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Understanding the role of acid-base interactions using architecturally-controlled, pyridyl-bearing sulfonated phenylated polyphenylenes

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1. Materials

4-Pyridinecarboxaldehyde, 2,5-dibromopyridine, triethylamine (99%, Anachemia Science), 1,4 - dibromonaphthalene (98%), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (95%) and 1-Bromo-4-iodobenzene (98%) were purchased from Combi-Blocks, Inc. Acetone, dichloromethane (DCM), diethyl ether (reagent grade) methanol (MeOH), petroleum ether (PE), potassium carbonate (K_2CO_3, reagent grade), tetrahydrofuran (THF) were purchased from Thermo Fisher Scientific. n-butanol, dichloroethane (DCE), dimethyl sulfoxide(DMSO), ethyl acetate (EtOAc) and potassium hydroxyde (KOH, reagent grade) were purchased from Caledon Laboratories Ltd. Nitrobenzene (ACS reagent, >99%), trimethylsilyl chlorosulfonate (99%), 2, 5-dibromopyridine (98%), 4′-Bromoacetophenone (98%), tetrakis(triphenylphosphine)palladium(0) (98%), n-Butyllithium solution (2.5 M in hexane), benzaldehyde and 4,4'-diiodobiphenyl (technical grade, 90%) were purchased from Sigma Aldrich Canada Co. Dimethylformamide (DMF, anhydrous HPLC grade) was purchased from J&K Scientific. Anhydrous ethanol was purchased from Commercial Alcohols. Diphenylphosphineferrocene palladium dichloride (97%) was purchased from Strem Chemicals, Inc. 1,3 - (diphenyl)propan-2-one (98%), bisbenzyl (98%), 1,3,5-tribromobenzene (98%) and trimethylsilylethynyl (98%) were purchased from Tokyo Chemical Industry Co., Ltd. America. Diphenylphosphine palladium dichloride (98%) was purchased from Strem Chemicals, Inc. Copper iodide (99.9%) was purchased from Santa Cruz Biotechnology, Inc. Chemicals and organic solvents were used as received except THF was dried with sodium using benzophenone as the indicator.

2. Synthetic pathways

2.1 Synthesis of the diene monomer, BTCS-TEA (compound 7)

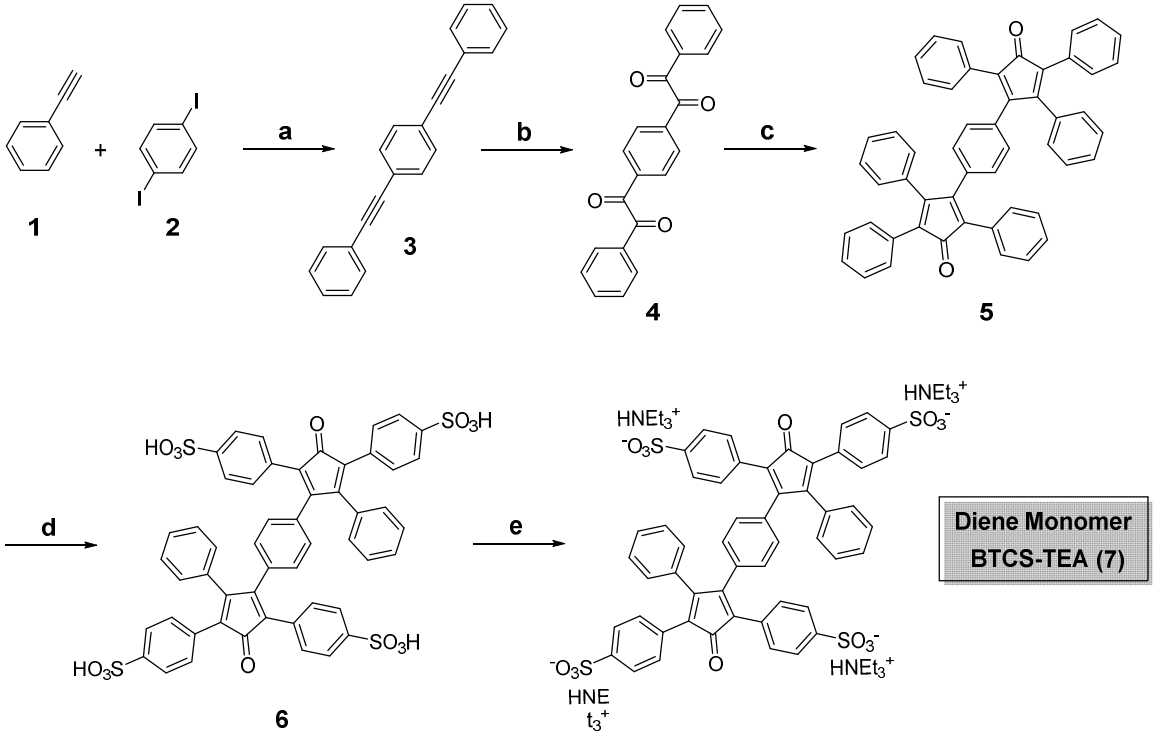

Figure S 1. Synthesis of diene monomer BTCS-TEA. Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, CuI, TEA, 50 °C, overnight; (b) I_2, DMSO, 155 °C, overnight; (c) dibenzyl ketone, KOH, reflux, 45 min; (d) TMS-OSO_2-Cl, DCE, overnight; (e) *n*-BuOH, triethylamine, THF.

3. Synthetic procedures and membrane preparation

Synthesis of the diene monomer, BTCS-TEA (7)

The target molecule **7** was synthesized following our previously reported methods and a detailed synthesis (from compound **3** to compound **7**) can be found in the literature.[1,2]

Synthesis of dienophile monomers TPP (11) and TPPy (13)

Both the oligophenylene **TPP** (molecule **11**) and 2,4,6-triphenylpyridine derivative **TPPy** (molecule **13**), as well as the intermediate compounds **8** through **10** were synthesized according to our previously reported methodologies.[3]

Synthesis of 1-(4-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (12)

Compound **12** was synthesized according to previous literature procedures with some modifications.[4,5] 1-(4-Bromophenyl)ethan-1-one (19.705 g, 100 mmol), $Pd(PPh_3)_2Cl_2$ (701 mg, 1 mmol) and trimethylsilylacetylene (18 mL, 120 mmol) were mixed in a combined solution of 70 mL trimethylamine and 120 mL THF under N_2. To the solution was added CuI (381 mg, 2 mmol). The mixture was stirred at 50 ^oC for 18 h. After cooling to RT, the volatiles were removed *in vacuo*. The crude product was purified via flash column chromatography (dichloromethane/hexanes = 1:20). A light yellow oil (18.0 g, 83.3%) was obtained. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.84 (d, 2H), 7.50 (d, 2H), 2.54 (s, 3H), 0.25 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 196.85, 136.43, 131.97, 129.73, 128.02, 104.05, 97.98, 26.40, -0.21; **HRMS** (EI) *m/z* calculated for $C_{13}H_{17}OSi^+$ (M + H^+) 271.1049, found 217.1040.

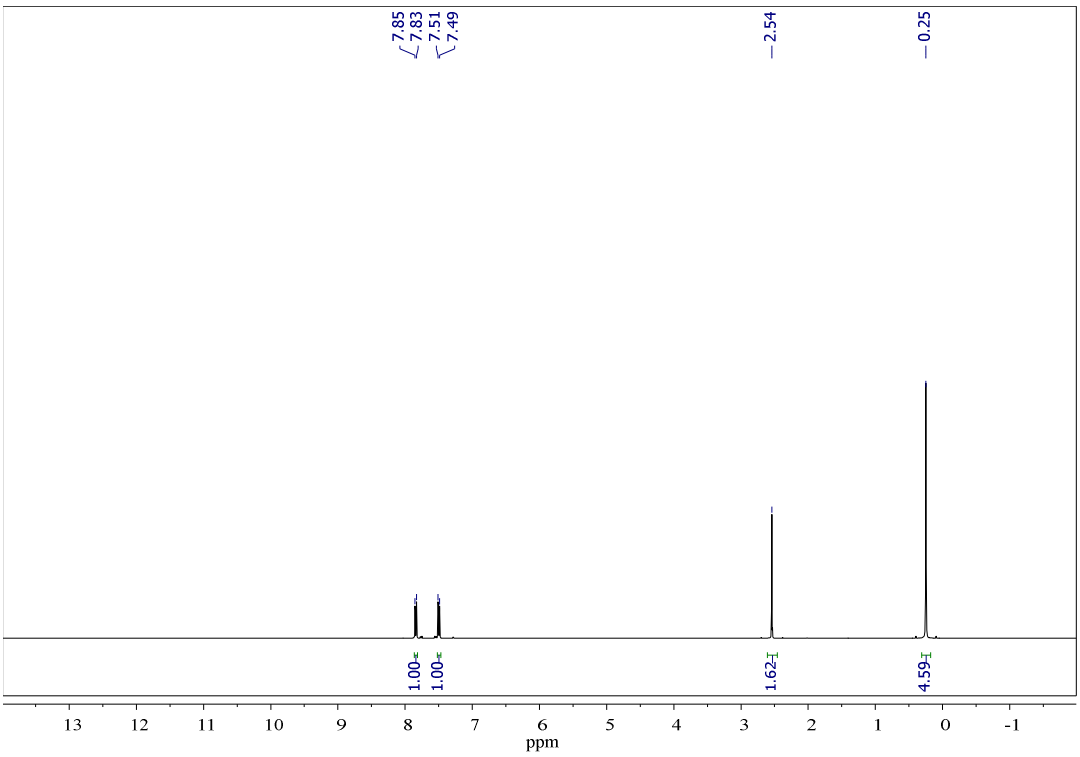

Figure S 2. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 12.

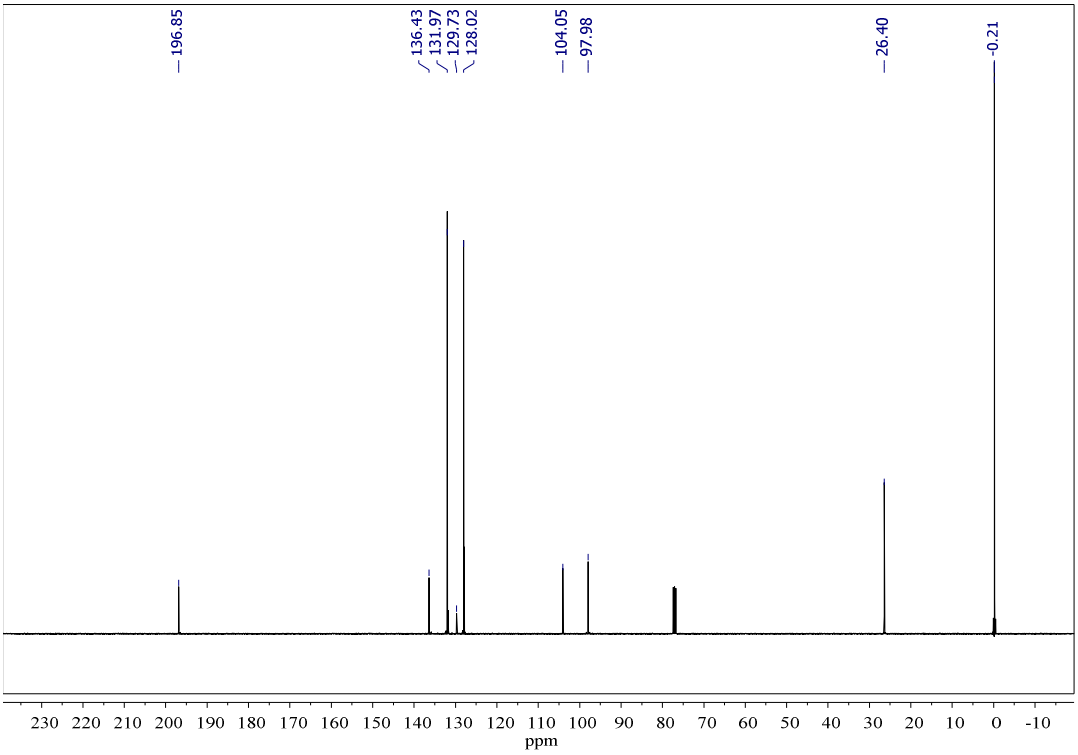

Figure S 3. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 12.

Synthesis of 2,6-bis(4-ethynylphenyl)-4,4'-bipyridine (BPBPy, 14)

Compound **14** was synthesized according to a previous literature procedure with some modifications.[6] To a solution of 4-pyridinecarboxaldehyde (536 mg, 5 mmol) in 25 mL ethanol was added 1-(4-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (2.16 g, 10 mmol). Then ammonium hydroxide (14.5 mL, 29.3%) and KOH pellets (561 mg, 10 mmol) were added to the mixture. The reaction was stirred at ambient temperature for 3 days. The crude solid was collected via filtration and washed with ethanol. Purification by flash chromatography (dichloromethane/hexanes = 1:3) gave a white powder (0.26 g, 14.2%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.87 (d, 2H), 8.20 (d, 4H), 7.94 (s, 2H), 7.86 (d, 2H), 7.69 (d, 2H), 3.24 (s, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 157.41, 149.39, 147.70, 146.52, 138.71, 132.65, 126.96, 123.52, 122.69, 116.89, 83.30, 78.84. **HRMS** (EI) *m/z* calculated for $C_{26}H_{17}N_2^+$ ($M + H^+$) 357.1392, found 357.1391

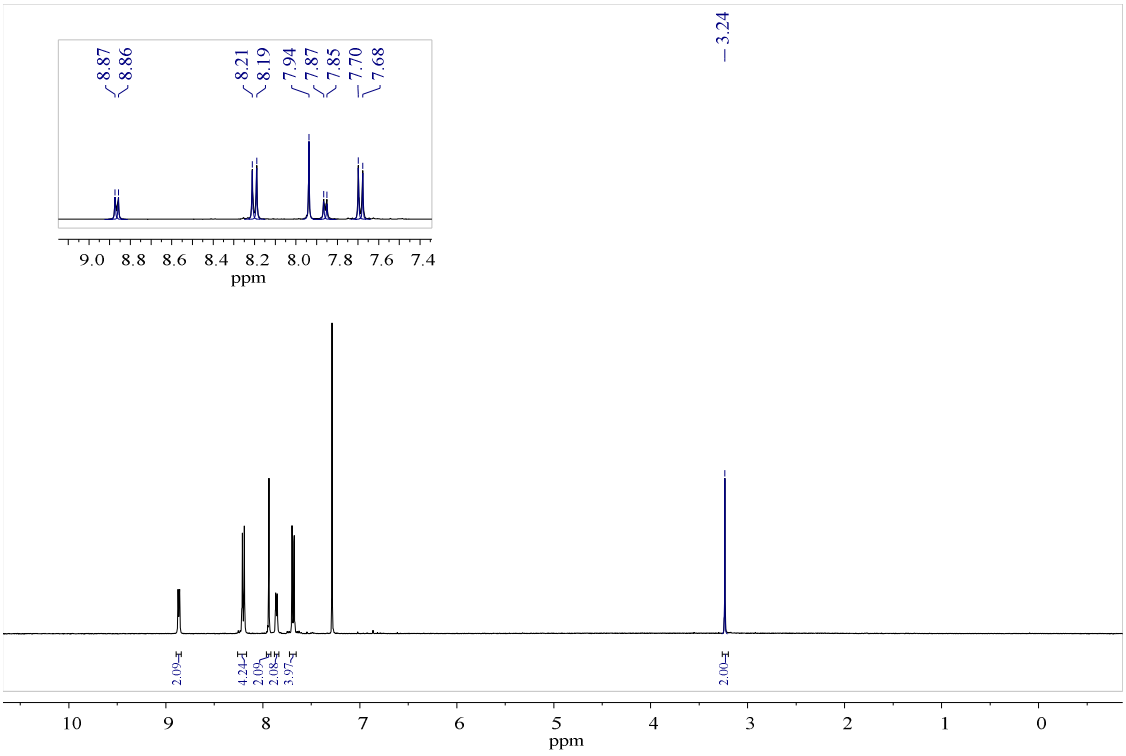

Figure S 4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 14.

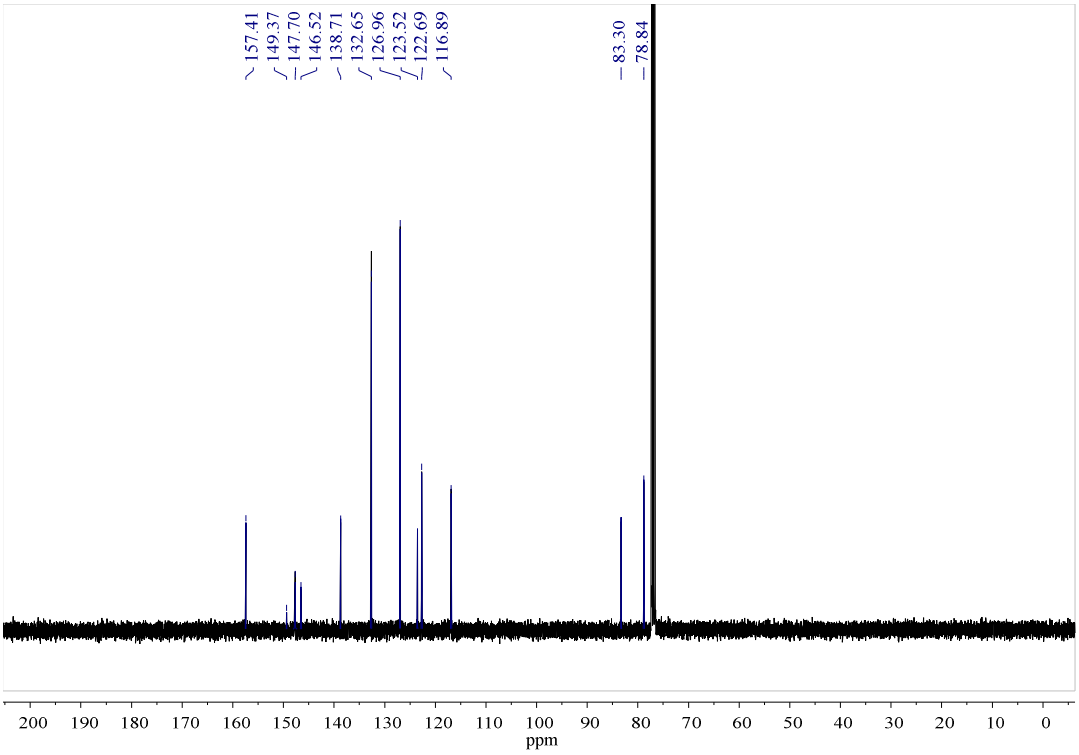

Figure S 5. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 14.

Synthesis of 1-(5-bromopyridin-2-yl)ethan-1-one (15)

Compound **15** was synthesized according to a previous literature procedure which was modified.[7] To a solution of 2,5-dibromopyridine (3.553 g, 15 mmol) in 60 mL anhydrous toluene was added n-BuLi (2.5 M in hexane, 6.6 mL, 16.5 mmol) dropwise manually within 15 min under Ar at -40 °C. The resulting mixture was stirred for 30 min, after which anhydrous dimethylacetamide (6.6 mL, 22.5 mmol) was added dropwise into the solution within 5 min and the mixture was allowed to warm to RT while stirring for 1 h. 80 mL of saturated NH_4Cl was added to quench the reaction. The product was extracted with dichloromethane (50 mL × 3). The organic layer was separated and washed with brine and water three times each. Purification via flash column chromatography (ethyl acetate/hexanes = 1:4) yielded the target product as a white solid (2.1 g, 70.0%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ δ 8.75 (d, 1H), 7.99 (dd, 1H), 7.97 (d, 1H), 2.72 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ δ 199.02, 151.93, 150.14, 139.50, 125.21, 122.88. **HRMS** (EI) *m/z* calculated for $C_7H_7BrNO^+$ (M + H^+) 199.9711, found 199.9701

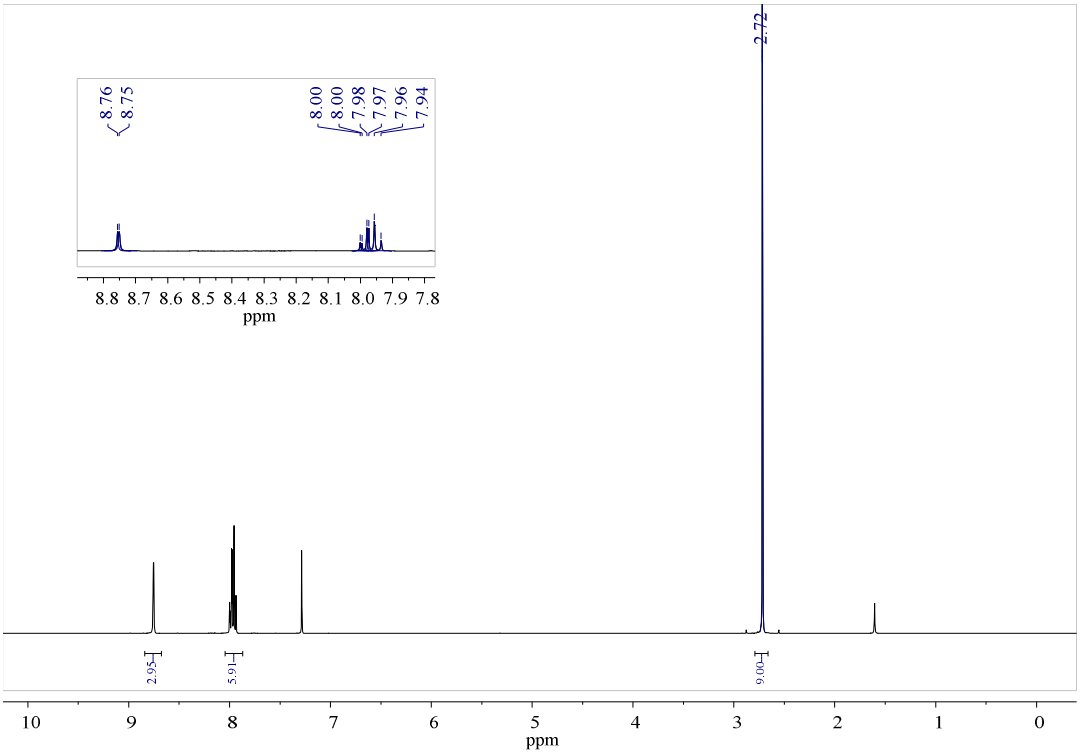

Figure S 6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 15.

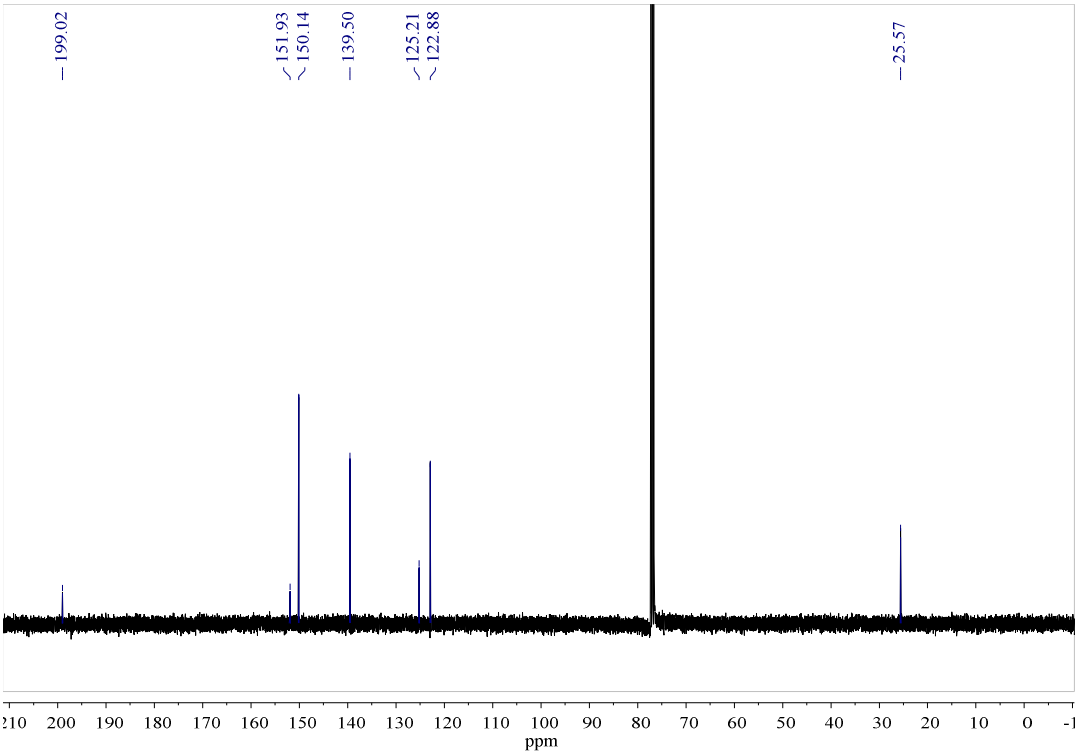

Figure S 7. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 15.

Synthesis of 1-(5-((trimethylsilyl)ethynyl)pyridin-2-yl)ethan-1-one (16)

1-(5-bromopyridin-2-yl)ethan-1-one (3.98 g, 20 mmol), $Pd(PPh_3)_2Cl_2$ (140.2 mg, 0.2 mmol) and trimethylsilylacetylene (3.13 mL, 22 mmol) were dissolved in a mixed solvent of 100 mL trimethylamine and 150 mL THF under Ar. To the solution was added CuI (76 mg, 0.4 mmol). The mixture was stirred at 60 °C for 18 h. After cooling down to RT, the mixture was filtered through Celite and the filtrate was concentrated *in vacuo*. The crude product was purified via flash column chromatography (hexanes). A brown oil (4.0 g, 92.0%) was obtained. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.71 (d, 1H), 7.98 (d, 1H), 7.96 (dd, 1H), 2.71 (s, 3H), 0.28 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 199.09, 151.77, 151.58, 139.56, 123.75, 120.77, 101.66, 100.93, 25.88, 0.34. **HRMS** (EI) *m/z* calculated for $C_{12}H_6NOSi^+$ ($M^+ + H^+$) 218.1001, found 218.0998

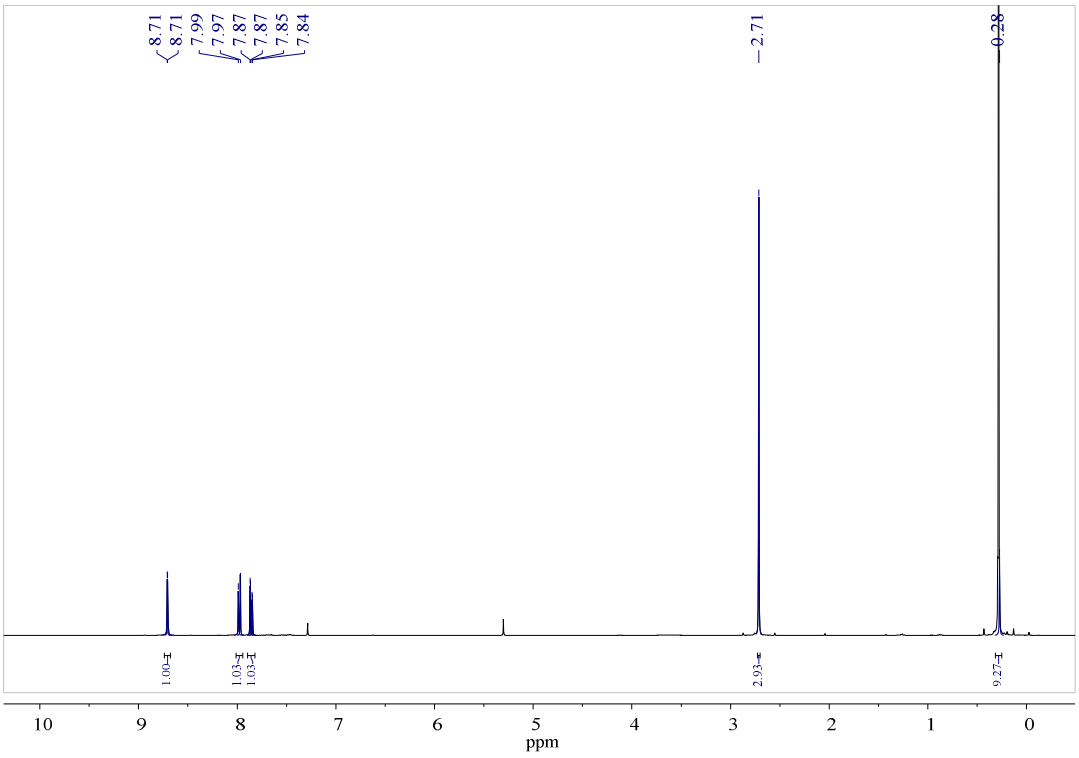

Figure S 8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 16.

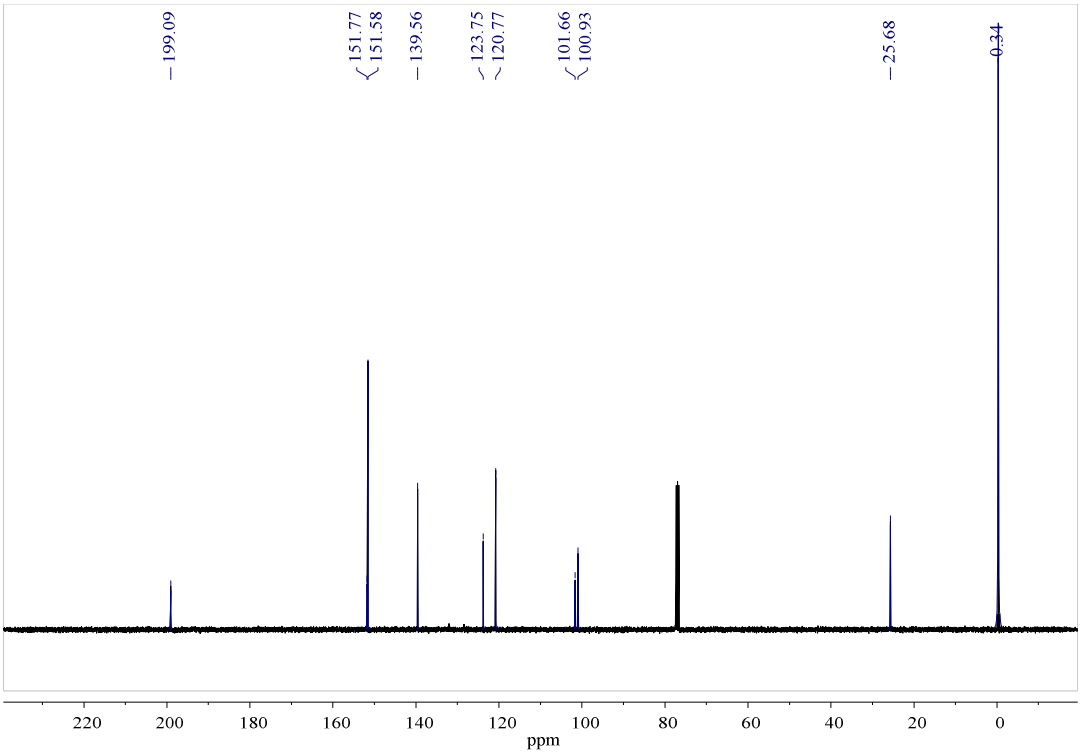

Figure S 9. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 16.

Synthesis of 5,5''-diethynyl-4'-phenyl-2,2':6',2''-terpyridine (PTPy, 17)

The synthesis of this compound followed a procedure similar to that of compound **14**. KOH (560 mg, 10 mmol), Benzaldehyde (531.0 mg, 5 mmol) and 1-(5-((trimethylsilyl)ethynyl)pyridin-2-yl)ethan-1-one (2.173 g, 10 mmol) were dissolved in 24 mL EtOH. To the resultant solution was added ammonium hydroxide (14.5 mL, 29.3%) and the mixture was stirred for 3 d. The crude solid was collected via filtration and washed with ethanol. Purification by flash chromatography (dichloromethane/hexanes = 1:1) gave a white powder (350.0 mg, 9.8%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (d, 2H), 8.79 (s, 2H), 8.68 (dd, 2H), 8.00 (d, 2H), 7.93 (d, 2H), 7. 55 (m, 3H), 3.35 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.75, 151.66, 160.69, 140.51, 137.92, 129.31, 129.05, 127.34, 120.88, 119.95, 119.54, 81.82, 80.242. **HRMS** (EI) *m/z* calculated for $C_{25}H_{16}N_3^+$ ($M^+ + H^+$) 358.1344, found 358.1337

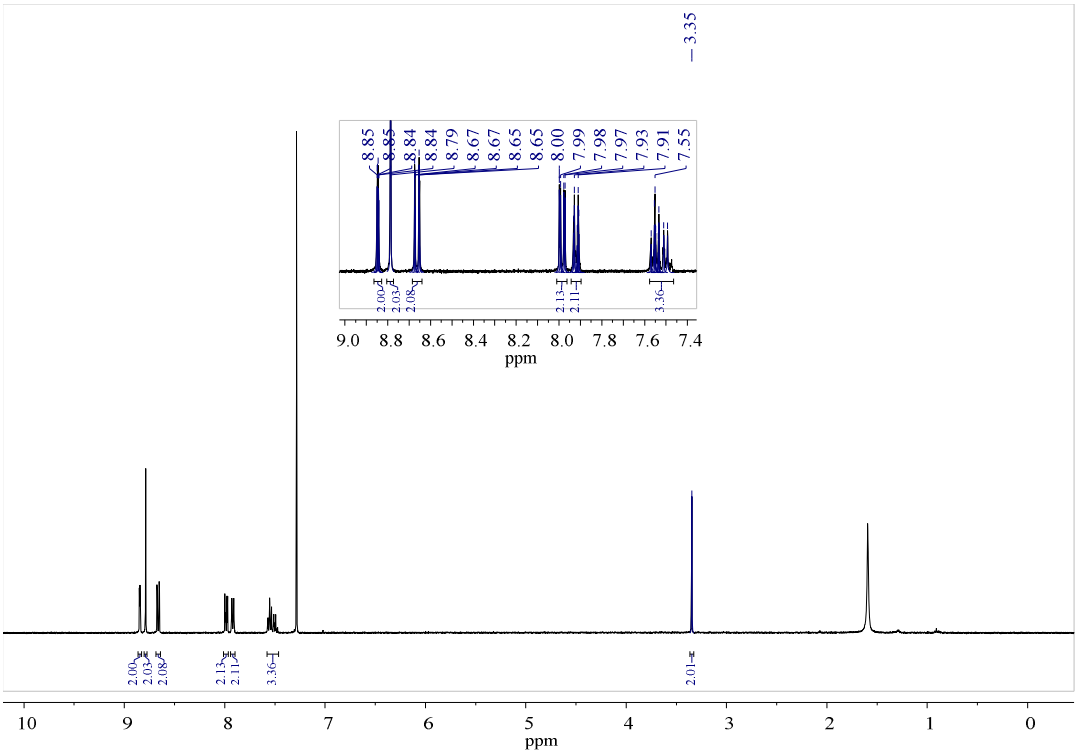

Figure S 10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 17.

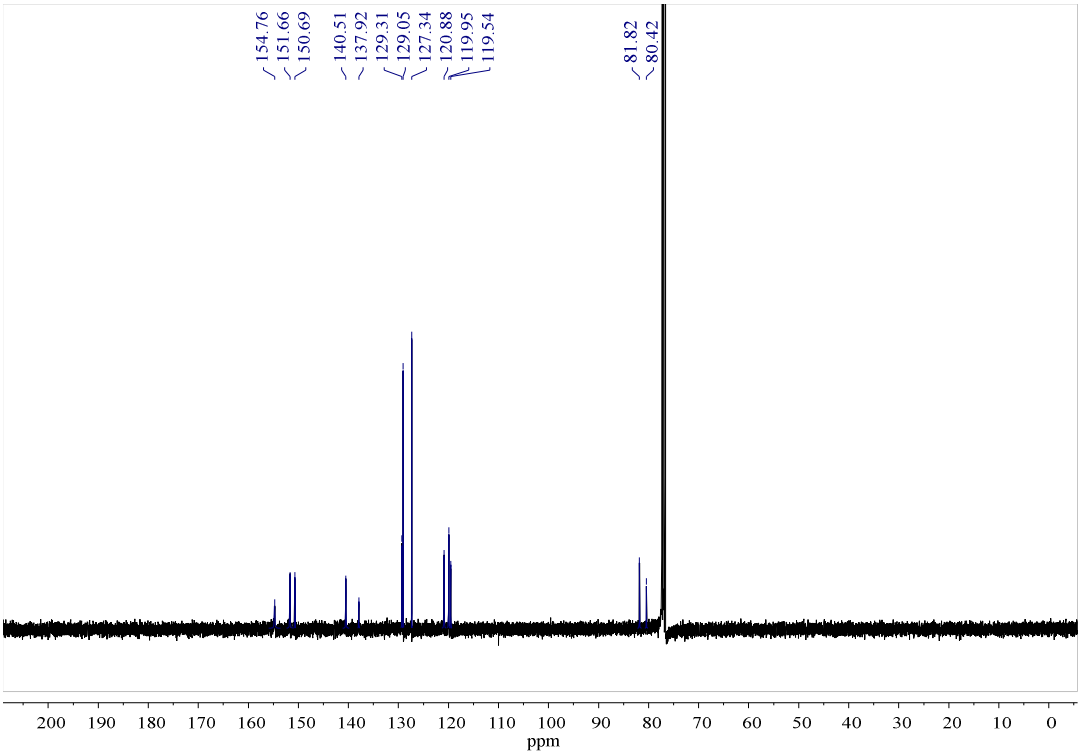

Figure S 11. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 17.

Synthesis of 5,5''-diethynyl-4'-(pyridin-4-yl)-2,2':6',2''-terpyridine (TPy, 18)

The synthesis of this compound followed a procedure similar to that of compound **14**. To a solution of 4-Pyridinecarboxaldehyde (404 mg, 4 mmol) in 18 mL ethanol was added 1-(5-((trimethylsilyl)ethynyl)pyridin-2-yl)ethan-1-one (1.738 g, 8 mmol). Then ammonium hydroxide (12 mL, 29.3%) and KOH pellets (440 mg, 4 mmol) were added to the mixture. The reaction was stirred at ambient temperature for 3 days. The crude solid was collected via filtration and washed with ethanol. Purification by flash chromatography (dichloromethane) gave a white powder (280.0 mg, 9.8%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.84 (m, 6H), 8.67 (d, 2H), 8.01 (dd, 2H), 8.93 (d, 2H), 3.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.85, 154.70, 152.25, 149.63, 147.27, 140.05, 121.96, 120.52, 119.70, 119.30, 81.71, 80.58. **HRMS** (EI) *m/z* calculated for $C_{24}H_{15}N_4^+$ ($M^+ + H^+$) 359.1297, found 359.1295

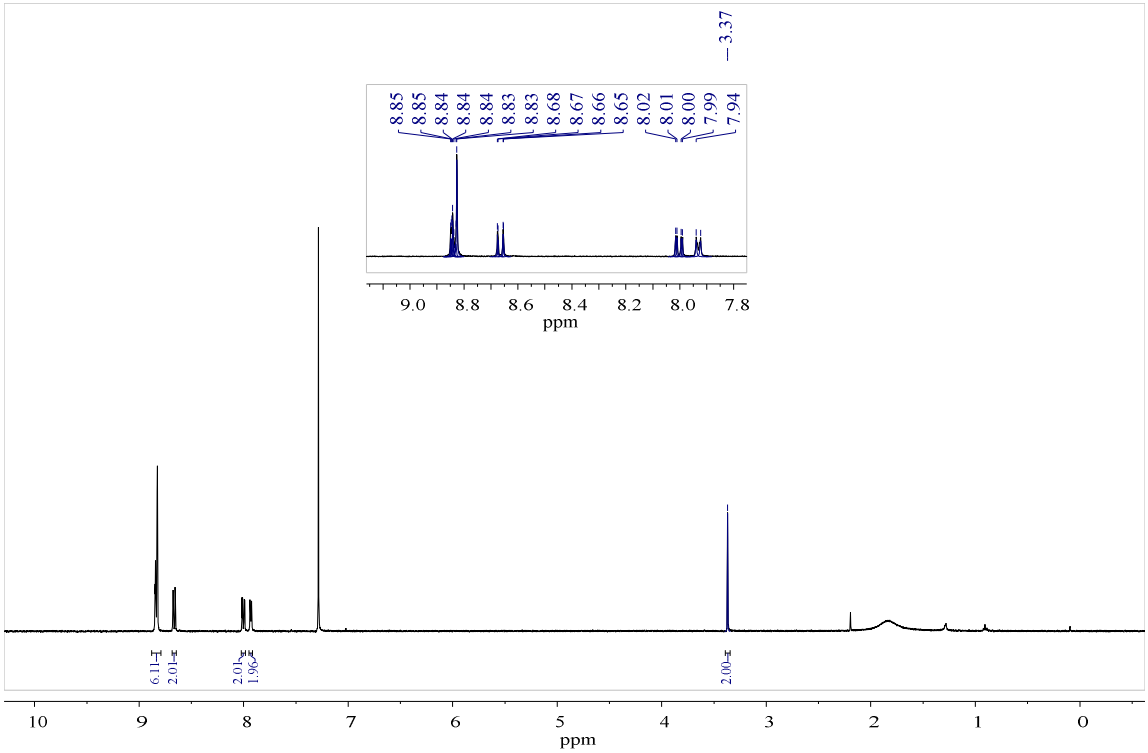

Figure S 12. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of 18.

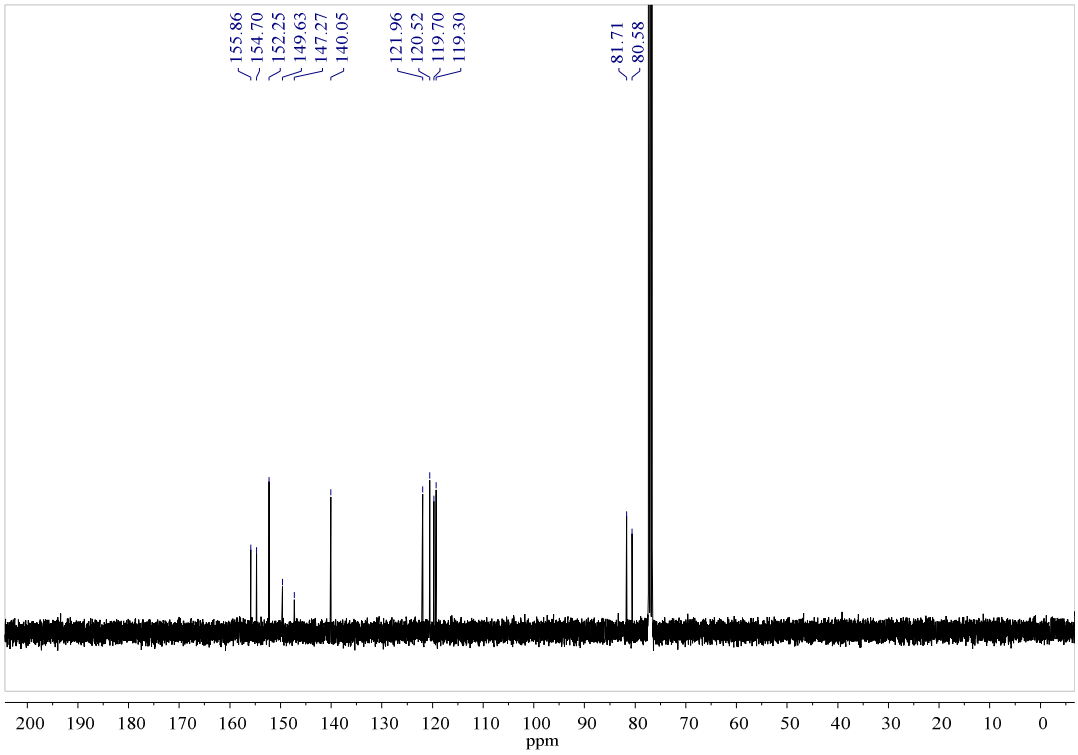

Figure S 13. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of 18.

General procedure for synthesis of sulfonated pyridyl polyphenylenes

The **0N**, **(1+0)N**, **(1+1)N**, **(3+0)N** and **(3+1)N** polymers were synthesized via Diels-Alder polymerization and purified following previous literature procedures.[1,2] Under Ar diene monomer **7** and the appropriate dienophile monomer were first mixed in nitrobenzene and then stirred at RT for 10 min. The mixture was heated at 180 °C for 3 d. After the reaction was cooled to RT, ethyl acetate was added to the mixture, which was subject to reflux for 6 h. The solid was filtered and washed with ethyl acetate to remove nitrobenzene. The polymer precipitate was then dissolved in DMSO at 80 °C, and re-precipitated into ethyl acetate. Filtration and drying under vacuum at 80 °C overnight yielded the polymer product of triethylammonium form (**Polymer-$HNEt_3^+$**).

To a solution of **Polymer-$HNEt_3^+$** in methanol was added NaOH methanolic solution. The mixture was stirred at RT for 48 h. Then **Polymer-Na^+** was filtered, washed with methanol and dried under vacuum, then suspended in water. To the resulting mixture of **Polymer-Na^+** in water was added 2 M H_2SO_4 and the mixture was stirred at RT for 24 h.

After filtration and drying *in vacuo* overnight, the **Polymer-H$^+$** was obtained.

Synthesis of the sTPPPP-H$^+$ polymer, 0N

Following the general procedure, monomer **7** (0.321 g, 0.226 mmol) and the dienophile monomer **11** (0.820 g, 0.232 mmol) were mixed in 45 mL nitrobenzene. The polymer (**sTPPPP-HNEt$_3^+$**) was dried in *in vacuo* overnight to afford a brown solid (0.325 g, 87.3%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.00 (s, 4H), 8.25-6.0 (m, 48H), 3.01 (q, 24H), 1.25 (t, 36H)

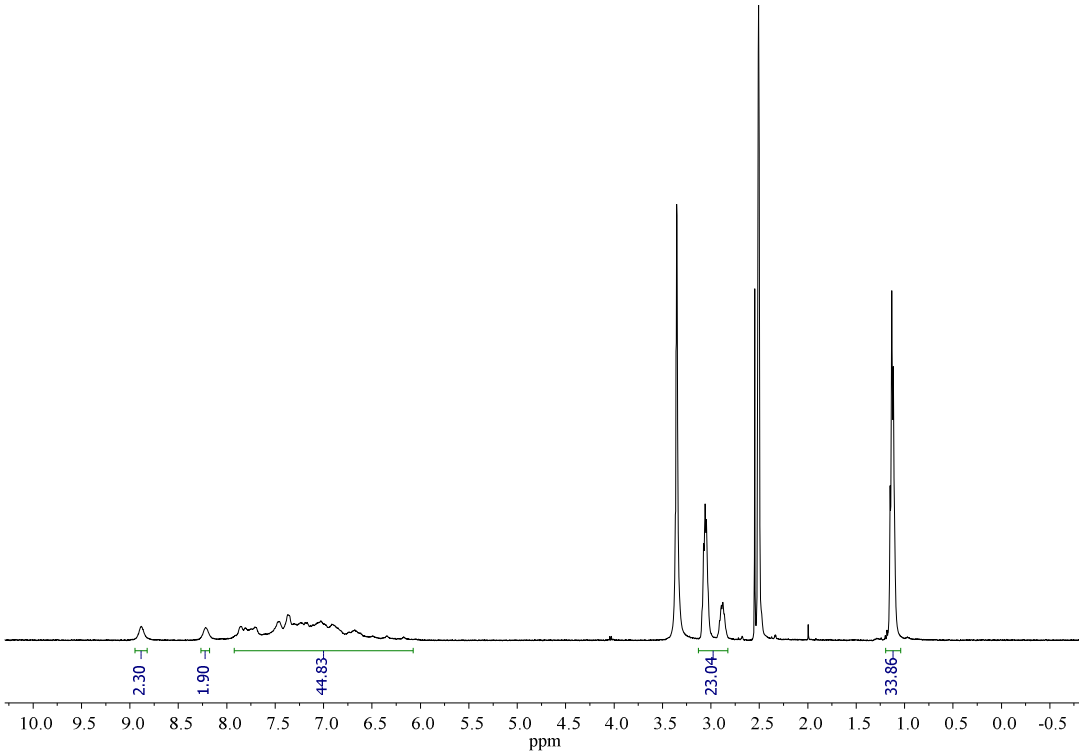

Figure S 14 ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sTPPPP-HNEt$^+$

To a solution of **sTPPPP-HNEt$_3^+$** (0.300 g) in 10 mL methanol was slowly added a solution of NaOH in methanol (2.0 g NaOH, 5 mL methanol) and the polymer of Na^+ form was isolated via filtration. The obtained **sTPPyPP-Na$^+$** was suspended in 10 mL water and combined with 15 mL of 2 M H_2SO_4. After filtration, **sTPPyPP-H$^+$** was dried *in vacuo* to afford a gray powder (0.225 g, 79.2%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 8.23-6.1 (m, 48H).

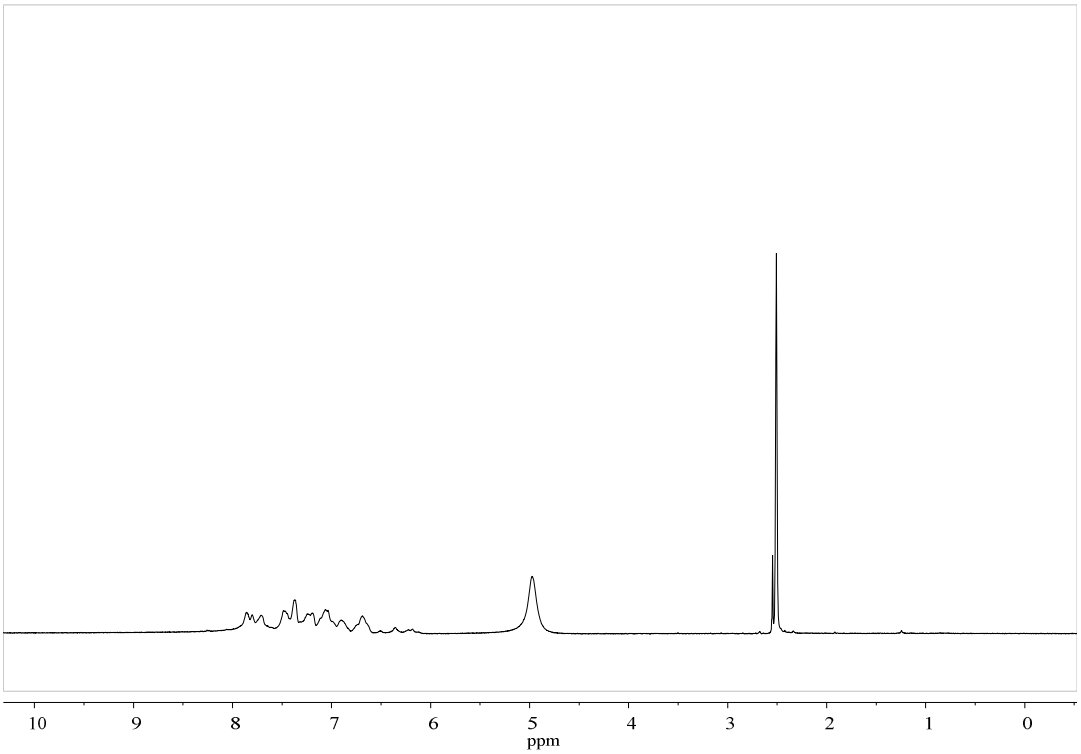

Figure S 15 ^{1}H NMR spectrum (DMSO-*d*$_6$, 400 MHz) of sTPPPP -H$^+$, 0N

Synthesis of the sTPPyPP-H$^+$ polymer, (1+0)N

Following the general procedure, monomer **7** (0.850 g, 0.7 mmol) and the dienophile monomer **12** (0.215 g, 0.7 mmol) were mixed in 45 mL nitrobenzene. The polymer (**sTPPyPP-HNEt$_3^+$**) was dried *in vacuo* overnight to afford a brown solid (1.02 g, 99.2%). **^{1}H NMR** (DMSO-*d*$_6$, 400 MHz) δ 8.9 (s, 4H), 8.23-6.50 (m, 47H), 3.00 (q, 24H), 1.26 (t, 36H)

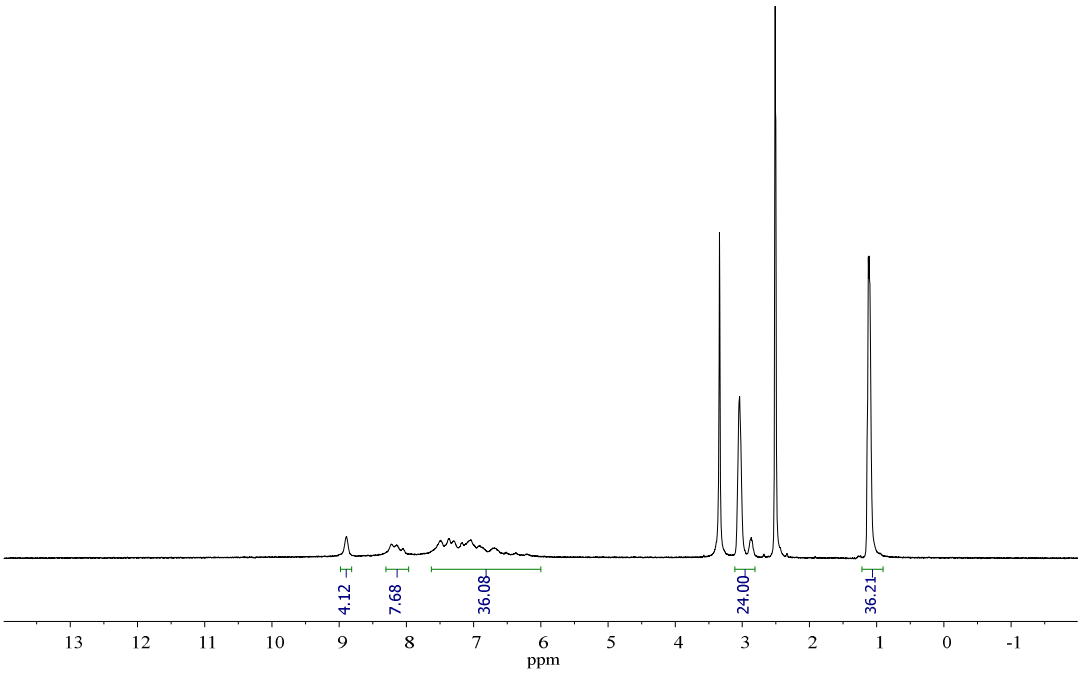

Figure S 16 ^{1}H NMR spectrum (DMSO-*d*$_6$, 400 MHz) of sTPPyPP -HNEt^{+}

To a solution of **sTPPyPP-HNEt$_3^+$** (1.01 g) in 50 mL methanol was slowly added a solution of NaOH in methanol (6.0 g NaOH, 45 mL methanol) and the polymer of Na^+ form was isolated via filtration. The obtained **sTPPyPP-Na$^+$** was suspended in 45 mL water and combined with 45 mL of 2 M H_2SO_4. After filtration, **sTPPyPP-H$^+$** was dried *in vacuo* to afford a gray powder (0.63 g, 79.2%). **^{1}H NMR** (DMSO-*d*$_6$, 400 MHz) δ 9.23-6.03 (m, 47H).

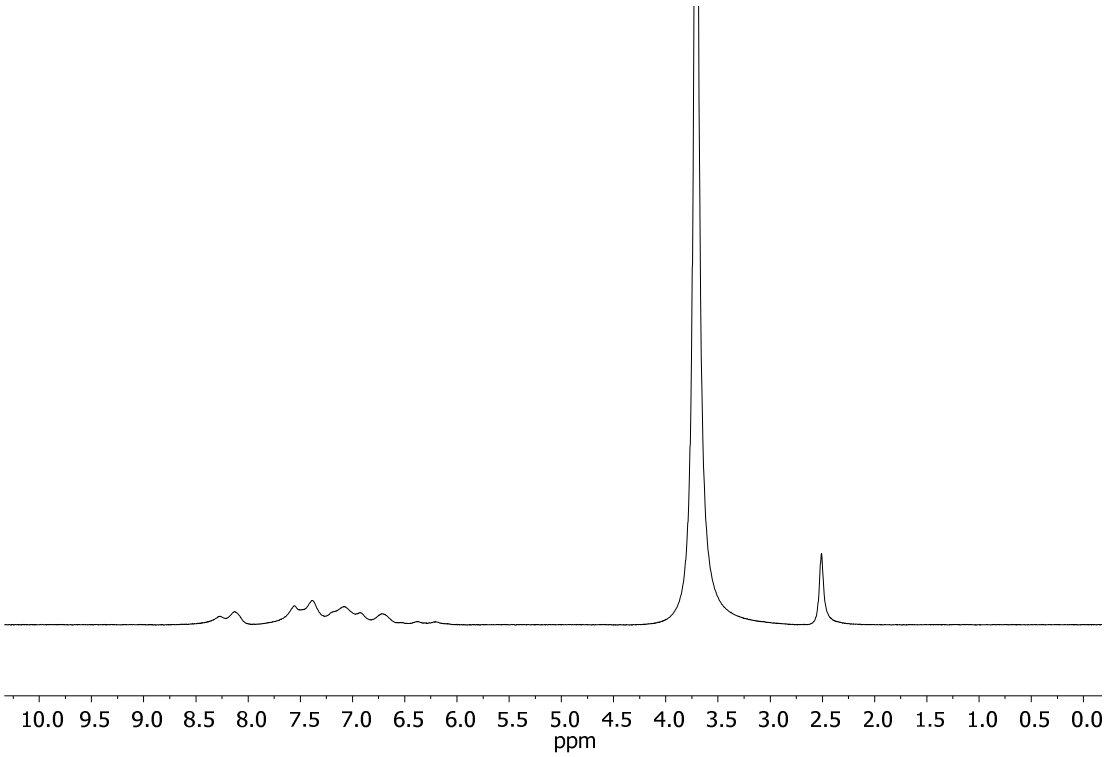

Figure S 17 ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sTPPyPP -H^+, (1+0)N

Synthesis of the sBPBPyPP-H^+ polymer, (1+1)N

Following the general procedure, monomer **7** (0.991 g, 0.7 mmol) and the dienophile monomer **9** (0.25 g, 0.7 mmol) were mixed in 45 mL nitrobenzene. The polymer (**sBPBPyPP-$HNEt_3^+$**) was dried *in vacuo* overnight to afford a brown solid (1.17 g, 96.7%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.02-6.27 (m, 46H), 3.00 (q, 24H), 1.22 (t, 36H)

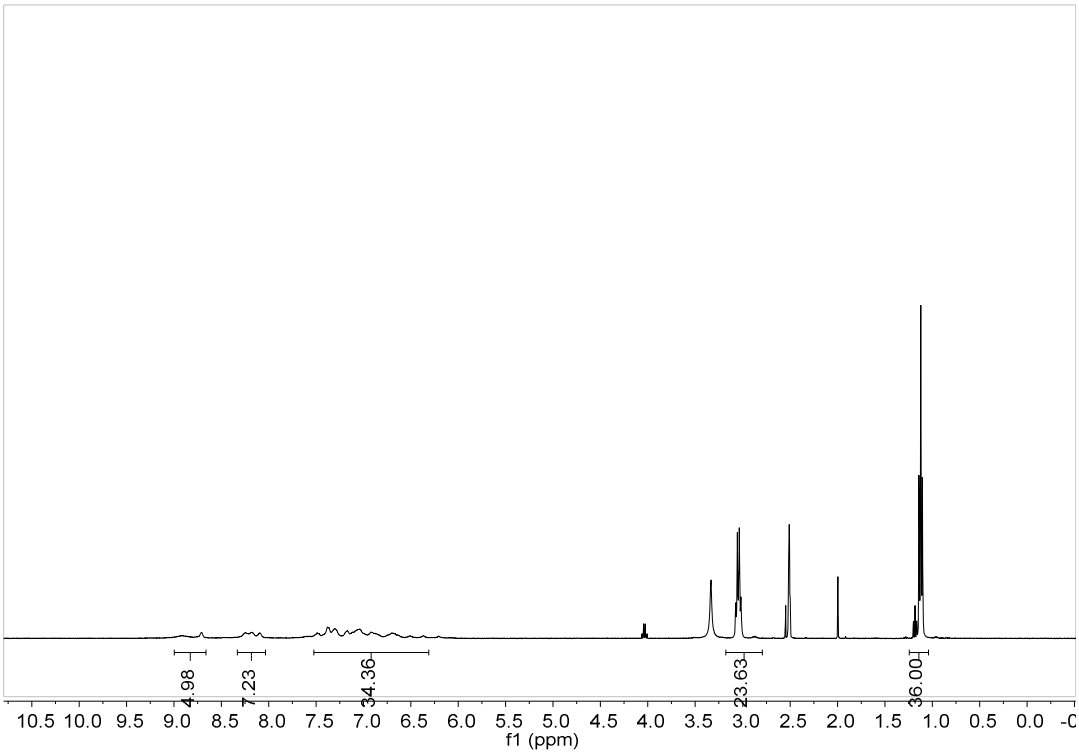

Figure S 18. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sPTPyPP-HNEt$^+$.

To a solution of **sBPBPyPP-HNEt$_3^+$** (1.17 g) in 45 mL methanol was slowly added a solution of NaOH in methanol (5.8 g NaOH, 45 mL methanol) and the polymer of Na^+ form was isolated via filtration. The obtained **sBPBPyPP-Na$^+$** was suspended in 45 mL water and combined with 45 mL of 2 M H_2SO_4. After filtration, **sBPBPyPP-H$^+$** was dried *in vacuo* to afford a gray powder (0.612 g, 66.7%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.25-6.0 (m, 46H).

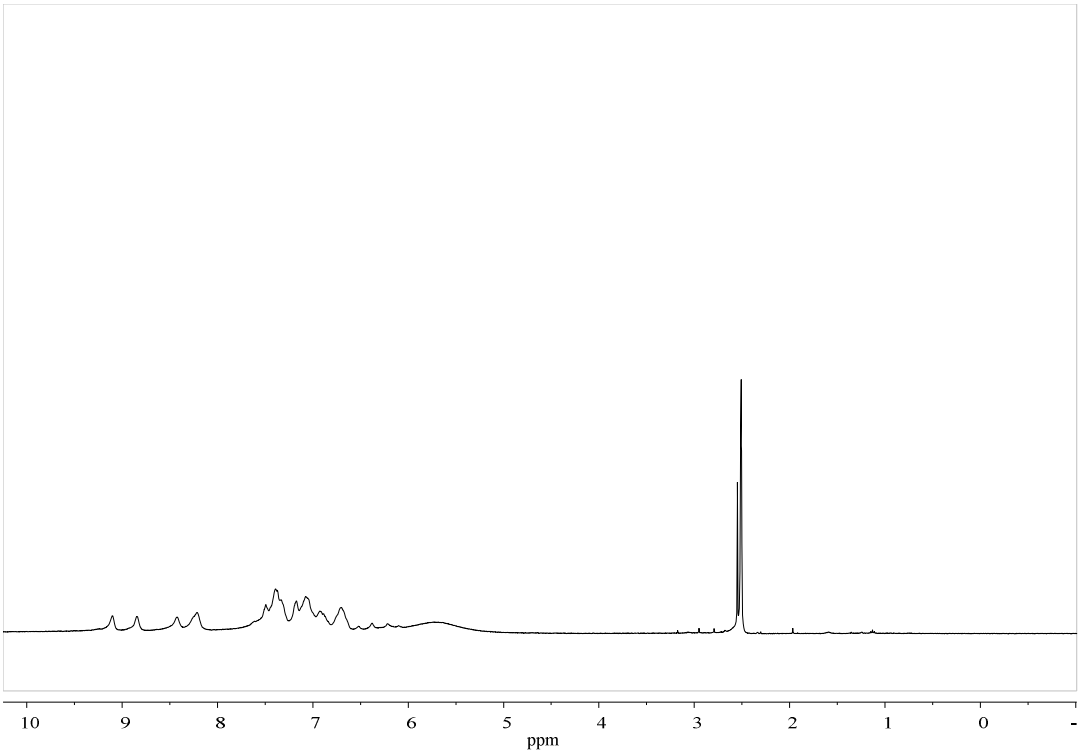

Figure S 19. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sBPBPyPP-H$^+$, (1+1)N.

Synthesis of the sPTPyPP-H$^+$ polymer, (3+0)N

Following the general procedure, monomer **7** (0.849 mg, 0.6 mmol) and the dienophile monomer **12** (0.217 g, 0.6 mmol) were mixed in 40 mL nitrobenzene. The polymer (**sPTPyPP-HNEt$_3^+$**) was dried in a vacuum oven overnight to afford a brown solid (0.720 g, 69.9%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.0-6.3 (m, 45H), 3.01 (q, 24H), 1.25 (t, 36H)

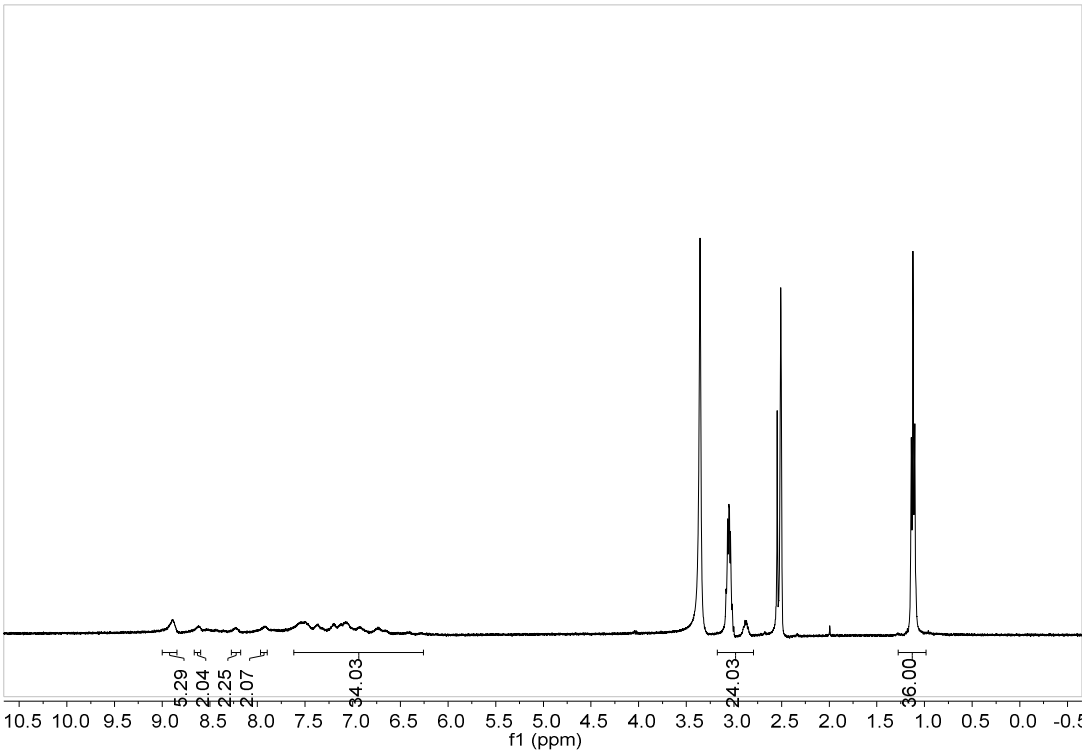

Figure S 20. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sPTPyPP-HNEt^{3+}.

To a solution of **sPTPyPP-HNEt$_3^+$** (0.700 g) in 40 mL methanol was slowly added a solution of NaOH in methanol (3.5 g NaOH, 40 mL methanol) and the polymer of Na^+ form was isolated via filtration. The obtained **sPTPyPP-Na$^+$** was suspended in in 40 mL water and combined with 40 mL of 2 M H_2SO_4. After filtration, **sPTPyPP-H$^+$** was dried *in vacuo* to afford a brown powder (520.0 mg, 66.1%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.0-6.0 (m, 45H).

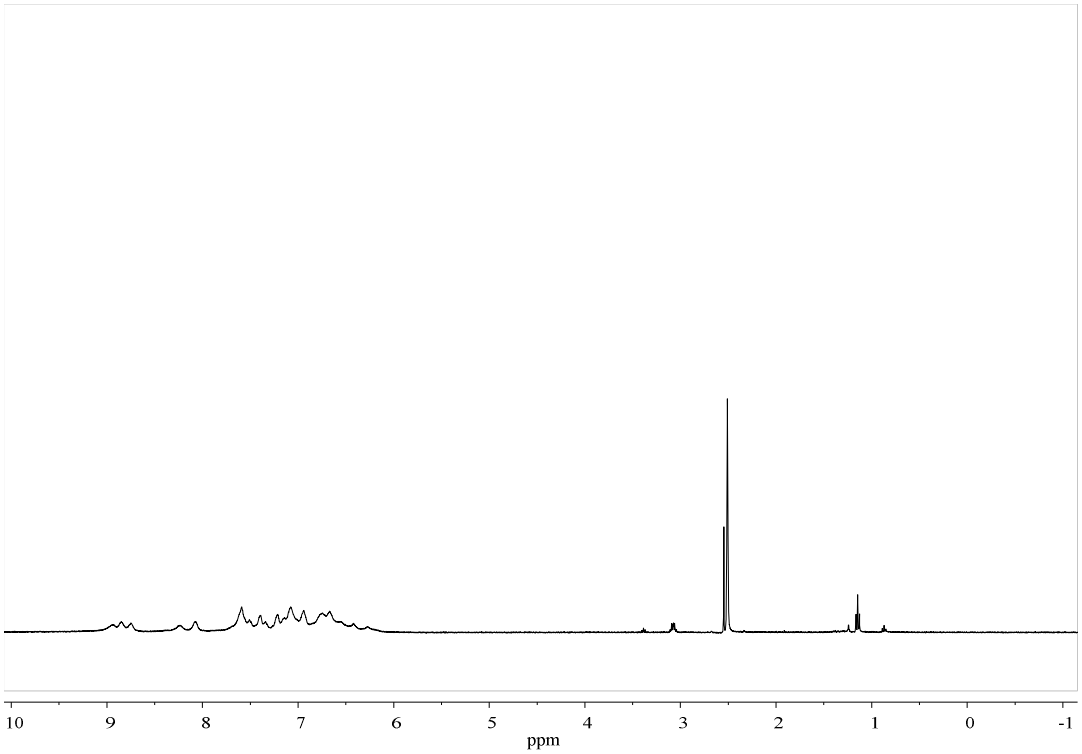

Figure S 21. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sPTPyPP-H+, (3+0)N.

Synthesis of the sTPyPP-H$^+$ polymer, (3+1)N

Following the general procedure, monomer **7** (0.707 mg, 0.5 mmol) and the dienophile monomer **13** (0.185 g, 0.5 mmol) were mixed in 35 mL nitrobenzene. The polymer (**sTPyPP -HNEt$_3^+$**) was dried in a vacuum oven overnight to afford a brown solid (0.610 g, 71.0%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.0-6.3 (m, 44H), 3.01 (q, 24H), 1.25 (t, 36H).

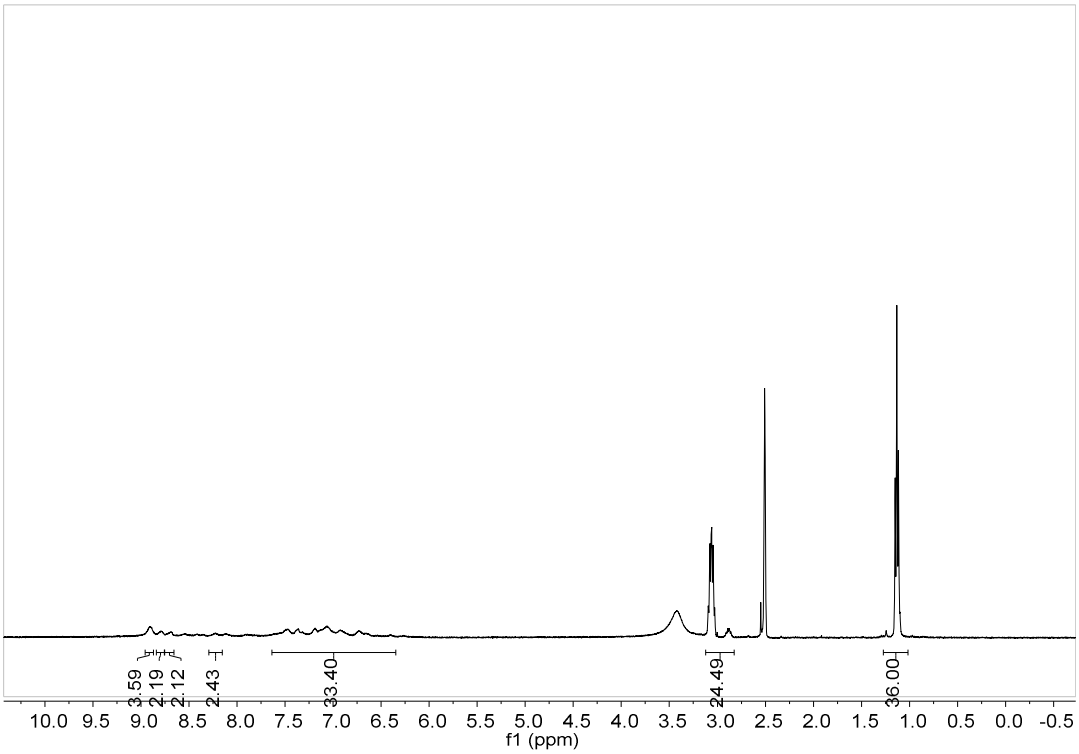

Figure S 22. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sTPyPP- H NEt^{3+}.

To a solution of **sTPyPP -HNEt$_3^+$** (0.600 g) in 34 mL methanol was slowly added a solution of NaOH in methanol (2.9 g NaOH, 34 mL methanol) and the polymer of Na^+ form was isolated via filtration. The obtained **sTPyPP -Na$^+$** was suspended in in 34mL water and combined with 34 mL of 2 M H_2SO_4. After filtration, **sTPyPP -H$^+$** was dried *in vacuo* to afford a gray powder (413.0 mg, 62.9%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 9.1-6.0 (m, 44H).

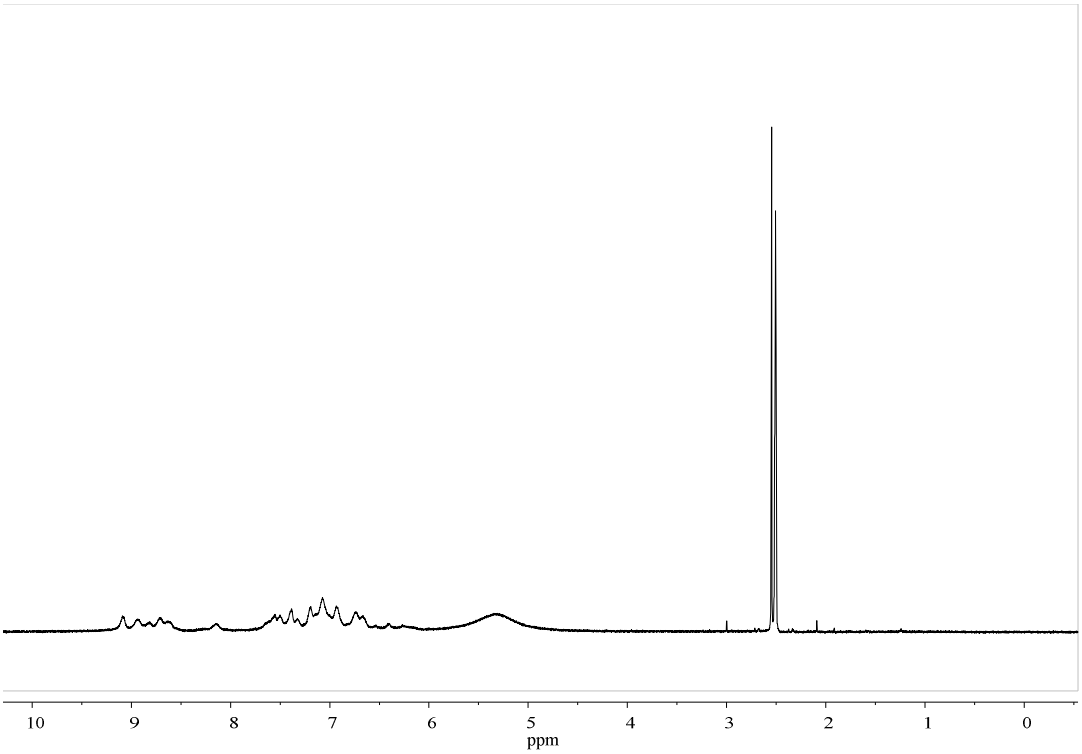

Figure S 23. ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of sTPyPP-H+, (3+1)N.

Membrane preparation

A 5 wt% polymeric solution was prepared and filtered through a sintered glass funnel. The resulting filtrate was poured into a glass petri dish, which was subject to a vacuum oven at 60 °C for 12 h. Water was added to help to obtain the polymer membrane. The membrane was then soaked in 0.5 M H_2SO_4 for 24 h, and subsequently washed with water for three times to remove residual acid. Membranes were dried under vacuum at 80 °C overnight.

4. Characterization methods and results

Mechanical strength measurements

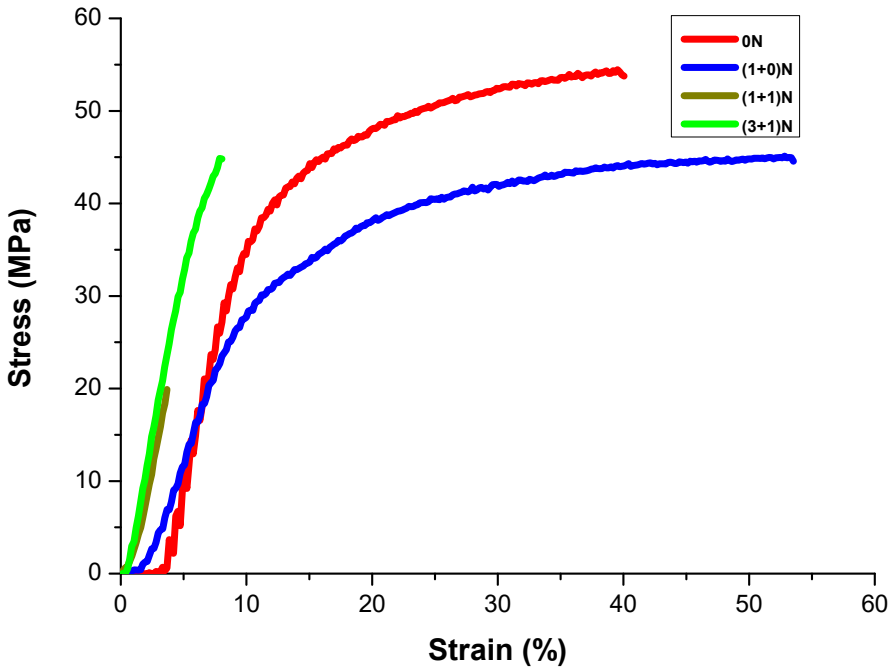

Figure S 24. Strain vs. Stress curves under ambient condition (23 °C, 50% RH).

Transient diffusion results

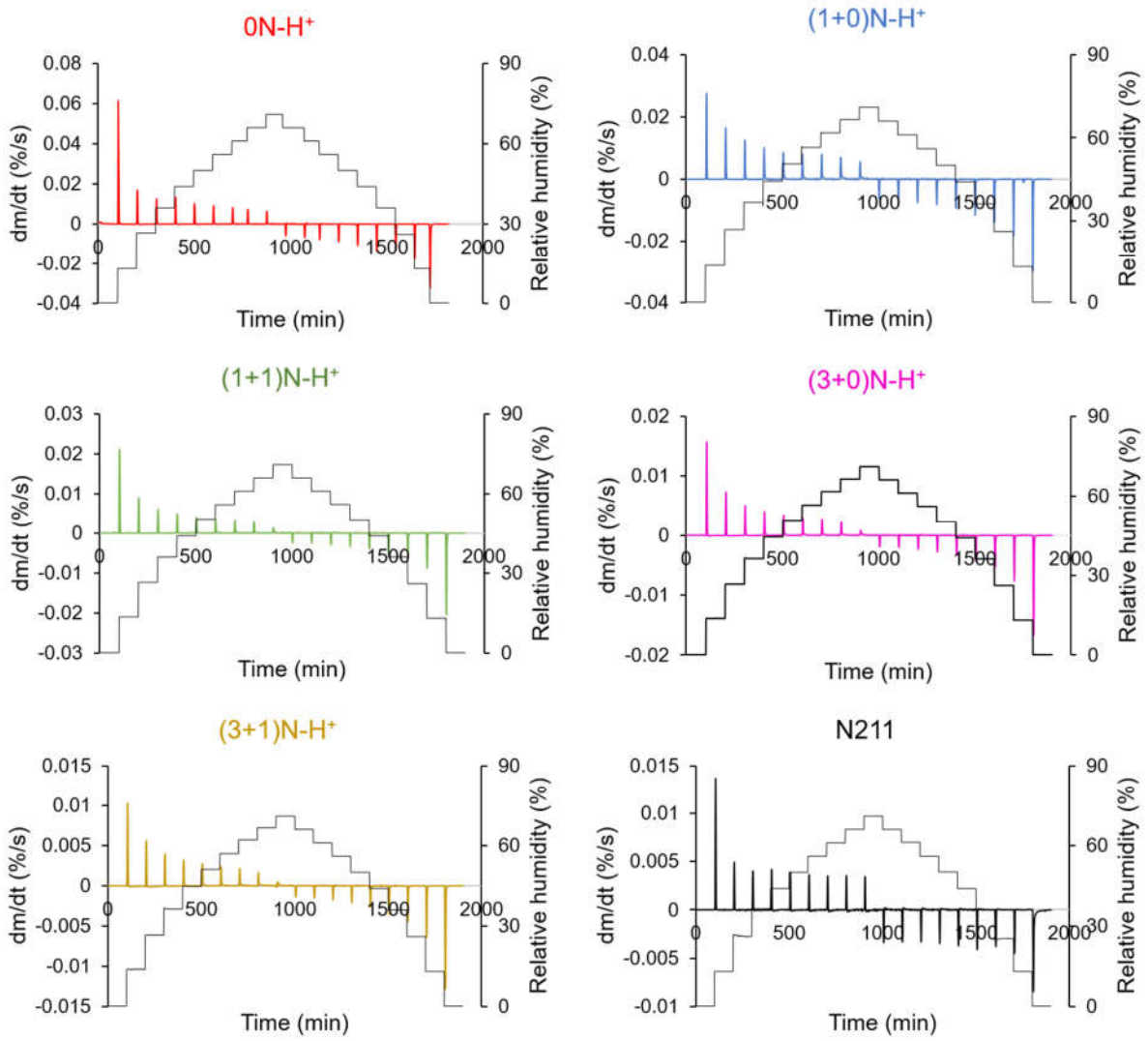

Figure S 25. Time-dependent transient water diffusion of membranes in a full isotherm cycle under 80 ℃, instantaneous mass-change rate (primary axis), dm/dt, and relative humidity steps (secondary axis) over time.

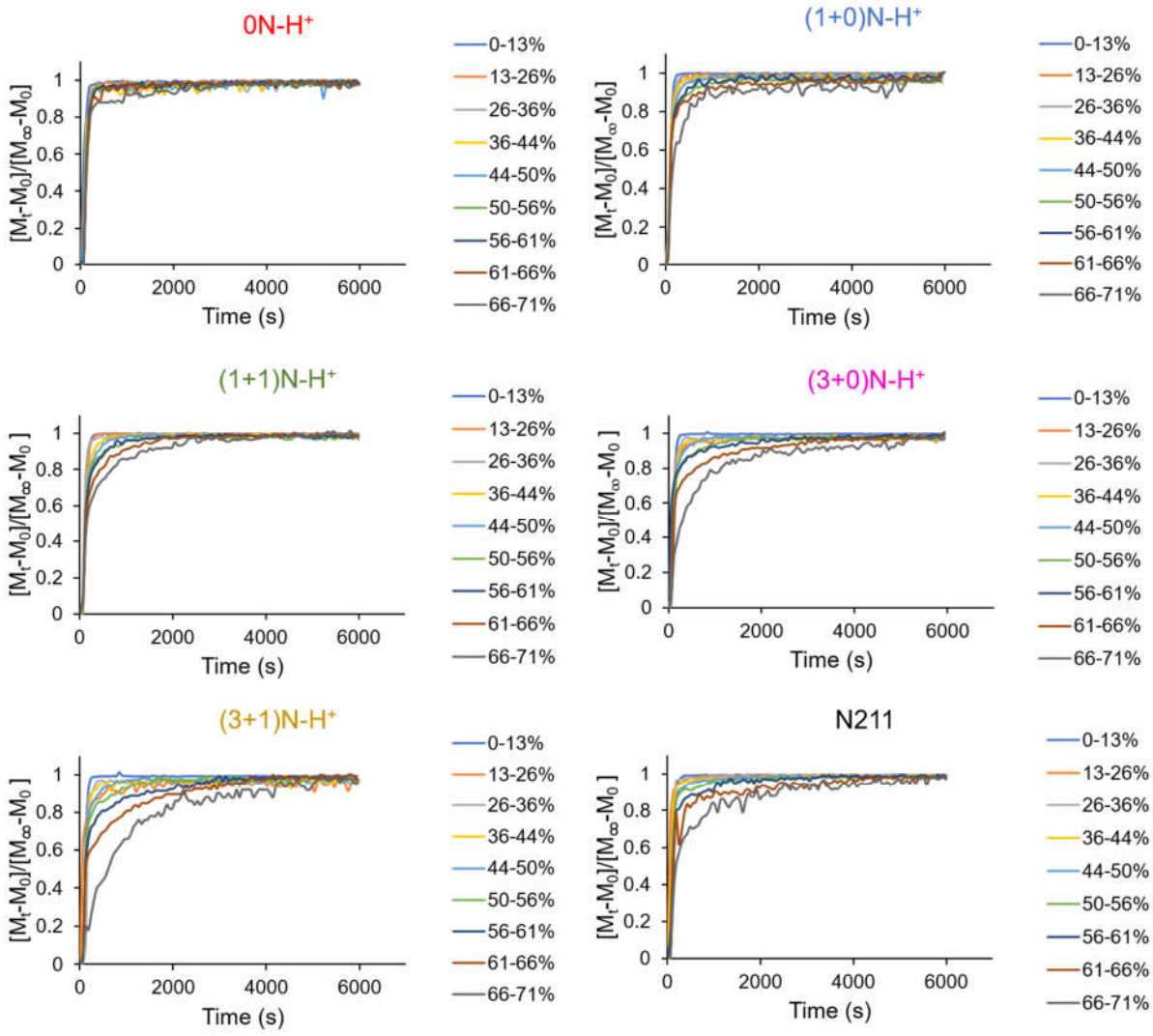

Figure S 26　Normalized water uptake, [M_t – M_0] / [M_∞ - M_0], over time in sorption period under 80 ℃.

Table S 1. Effective rate constant of diffusion, k_{sorp}, for membranes under 80 ℃

RH range	k_{sorp} (s^{-1})					
	0N	**(1+0)N**	**(1+1)N**	**(3+0)N**	**(3+1)N**	**N211**
0-13%	0.81	0.52	1.3	0.67	0.69	0.71
13-26%	0.56	0.27	0.54	0.29	0.29	0.49
26-36%	0.39	0.12	0.30	0.16	0.17	0.28
36-44%	0.099	0.086	0.19	0.096	0.10	0.14
44-50%	0.077	0.069	0.17	0.065	0.056	0.045
50-56%	0.042	0.051	0.11	0.031	0.018	0.024
56-61%	0.033	0.045	0.061	0.016	0.0079	0.014
61-66%	0.019	0.032	0.026	0.0080	0.0050	0.0082
66-71%	0.0067	0.013	0.018	0.0050	0.0027	0.0053

Table S 2. Transient diffusivity, *D*, for membranes under 80 ℃

RH step	D (cm^2/s)					
	0N [a]	**(1+0)N** [b]	**(1+1)N** [c]	**(3+0)N** [d]	**(3+1)N** [e]	**N211** [f]
0-13%	9.9×10^{-6}	5.3×10^{-6}	5.2×10^{-6}	4.9×10^{-6}	4.7×10^{-6}	4.4×10^{-6}
13-26%	6.9×10^{-6}	2.8×10^{-6}	2.2×10^{-6}	2.1×10^{-6}	2.0×10^{-6}	3.1×10^{-6}
26-36%	4.8×10^{-6}	1.3×10^{-6}	1.2×10^{-6}	1.2×10^{-6}	1.2×10^{-6}	1.8×10^{-6}
36-44%	1.4×10^{-6}	9.4×10^{-7}	7.6×10^{-7}	7.0×10^{-7}	6.8×10^{-7}	8.8×10^{-7}
44-50%	1.0×10^{-6}	8.0×10^{-7}	6.8×10^{-7}	4.8×10^{-7}	3.8×10^{-7}	2.8×10^{-7}
50-56%	8.1×10^{-7}	5.9×10^{-7}	4.4×10^{-7}	2.3×10^{-7}	1.2×10^{-7}	1.5×10^{-7}
56-61%	6.4×10^{-7}	5.2×10^{-7}	2.4×10^{-7}	1.2×10^{-7}	5.3×10^{-8}	8.7×10^{-8}
61-66%	4.1×10^{-7}	3.9×10^{-7}	1.0×10^{-7}	5.8×10^{-8}	3.4×10^{-8}	5.1×10^{-8}
66-71%	1.6×10^{-7}	1.6×10^{-7}	7.2×10^{-8}	3.7×10^{-8}	1.8×10^{-8}	3.3×10^{-8}

[a] thickness at 0-36% RH was 35 μm, 36-50% RH was 37 μm, 50-61% RH was 44 μm, 61-66 % RH was 46 μm, and 66-71 %RH was 49 μm.

[b] thickness at 0-26% RH was 32 μm, 26-44% RH was 33 μm, 44-61% RH was 34 μm, 61-71% RH was 35 μm.

[c] thickness throughout RH range was 20 μm.

[d] thickness throughout RH range was 27 μm.

[e] thickness throughout RH range was 26 μm.

[f] thickness throughout RH range was 25 μm.

5. References

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