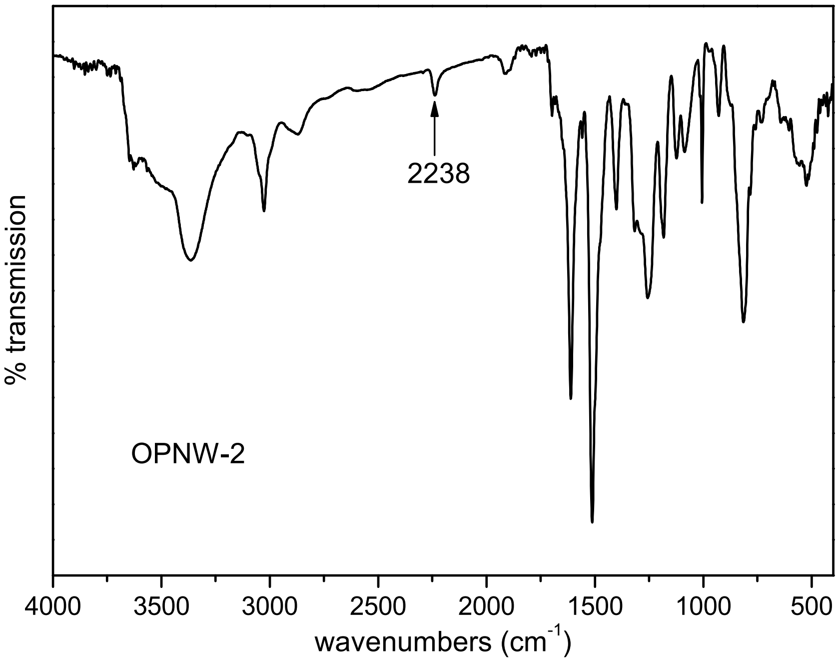


Figure S6. FT-IR spectrum of OPNW-2.

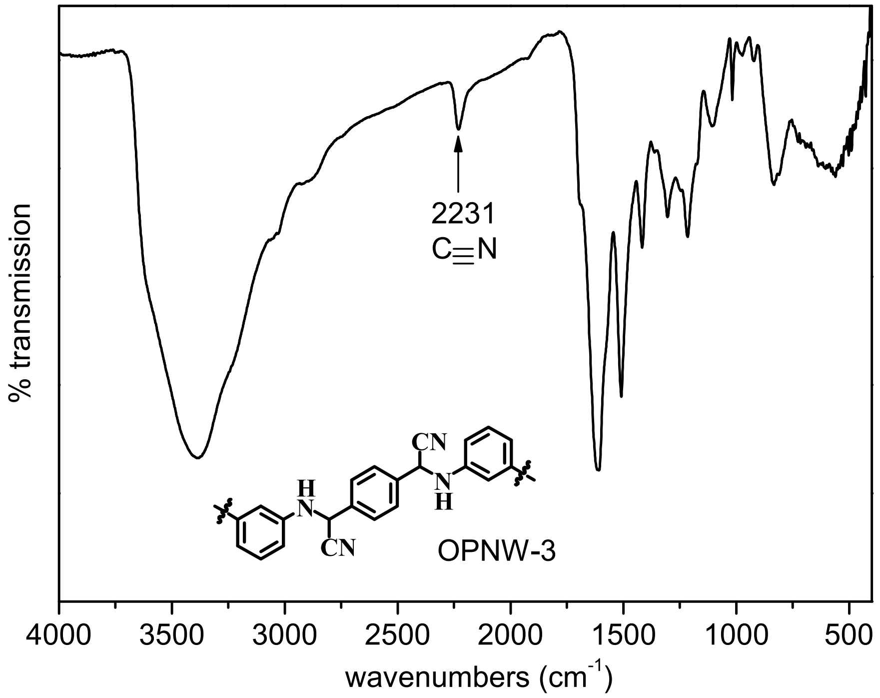


Figure S7. FT-IR spectrum of OPNW-3.

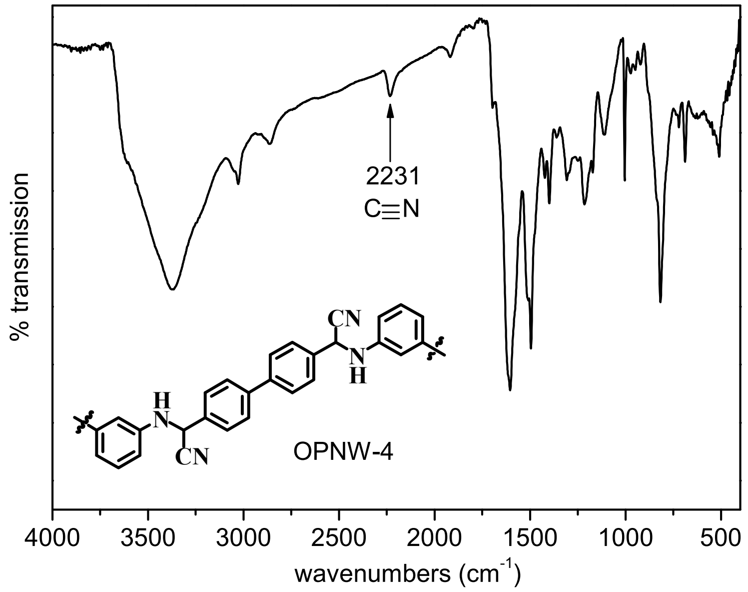


Figure S8. FT-IR spectrum of OPNW-4.

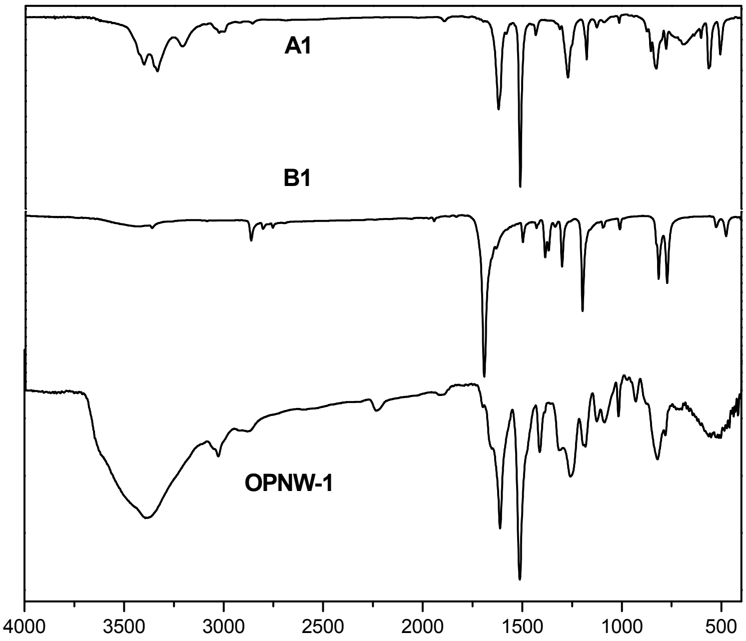


Figure S9. Stack plot of FTIR spectra of tris(4-aminophenyl)methane (**A1**), terephthalaldehyde (**B1**), and **OPNW-1**.

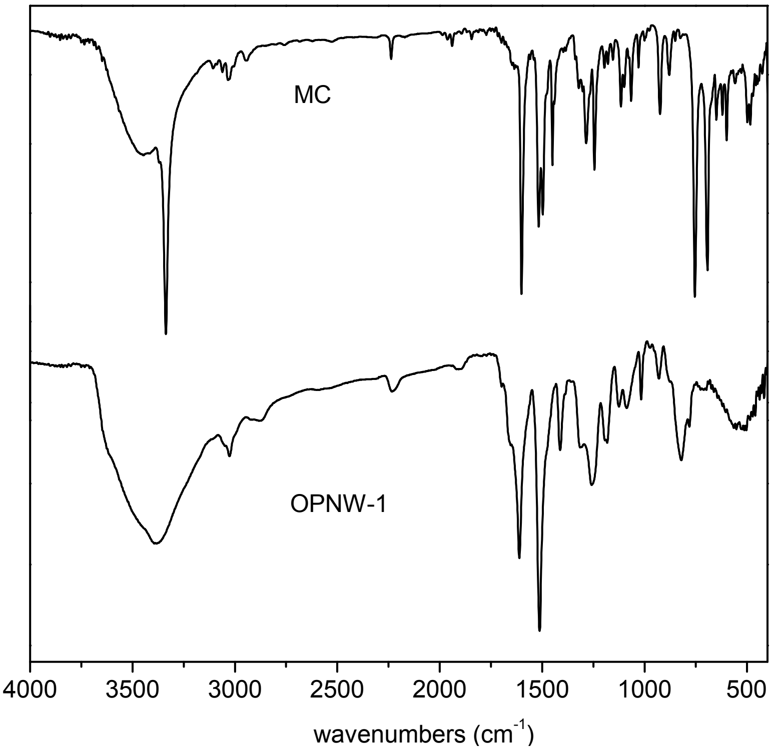


Figure S10. Stack plot of FTIR spectra of model compound (**MC**, 2-phenyl-2-(phenylamino)ethanenitrile) and **OPNW-1**.

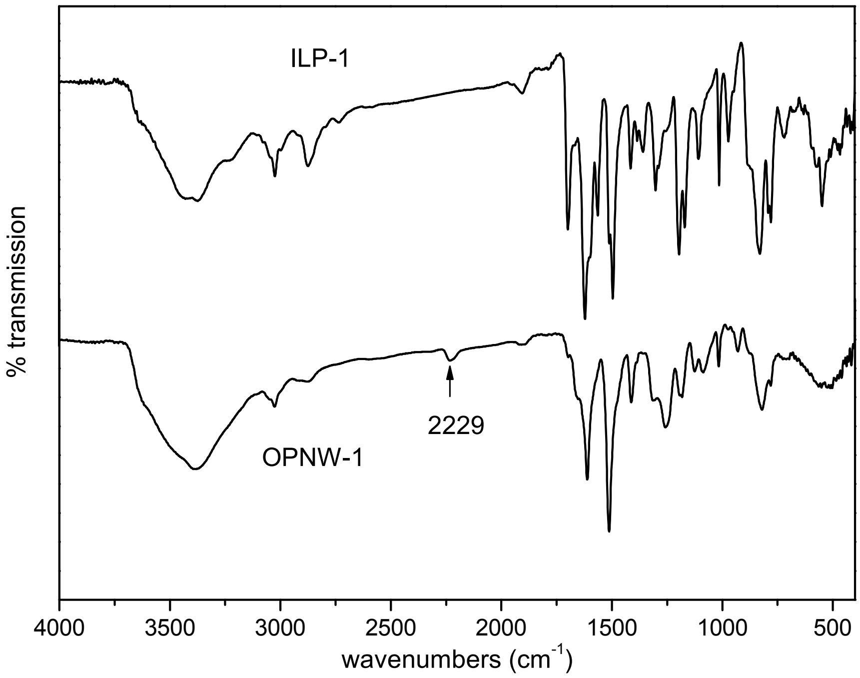


Figure S11. Stack plot of FTIR spectra of **ILP-1** and **OPNW-1**.

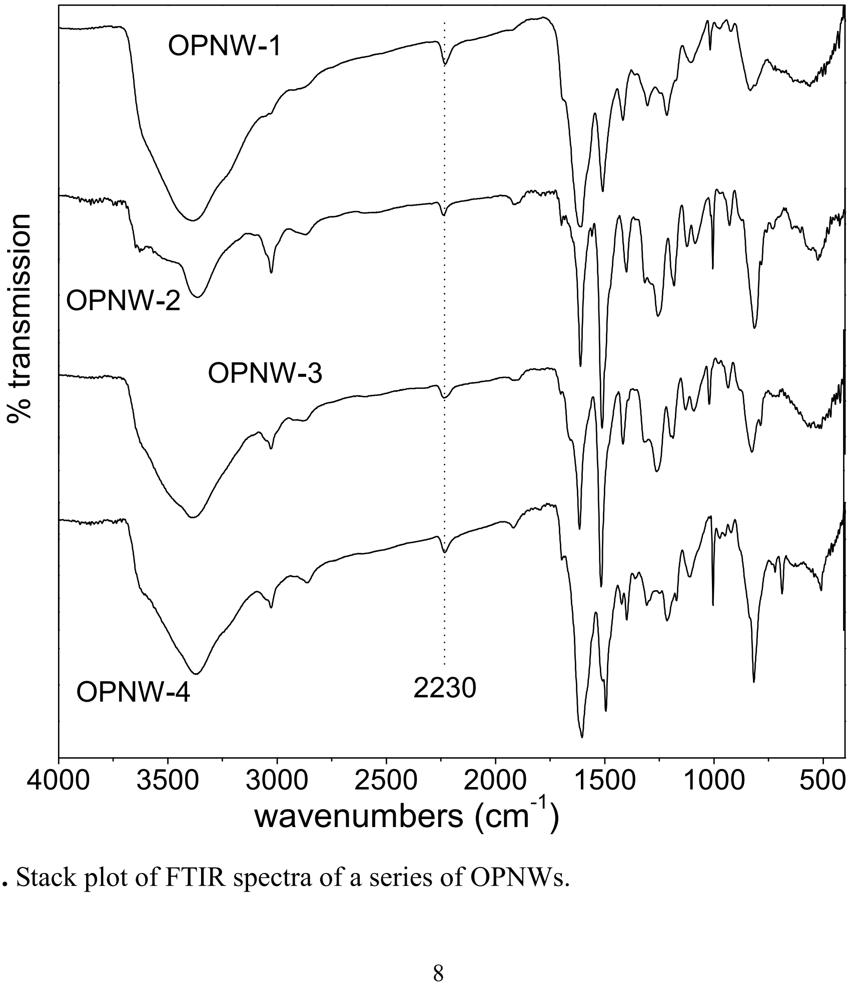


Figure S12. Stack plot of FTIR spectra of a series of OPNWs.

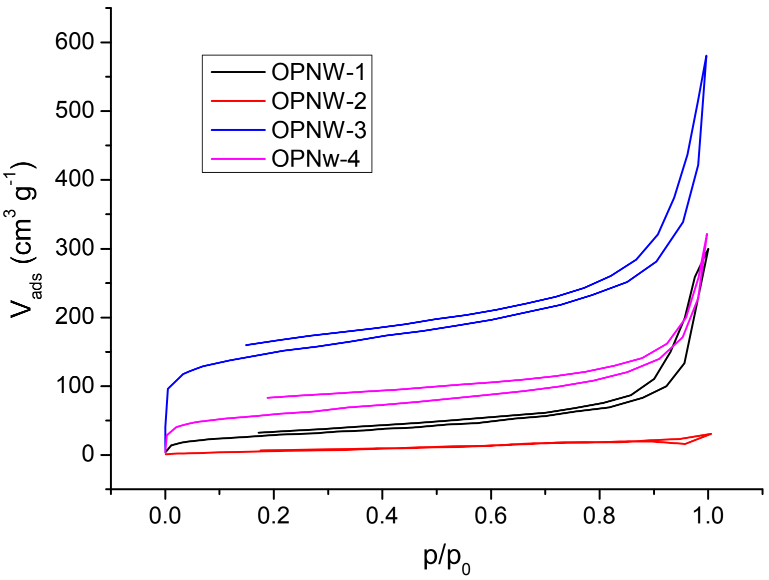


Figure S13. Nitrogen sorption isotherms of the OPNWs.

Table S1. Textural properties of OPNWs.

$$\text{Amine} + \text{Aldehyde} + Me_3SiCN \xrightarrow[\Delta]{\text{DMSO}} \text{OPNW}$$

Entry	Polymer	Specific surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
1	OPNW-1	99	0.40
2	OPNW-2	25	0.11
3	OPNW-3	527	0.79
4	OPNW-4	206	0.43

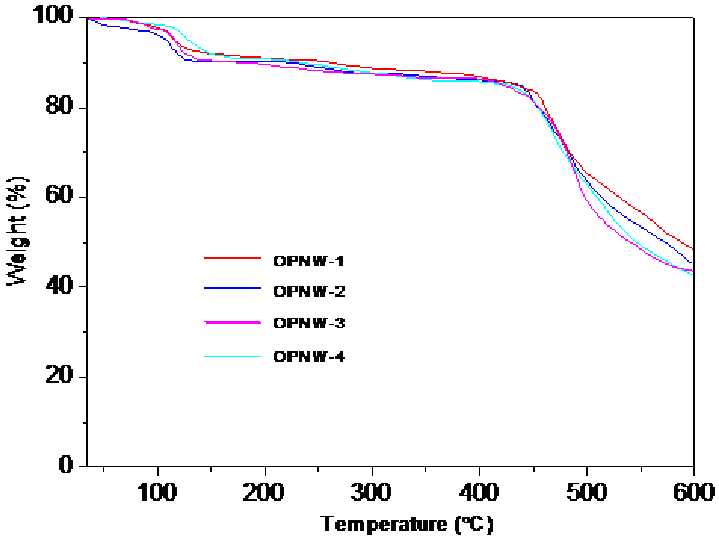


Figure S14. Thermal gravimetric curves of the OPNWs in a nitrogen flow.

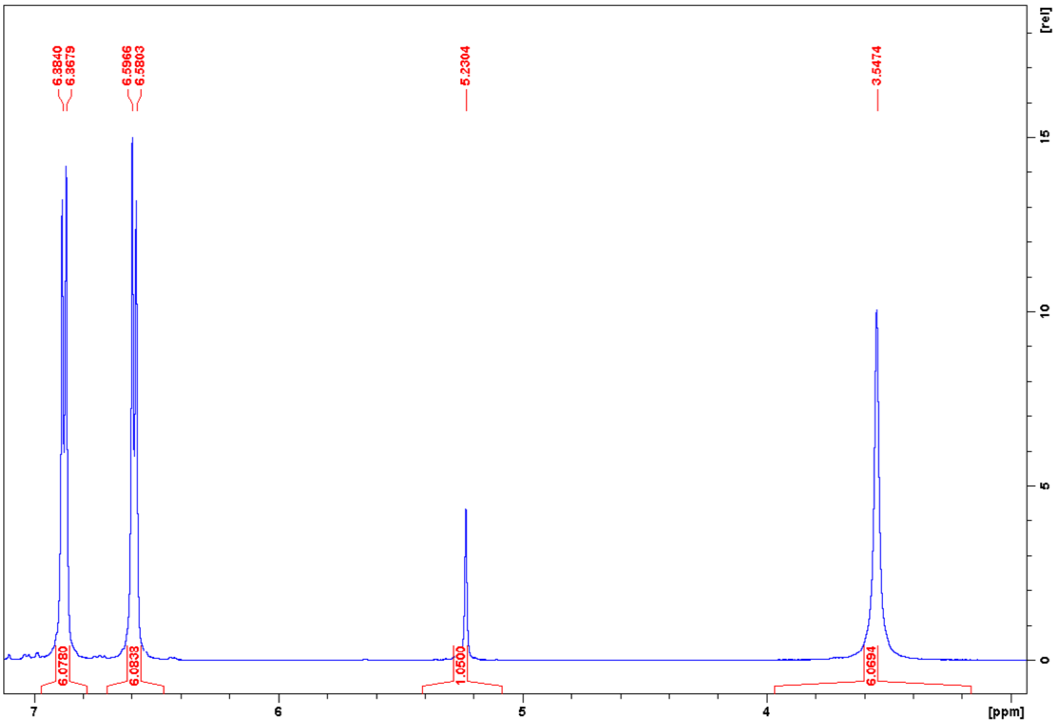


Figure S15. ^{1}H NMR spectrum for tris(4-aminophenyl)methane (**A1**) in CDCl3.

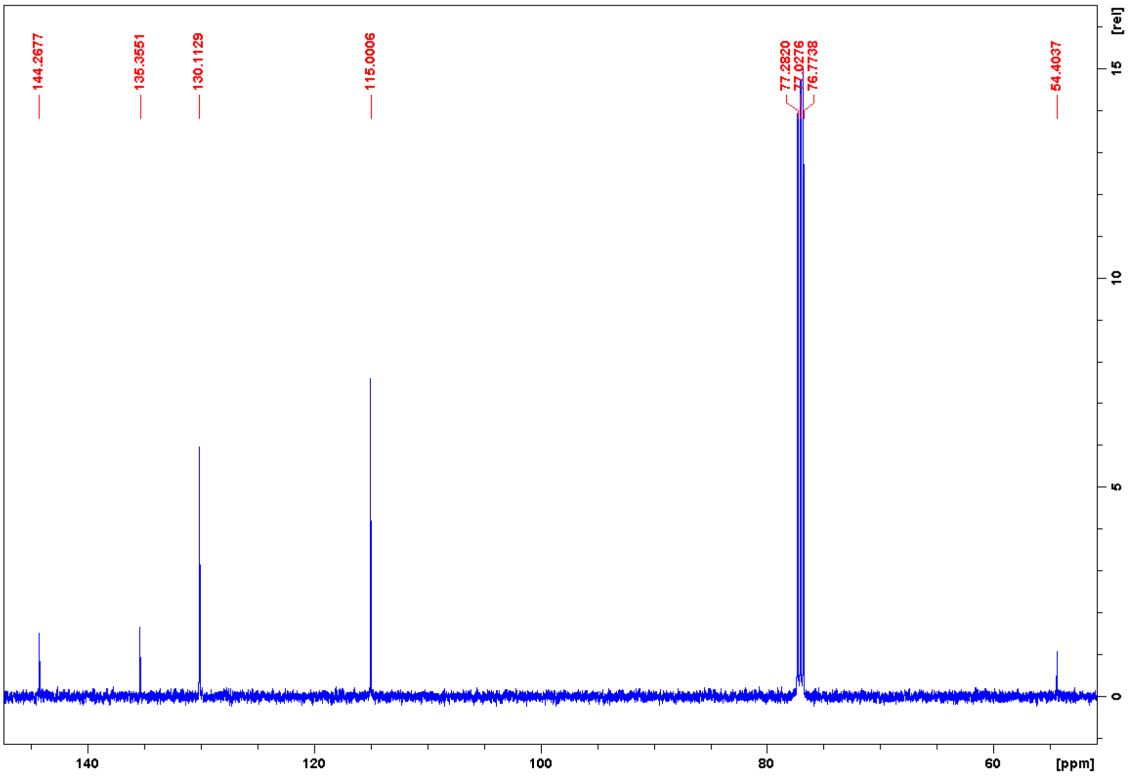
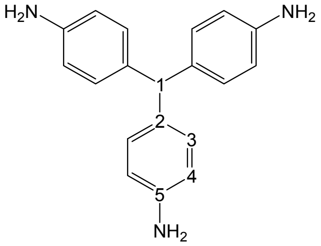


Figure S16. ^{13}C NMR spectrum for tris(4-aminophenyl)methane (A1) in CDCl3.

Table S2. ^{13}C NMR signals for tris(4-aminophenyl)methane (A1) in CDCl3.



Signal (ppm)	assignment	comments
54.4037	1	Methane quaternary
115.0006	3	Aromatic
130.1129	2	Aromatic
135.3551	4	Aromatic
144.2677	5	Aromatic

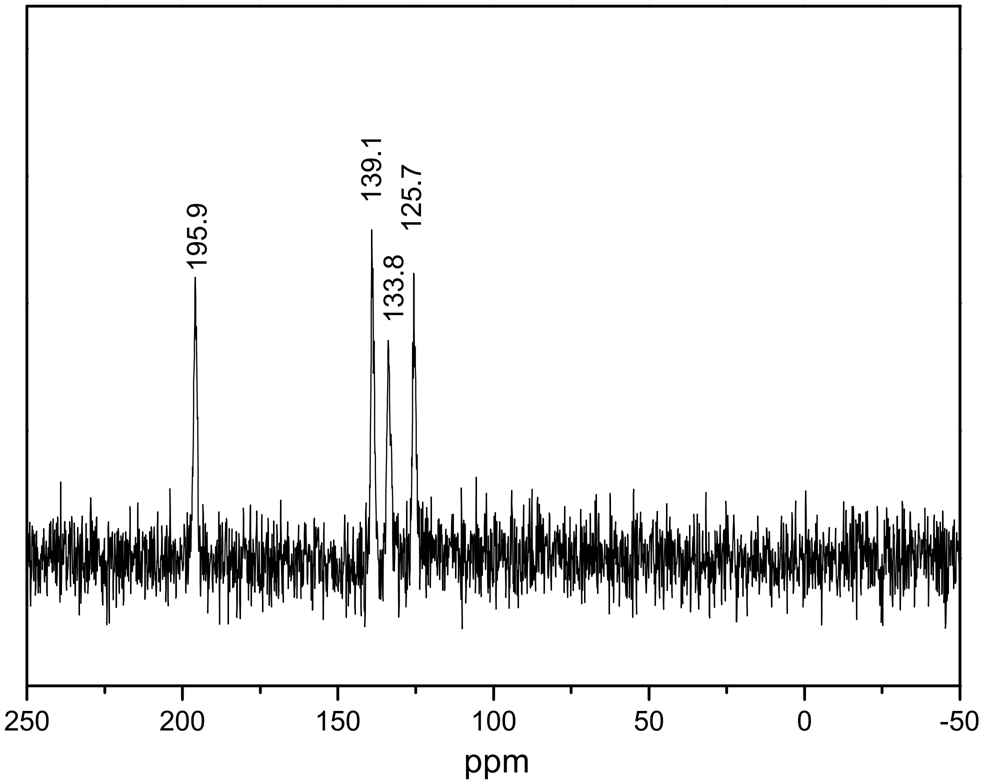
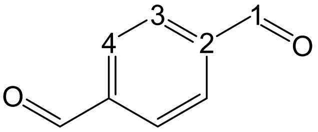


Figure S17. Solid-state ^{13}C CP-MAS spectrum for terephthaldehyde (**B1**).

Table S3. ^{13}C NMR signals for terephthaldehyde (**B1**) in CDCl3.



Signal (ppm)	assignment	comments
125.7 133.8	3, 4	Aromatic
139.1	2	Aromatic
195.9	1	Carbonyl

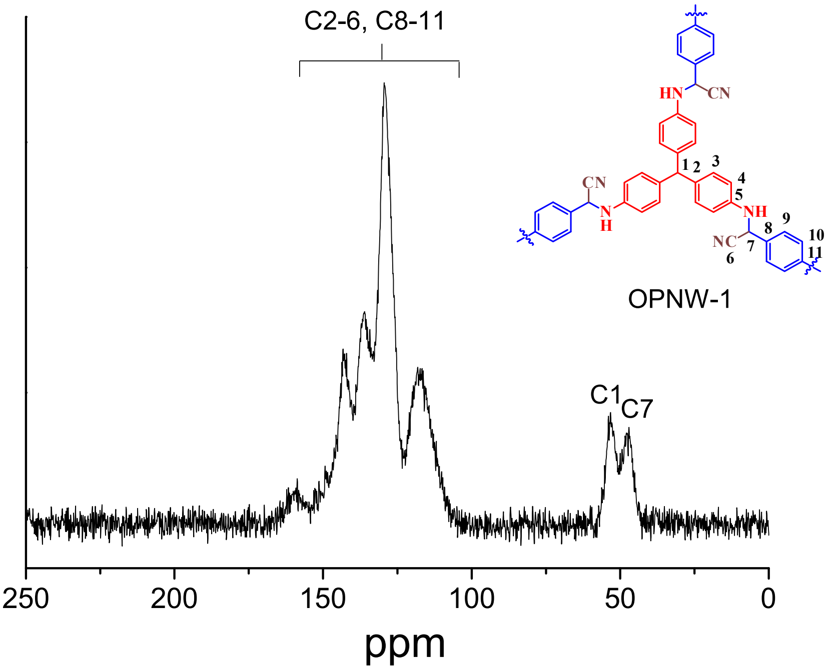


Figure S18. ^{13}C CP-MAS NMR spectrum of OPNW-1.

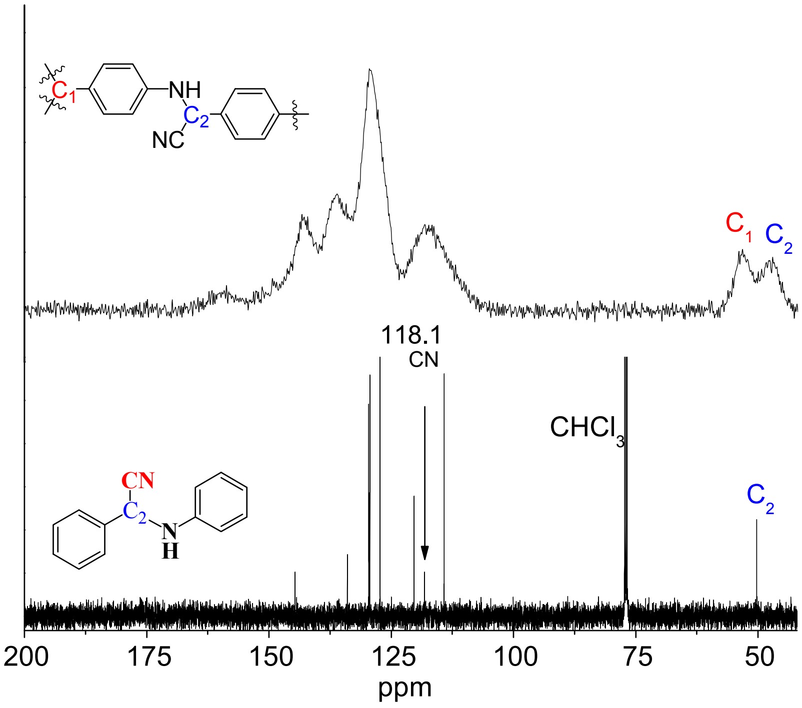


Figure S19. Stack plots of ^{13}C NMR spectra of **OPNW-1** and 2-phenyl-2-(phenylamino)ethanenitrile (**MC**)

References

1. H. Houjou, T. Koga, M. Akiizumi, I. Yoshikawa and K. Araki, *Bull. Chem. Soc. Jpn.*, 2009, **82**, 730.
2. J. C. Wang, Y. Masui and M. Onaka, *Eur. J. Org. Chem.*, 2010, 1763.
3. G. K. S. Prakash, T. Mathew, C. Panja, S. Alconcel, H. Vaghoo, C. Do and G. A. Olah, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 3703.