

Supplementary Information

Highly-Metallized Phosphonium Polyelectrolytes

*Amir Rabiee Kenaree,^a Bradley M. Berven,^{a,b} Paul J. Ragona,^{*a} and Joe B. Gilroy^{*a}*

^a Department of Chemistry and the Centre for Advanced Materials and Biomaterials Research (CAMBR), The University of Western Ontario, 1151 Richmond St. N., London, Ontario, Canada, N6A 5B7. Fax: +1-519-661-3022; Tel: +1-519-661-2111 ext. 81561.

E-mail: pragogna@uwo.ca, joe.gilroy@uwo.ca

^b Current Address: 3M Canada, 1840 Oxford Street East, London, Ontario, Canada, N5V 3R6.

Table of Contents

Experimental Details.....	S2
Additional Figures.....	S15
References.....	S38

Experimental:

General considerations

All reactions and manipulations were carried out under a nitrogen atmosphere using standard glove box or Schlenk techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received, aside from phosphine gas, which was supplied by Cytec Industries Inc. and vinylferrocene which was synthesized according to literature procedures.¹ NMR spectra were recorded on a 400 MHz (¹H: 399.8 MHz, ¹³C: 100.5 MHz, ¹⁹F: 376.4 MHz, ³¹P: 161.8 MHz) or a 600 MHz (¹H: 599.5 MHz, ¹³C: 150.8 MHz, ³¹P: 242.6 MHz) Varian INOVA instrument, or a 400 MHz (¹H: 400.8 MHz, ¹³C: 100.6 MHz, ³¹P: 161.9 MHz) Varian Mercury instrument. ¹H NMR spectra were referenced to residual CHCl₃ (7.27 ppm) or CHD₂SOCD₃ (2.50 ppm) and ¹³C NMR spectra were referenced to CDCl₃ (77.2 ppm) or CD₃SOCD₃ (39.5 ppm). ³¹P spectra were referenced to PPh₃ at –6.0 ppm. gHSQCAD NMR spectra were used to support ¹³C NMR spectral assignments. Mass spectrometry data were recorded using a Micromass LCT electrospray ionization time-of-flight mass spectrometer and high resolution Finnigan MAT 8200 spectrometer, in positive-ion mode and using electron impact ionization. UV-vis spectra were recorded using a Cary 300 Scan instrument. Infrared spectra were recorded as KBr pellets using a Bruker Tensor 27 FT-IR spectrometer. Elemental analyses (C, H, and S) were carried out by Laboratoire d'Analyse Élémentaire de l'Université de Montréal, Montréal, QC, Canada.

Electrochemistry

Cyclic voltammetry experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon potentiostat and analyzed using BASi Epsilon software. Typical electrochemical cells consisted of a three-electrode setup including a glassy carbon working electrode, platinum wire counter electrode, and silver wire *pseudo*-reference electrode. Experiments were run at variable scan rates in degassed 2:1 dichloromethane:acetonitrile solutions of the analyte (~1 mM) and 0.1 M tetrabutylammonium trifluoromethanesulfonate ([Bu₄N][OTf]) supporting electrolyte. Cyclic voltammograms were referenced against an internal standard (~1 mM decamethylferrocene: -520 mV vs. ferrocene/ferrocenium) and corrected for internal cell resistance using the BASi Epsilon software. The number of electrons corresponding to each oxidation wave was confirmed by comparison of the peak current response of the analyte to a stoichiometric amount of decamethylferrocene/decamethylferrocenium.

X-ray Crystallography

Single crystals of **4a** (unit cell previously reported),² **4b**, and **5b** suitable for X-ray diffraction studies were grown by vapor diffusion of pentane into a concentrated solution of the compound in chloroform. Single crystals of **4c** suitable for X-ray diffraction studies were grown from a warm concentrated solution in tetrahydrofuran/pentane. The samples were mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. X-ray measurements of **4b** and **4c** were made on a Bruker APEX-II CCD diffractometer and **4a** and **5b** were made on a Nonius Kappa CCD diffractometer. The unit cell dimensions for **4a**, **4b**, **4c** and **5b** were determined from a symmetry constrained fit of 7670 reflections with $5.72^\circ < 2\theta < 56.02^\circ$, 6051 reflections with $6.12^\circ < 2\theta < 58.56^\circ$, 9103 reflections with $5.44^\circ < 2\theta < 70.18^\circ$, and 9891 reflections with $5.14^\circ < 2\theta < 50.28^\circ$. The data collection strategy was a number of ω and ϕ scans which collected

data up to 58.626° (2 θ), 50.05° (2 θ), 70.16° (2 θ) and 57.156° (2 θ), for **4a**, **4b**, **4c** and **5b**, respectively. The frame integration was performed using SAINT.³ The resulting raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.⁴ The structures for **4a**, **4b** and **4c** were solved using the XS program⁵ and for **5b** was solved by direct methods using the SIR92 program.⁶ All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The structural model was fit to the data using full matrix least-squares based on F² corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL-2014 program from the SHELXTL program package.⁷ Graphic plots were produced using Mercury software. Crystallographic data for **4a–c** and **5b** have been deposited to the Cambridge Crystallographic Data Centre (CCDC) (1012820–1012823). See Table S1 for additional crystallographic data.

Table S1. Crystallographic data for **4a**, **4b**, **4c** and **5b**.

	4a	4b	4c	5b
Chemical formula	C ₁₂ H ₁₅ FeP	C ₂₄ H ₂₇ Fe ₂ P	C ₃₆ H ₃₉ Fe ₃ P	C ₃₉ H ₄₆ BF ₄ Fe ₃ OP
FW (g mol ⁻¹)	246.07	458.13	670.20	816.10
Temp(K)	110	110	110	150
Crystal syst.	monoclinic	monoclinic	triclinic	monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /c	P-1	P 2 ₁ /c
λ (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	14.330(6)	5.7236(13)	11.1849(5)	7.342(8)
b (Å)	7.584(3)	9.910(3)	11.6315(4)	29.84(4)
c (Å)	10.513(3)	35.994(11)	11.8872(5)	17.170(19)
α (deg)	90	90	85.1800(10)	90
β (deg)	97.029(16)	90.579(12)	82.1170(10)	106.475(19)
γ (deg)	90	90	74.9990(10)	90
V (Å ³)	1133.9(8)	2041.6(10)	1477.77(10)	3607(7)
Z	4	4	2	4
ρ_c (g cm ⁻³)	1.441	1.481	1.506	1.503
μ (cm ⁻¹)	1.428	1.505	1.532	1.286
R_1 [$I > 2\theta$]	0.0398	0.052	0.0336	0.0582
wR_2 [$I > 2\theta$]	0.1025	0.0974	0.0949	0.138
R_1 (all data)	0.0709	0.0738	0.0432	0.0869
wR_2 (all data)	0.1315	0.1044	0.1018	0.1522
GOF	1.12	1.093	0.949	1.031

$$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o; \quad wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2},$$

$$GOF = [\theta(w(F_o^2 - F_c^2)^2)/(\text{No. of reflns.} - \text{No. of params.})]^{1/2}.$$

Gel Permeation Chromatography (GPC)

GPC experiments were performed by PolyAnalytik Inc. (London, Ontario, Canada). Molecular weights and polydispersity indices ($PDI = M_w / M_n$) of all polymers were obtained using a Viscotek TDA302/GPCmax triple detection gel permeation chromatograph equipped with automatic sampler, isocratic pump, injector, in-line degasser, column and detector oven (60 °C), refractive index detector, right-angle (90°) and low-angle (7°) light scattering detectors, a four bridge capillary viscometer, and Viscotek Inert Series Columns: 2 x Mixed Bed Low Molecular Weight (I-MBLMW, exclusion limit of 20 kDa PS) and 1 x Mixed Bed High Molecular Weight (I-MBHMW, exclusion limit of 10,000 kDa PS). The eluent employed was dimethylformamide containing 0.02 M tetrabutylammonium trifluoromethanesulfonate, at a flow rate of 0.7 mL min⁻¹. Samples were dissolved in the eluent (5 mg mL⁻¹), heated for 1.5 h at 70 °C, and filtered (Nylon membrane, 0.22 µm) before analysis. Conventional calibration of the refractive index detector was performed using a series of monodisperse poly(methyl methacrylate) standards (PolyAnalytik). All data were processed using Viscotek's OmniSEC v4.6.2 software.

Thermal Analysis

Thermal degradation studies were performed using a TA Instruments Q600 SDT TGA instrument. Samples were placed in an alumina cup and heated at a rate of 10 °C min⁻¹ from room temperature to 800 °C under a flow of nitrogen (100 mL min⁻¹). Glass transition temperatures were determined using Differential Scanning Calorimetry (DSC) on a TA Instruments DSC Q20. The polymer samples were placed in an aluminum Tzero pan and heated from room temperature to 280 °C at 10 °C min⁻¹ under a flow of nitrogen (50 mL min⁻¹) and cooled down to 0 °C at 5 °C min⁻¹, before they underwent 2 more heating/cooling cycles. The glass transitions were determined from the second heating/cooling cycle.

Pyrolysis Studies and Scanning Electron Microscopy

Silicon wafers were cut into approximately 1 cm × 1 cm squares using a diamond tip stylus and immersed in a Piranha solution (3:1 concentrated sulfuric acid:30% hydrogen peroxide) for 16 h before they were removed, immersed in DI water for 10 min and washed thoroughly with DI water. This immersing and washing cycle was repeated twice more before the wafers were placed in petri dishes and dried in a vacuum oven at 50 °C in 2 h. Thin films of polyelectrolyte **7b** were prepared by spin coating (2000 rpm, 30 s, acceleration time < 2 s) 20 μL of a 80 mg mL⁻¹ solution of polyelectrolyte **7b** in a 3:2 mixture of chlorobenzene:chloroform onto the freshly cleaned silicon wafers using a Laurell WS-400BZ-6NPP/LITE spin-coater. The samples were allowed to dry in a vacuum oven at 50 °C for 16 h before they were heated at a rate of 10 °C min⁻¹ to a temperature of 800 °C under a gentle flow of N₂ gas in a Lindberg Blue M tube furnace. The temperature was maintained at 800 °C for an additional 2 h before the furnace was cooled to room temperature at a rate of 10 °C min⁻¹. The surface morphology was assessed directly by scanning electron microscopy (SEM) at 1 keV beam energy using the LEO/Zeiss 1540XB instrument at the Western Nanofabrication Facility. Elemental analysis was performed at 10 keV beam energy on the 1540XB with the equipped Oxford x-sight x-ray detector and INCA analysis software.

Preparation of phosphines **4a–c**

In a 300 mL autoclave, vinylferrocene (2.00 g, 9.43 mmol) and AIBN (0.06 g, 0.4 mmol) were dissolved in dry toluene (170 mL). The autoclave was degassed by N₂ purging for 10 min before it was pressurized with PH₃ gas to 80 psi. The solution was allowed to stir for 16 h at 45 °C. Pressurized PH₃ gas was released in a controlled environment where it was ignited and allowed to burn (Caution: PH₃ gas is toxic and pyrophoric). The resulting solution was then

transferred to a 350 mL grease-free Schlenk flask in a glove box, which was charged with vinylferrocene (2.00 g, 9.43 mmol) and AIBN (0.06 g, 0.4 mmol) before it was allowed to stir for 16 h at 45 °C and 8 h at 65 °C, respectively. The reaction flask was charged a second time with vinylferrocene (1.00 g, 4.71 mmol) and AIBN (0.03 g, 0.2 mmol) and stirred for 16 h at 45 °C and then 8 h at 65 °C, respectively. Vinylferrocene (0.50 g, 2.4 mmol) and AIBN (0.015 g, 0.091 mmol) were added to the reaction flask for a third time and the orange solution was allowed to stir at 45 °C for 16 h, followed by stirring at 65 °C for 8 h and 85 °C for 2 h, respectively, before the mixture was concentrated *in vacuo*. The oily solid was divided into four fractions, each of which was dissolved in a minimum amount of dichloromethane and transferred to a silica column (1" × 12") for subsequent purification by chromatography, using a gradient solvent strategy (see below).

Primary phosphine **4a**

Primary phosphine **4a** was removed from the column using hexanes as a yellow band ($R_f = 0.21$). The solutions containing **4a** were collected, combined and concentrated *in vacuo* to yield **4a** as a yellow solid, which was recrystallized from ethanol. Yield = 1.34 g, 20%. M.p. = 51–53 °C. ^1H NMR (599.5 MHz, CDCl_3): δ 4.12 (s, 5H, C_5H_5), 4.09 (t, $^3J_{\text{HH}} = 2$ Hz, 2H, $\beta\text{-C}_5\text{H}_4\text{R}$), 4.07 (t, $^3J_{\text{HH}} = 2$ Hz, 2H, $\alpha\text{-C}_5\text{H}_4\text{R}$), 2.72 (d of m, $^1J_{\text{HP}} = 204$ Hz, 2H, PH_2 , the signal is overlapped with signal at δ 2.57), 2.57 (m, 2H, $\text{C}_5\text{H}_4\text{CH}_2$, the signal is overlapped with signal at δ 2.72), 1.72 (m, 2H, CH_2PH_2). ^{31}P NMR (161.8 MHz, CDCl_3): δ -137.1 (t, $^1J_{\text{PH}} = 196$ Hz). Mass Spec. (EI, +ve mode): exact mass calculated for $[\text{C}_{12}\text{H}_{15}\text{FeP}]^+$: 246.0260; exact mass found: 246.0256; difference: -1.6 ppm. These data are consistent with a previous report describing the synthesis of phosphine **4a** by a different synthetic strategy.²

Secondary phosphine **4b**

Secondary phosphine **4b** was collected by changing the elution solvent to 98:2 hexanes:diethyl ether ($R_f = 0.13$). The solutions containing **4b** were collected, combined and concentrated *in vacuo* to yield **4b** as a yellow solid, which was recrystallized from 4:1 dichloromethane:pentane. Yield = 1.91 g, 31%. M.p. = 93–95 °C. ^1H NMR (399.8 MHz, CDCl_3): δ 4.20 (s, 10H, C_5H_5), 4.18 (t, $^3J_{\text{HH}} = 2\text{ Hz}$, 4H, $\beta\text{-C}_5\text{H}_4\text{R}$), 4.16 (t, $^3J_{\text{HH}} = 2\text{ Hz}$, 4H, $\alpha\text{-C}_5\text{H}_5\text{R}$), 3.25 (d of quintets, $^1J_{\text{HP}} = 200\text{ Hz}$, $^3J_{\text{HH}} = 7\text{ Hz}$, 1H, PH), 2.60 (m, 4H, $\text{C}_5\text{H}_4\text{CH}_2$), 1.87 (d of m, $^2J_{\text{HP}} = 52\text{ Hz}$, 4H, CH_2PH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CDCl_3): δ 89.1 (d, $^3J_{\text{CP}} = 10\text{ Hz}$, *ipso*- $\text{C}_5\text{H}_4\text{R}$), 68.2 (s, C_5H_5), 67.7 (d, $^5J_{\text{CP}} = 3\text{ Hz}$, $\beta\text{-C}_5\text{H}_4\text{R}$), 67.0 (d, $^4J_{\text{CP}} = 1\text{ Hz}$, $\alpha\text{-C}_5\text{H}_4\text{R}$), 28.3 (d, $^2J_{\text{CP}} = 10\text{ Hz}$, $\text{C}_5\text{H}_4\text{CH}_2$), 21.7 (d, $^1J_{\text{CP}} = 11\text{ Hz}$, CH_2PH). ^{31}P NMR (161.8 MHz, CDCl_3): δ -68.8 (d, $^1J_{\text{PH}} = 201\text{ Hz}$). FT-IR (KBr): 815 (s), 1001 (m), 1100 (m), 1443 (w), 2254 (s), 3097 (w) cm^{-1} . UV-vis (CH_2Cl_2): λ_{max} 439 nm ($\epsilon = 232\text{ M}^{-1}\text{ cm}^{-1}$). Mass Spec. (EI, +ve mode): exact mass calculated for $[\text{C}_{24}\text{H}_{27}\text{Fe}_2\text{P}]^+$: 458.0549; exact mass found: 458.0549; difference: 0 ppm. Anal. Calcd. (%) for $\text{C}_{24}\text{H}_{27}\text{Fe}_2\text{P}$: C, 62.92; H, 5.94. Found: C, 62.88; H, 6.04.

Tertiary phosphine **4c**

Tertiary phosphine **4c** was collected by changing the elution solvent to a 9:1 mixture of hexanes:diethyl ether ($R_f = 0.29$). The solutions containing **4c** were collected, combined and concentrated *in vacuo* to yield an orange solid. Recrystallization from 4:1 ethyl acetate:ethanol yielded **4c** as an air stable yellow powder. Yield = 1.63 g, 27%. M.p. = 119–121 °C. ^1H NMR (399.8 MHz, CDCl_3): δ 4.15 (s, 15H, C_5H_5), 4.13 (t, $^3J_{\text{HH}} = 2\text{ Hz}$, 6H, $\beta\text{-C}_5\text{H}_4\text{R}$), 4.11 (t, $^3J_{\text{HH}} = 2\text{ Hz}$, 6H, $\alpha\text{-C}_5\text{H}_4\text{R}$), 2.56 (m, 6H, $\text{C}_5\text{H}_4\text{CH}_2$), 1.84 (m, 6H, CH_2P). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.7 MHz, CDCl_3): δ 89.3 (d, $^3J_{\text{CP}} = 11\text{ Hz}$, *ipso*- $\text{C}_5\text{H}_4\text{R}$), 68.1 (s, C_5H_5), 67.5 (s, $\beta\text{-C}_5\text{H}_4\text{R}$), 66.9 (s, $\alpha\text{-C}_5\text{H}_4\text{R}$), 28.0 (d, $^2J_{\text{CP}} = 11\text{ Hz}$, $\text{C}_5\text{H}_4\text{CH}_2$), 25.6 (d, $^1J_{\text{CP}} = 12\text{ Hz}$, CH_2P). ^{31}P NMR (161.8 MHz,

CDCl₃): δ -27.9 (s). FT-IR (KBr): 808 (s), 1001 (m), 1105 (m), 1441 (w), 3097 (w) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 440 nm (ϵ = 311 M⁻¹ cm⁻¹). Mass Spec. (EI, +ve mode): exact mass calculated for [C₃₆H₃₉Fe₃P]⁺: 670.0838; exact mass found: 670.0822; difference: -2.4 ppm. Anal. Calcd. (%) for C₃₆H₃₉Fe₃P: C, 64.52; H, 5.87. Found: C, 64.63; H, 5.81.

Preparation of phosphonium chloride salt **5a**

In a 250 mL Schlenk flask equipped with a condenser, tertiary phosphine **4c** (1.00 g, 1.49 mmol) and 3-chloro-1-propanol (2.00 mL, 23.4 mmol) were dissolved in 25 mL dry dimethylformamide. The solution was refluxed for 16 h at 100 °C, cooled and concentrated *in vacuo*. The orange oily residue was then dissolved in about 50 mL degassed dichloromethane, washed with 3 × 20 mL of degassed H₂O, dried over magnesium sulfate, transferred to a silica plug (1" × 2") for subsequent purification *in vacuo*. Unreacted tertiary phosphine **4c** was removed by eluting degassed dichloromethane through the plug. Phosphonium chloride salt **5a** remained on top of the plug while 150 mL degassed dichloromethane passed through the column before the elution solvent was changed to degassed ethanol to remove **5a**. The ethanol solution containing **5a** was collected and concentrated *in vacuo* before dissolved in a minimum amount of degassed dichloromethane, and precipitated by adding degassed hexanes. The resulting powder was filtered *in vacuo* before it was once again dissolved, precipitated, and filtered to yield **5a** as a yellow solid. Yield = 1.01 g, 88%. M.p. = 102–104 °C. ¹H NMR (599.4 MHz, CDCl₃): δ 5.19 (t, ³J_{HH} = 6 Hz, 1H, OH), 4.17 (s, 15H, C₅H₅), 4.16 (d, ³J_{HH} = 2 Hz, 6H, β -C₅H₄R), 4.16 (t, ³J_{HH} = 2 Hz, 6H, α -C₅H₄R), 3.78 (m, 2H, CH₂OH), 2.68 (m, 6H, C₅H₄CH₂), 2.57 (m, 2H, PCH₂CH₂CH₂), 2.44 (m, 6H, C₅H₄CH₂CH₂), 1.92 (m, 2H, PCH₂CH₂CH₂). ¹³C{¹H} NMR (150.7 MHz, CDCl₃): δ 85.5 (d, ³J_{CP} = 12 Hz, *ipso*-C₅H₄R), 68.8 (s, C₅H₅), 68.1 (d, ⁵J_{CP} = 2 Hz, β -C₅H₄R), 67.9 (d, ⁴J_{CP} = 2 Hz, α -C₅H₄R), 60.7 (d, ³J_{CP} = 14 Hz, CH₂OH), 24.8 (s, ²J_{CP} = 2 Hz,

PCH₂CH₂CH₂), 22.1 (s, C₅H₄CH₂), 21.3 (d, ¹J_{CP} = 45 Hz, C₅H₄CH₂CH₂), 16.5 (d, ¹J_{CP} = 48 Hz, PCH₂CH₂CH₂). ³¹P NMR (242.7 MHz, CDCl₃): δ 32.6. FT-IR (KBr): 813 (s), 1001 (m), 1105 (m), 1411 (w), 3095 (br, w), 3267 (br, m) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 439 nm (ε = 326 M⁻¹ cm⁻¹). Mass Spec. (ESI, +ve mode): exact mass calculated for [C₃₉H₄₆PFe₃O]⁺: 729.1334; exact mass found: 729.1351; difference: +2.3 ppm. Anal. Calcd. (%) for C₃₉H₄₆PFe₃OCl: C, 61.25; H, 6.06. Found: C, 61.82; H, 6.31.

Preparation of phosphonium tetrafluoroborate salt **5b**

In a 100 mL Schlenk flask, **5a** (0.50 g 0.65 mmol) was dissolved in 25 mL dry, and degassed chloroform before sodium tetrafluoroborate (0.70 g, 6.2 mmol) was charged into the reaction flask. The resulting mixture was allowed to stir at 20 °C for 16 h, gravity filtered to remove precipitate, washed with 3 × 20 mL of H₂O, dried over magnesium sulfate, and gravity filtered. Sodium tetrafluoroborate (0.07 g, 0.06 mmol) was once again charged into a 100 mL flask containing the filtrate before the mixture was allowed to stir for another 16 h. It was then gravity filtered to remove the precipitate, washed with 3 × 20 mL of H₂O, dried over magnesium sulfate, and gravity filtered before it was concentrated to yield an orange solid. Recrystallization from 9:1 dichloromethane:pentane yielded **5b** as a yellow solid. Yield = 0.39 g, 74%. M.p. = 203–205 °C. ¹H NMR (399.8 MHz, *d*₆-DMSO): δ 4.90 (t, ³J_{HH} = 5 Hz, 1H, OH), 4.24 (s, 6H, β-C₅H₄R), 4.20 (s, 15H, C₅H₅), 4.15 (s, 6H, α-C₅H₄R), 3.52 (m, 2H, CH₂OH), 2.54–2.70 (m, 12H, C₅H₄CH₂ and C₅H₄CH₂CH₂), 2.38 (m, 2H, PCH₂CH₂CH₂), 1.73 (m, 2H, PCH₂CH₂CH₂). ¹³C{¹H}NMR (100.6 MHz, *d*₆-DMSO): δ 86.9 (d, ³J_{CP} = 17 Hz, *ipso*-C₅H₄R), 68.5 (s, C₅H₅), 67.7 (s, β-C₅H₄R), 67.4 (s, α-C₅H₄R), 60.4 (d, ³J_{CP} = 16 Hz, CH₂OH), 24.2 (s, PCH₂CH₂CH₂), 20.8 (s, C₅H₄CH₂), 18.9 (d, ¹J_{CP} = 45 Hz, C₅H₄CH₂CH₂), 14.7 (d, ¹J_{CP} = 49 Hz, PCH₂CH₂CH₂). ¹⁹F NMR (376.4 MHz, *d*₆-DMSO): δ -1483. ³¹P NMR (162.0 MHz, *d*₆-DMSO): δ 34.2 (s). FT-

IR (KBr): 825 (s), 1068 (br, s), 1085 (s), 1224 (m), 1409 (br, m), 2930 (br, m), 3100 (br, w), 3437 (br, m) cm^{-1} . UV-vis (CH_2Cl_2): λ_{max} 443 nm ($\epsilon = 331 \text{ M}^{-1} \text{ cm}^{-1}$). Mass Spec. (ESI, +ve mode): exact mass calculated for $[\text{C}_{39}\text{H}_{46}\text{PFe}_3\text{O}]^+$: 729.1334; exact mass found: 729.1338; difference: +0.5 ppm. Anal. Calcd. (%) for $\text{C}_{39}\text{H}_{46}\text{PFe}_3\text{OBF}_4$: C, 57.40; H, 5.68. Found: C, 57.51; H, 5.76.

Preparation of monomer 6

In a 250 mL Schlenk flask, **5a** (0.50 g 0.65 mmol) was dissolved in dry dichloromethane (100 mL). Triethylamine (1.4 mL, 10 mmol) was added to the reaction flask at the room temperature. After stirring at 20 °C for 20 min, methacryloyl chloride (1.10 mL, 10.9 mmol) was added to the reaction flask and the resulting solution was allowed to stir for 2 h. The reaction mixture was then allowed to stir at 20 °C for 16 h before it was washed with $2 \times 25 \text{ mL}$ of saturated solution of sodium bicarbonate and $3 \times 25 \text{ mL}$ of H_2O , respectively, dried over magnesium sulfate, and transferred to a silica plug (1'' \times 3'') for subsequent purification *in vacuo*. The chloride salt remained on top of the plug while 150 mL degassed dichloromethane eluted before the solvent was changed to degassed ethanol to remove the monomer as a chloride salt. The ethanol solution containing the chloride salt was collected and concentrated *in vacuo*. The resulting residue was dissolved in 25 mL dry and degassed chloroform before sodium trifluoromethanesulfonate (1.00 g, 5.70 mmol) was charged into the reaction flask. The resulting mixture was allowed to stir at 20 °C for 16 h, gravity filtered to remove precipitate, washed with $3 \times 20 \text{ mL}$ of H_2O , dried over magnesium sulfate, and gravity filtered. Sodium trifluoromethanesulfonate (0.10 g, 0.57 mmol) was once again charged into a 100 mL flask containing the filtrate before the mixture was allowed to stir for another 16 h. It was then gravity filtered to remove the precipitate that formed, washed with $3 \times 20 \text{ mL}$ of H_2O , dried over

magnesium sulfate, and gravity filtered before it was concentrated *in vacuo*. The resulting orange residue was then dried *in vacuo* for 2 h at 35 °C to remove residual solvents to afford monomer **6** as an orange solid. Yield = 0.54 g, 89%. M. p. = 68–70 °C. ¹H NMR (599.4 MHz, CDCl₃): δ 6.16 (m, 1H, *trans*-CCH₂), 5.66 (m, 1H, *cis*-CCH₂), 4.22 (s, 15H, C₅H₅), 4.21 (s, 6H, β-C₅H₄R), 4.20 (s, 6H, α-C₅H₄R), 4.15 (m, 2H, CH₂CH₂O), 2.59 (m, 6H, C₅H₄CH₂), 2.32 (m, 6H, C₅H₄CH₂CH₂), 2.10 (m, 2H, PCH₂CH₂CH₂), 1.98 (s, 3H, CH₃), 1.81 (m, 2H, PCH₂CH₂CH₂). ¹³C{¹H} NMR (100.5 MHz, CDCl₃): δ 166.8 (s, CO), 135.7 (s, CCH₃), 126.1 (s, CCH₂), 120.8 (q, ¹J_{CF} = 321 Hz, SO₃CF₃[−]), 85.2 (d, ³J_{CP} = 13 Hz, *ipso*-C₅H₄R), 68.8 (s, C₅H₅), 68.0 (s, β-C₅H₄R and α-C₅H₄R), 63.5 (d, ³J_{CP} = 16 Hz, CH₂CH₂O), 21.9 (d, ²J_{CP} = 5 Hz, C₅H₄CH₂), 21.0 (d, ²J_{CP} = 4 Hz, PCH₂CH₂CH₂), 20.6 (d, ¹J_{CP} = 46 Hz, C₅H₄CH₂CH₂), 18.24 (s, CH₃), 15.8 (d, ¹J_{CP} = 48 Hz, PCH₂CH₂CH₂). ¹⁹F NMR (376.4 MHz, CDCl₃): δ −78.1. ³¹P NMR (242.7 MHz, CDCl₃): δ 31.9 (s). FT-IR (KBr): 825 (m), 1032 (s), 1163 (s), 1275 (br, s), 1645 (br, m), 1722 (br, m), 3109 (br, w), 3468 (br, s) cm^{−1}. UV-vis (CH₂Cl₂): λ_{max} 440 nm (ε = 294 M^{−1} cm^{−1}). Mass Spec. (ESI, +ve mode): exact mass calculated for [C₄₄H₅₀PFe₃O₅]⁺: 797.1597; exact mass found: 797.1598; difference: +0.1 ppm. Anal. Calcd. (%) for C₄₄H₅₀PFe₃O₅SF₃: C, 55.84; H, 5.32; S, 3.39. Found: C, 56.03; H, 5.49; S, 3.52.

Preparation of polyelectrolyte **7a**

In a 20 mL grease-free Schlenk flask, monomer **6** (0.400 mg, 0.423 mmol) was dissolved in 0.400 mL of a tetrahydrofuran solution containing AIBN (0.695 mg, 0.00423 mmol). The resulting solution was degassed using 3 freeze-pump-thaw cycles before it was allowed to stir at 75 °C for 17 h. The solution was concentrated *in vacuo* to yield a dark orange residue before it was dissolved in a minimum amount of dichloromethane, precipitated in benzene, and centrifuged for 1 min to separate the solids. The solids were collocated and the precipitation

process was repeated once in benzene and twice in pentane, respectively, and dried in a drying tube at 50 °C for 40 h to yield polyelectrolyte **7a** as a yellow powder. Yield = 0.28 g, 70%. ¹H NMR (599.4 MHz, CDCl₃): δ 3.30–5.40 (broad, C₅H₅, C₅H₄R and CH₂CH₂O), 0.50–3.05 (broad, saturated polymer backbone CH₂, C₅H₄CH₂, C₅H₄CH₂CH₂, PCH₂CH₂CH₂, CH₃, PCH₂CH₂CH₂). ¹⁹F NMR (376.4 MHz, CDCl₃): δ –77.2. ³¹P NMR (242.7 MHz, CDCl₃): δ 31.8 (s). FT-IR (KBr): 638 (m), 829 (w), 1032 (m), 1161 (m), 1265 (s), 1660 (br, w), 1734 (br, w), 2934 (br, w), 3099 (br, w) cm^{–1}. UV-vis (CH₂Cl₂): λ_{max} 437 nm (ε = 322 M^{–1} cm^{–1}). Anal. Calcd. (%) for (C₄₄H₅₀PFe₃O₅SF₃)_n: C, 55.84; H, 5.32; S, 3.39. Found: C, 56.14; H, 5.42; S, 3.69.

Preparation of polyelectrolyte **7b**

In a 20 mL grease-free Schlenk flask, monomer **6** (0.400 mg, 0.423 mmol) was dissolved in 0.533 mL of a tetrahydrofuran solution containing AIBN (0.347 mg, 0.00211 mmol). The resulting solution was degassed using 3 freeze-pump-thaw cycles before it was allowed to stir at 75 °C for 25 h. The solution was concentrated *in vacuo* to yield a dark orange residue before it was dissolved in a minimum amount of dichloromethane, precipitated in benzene, and centrifuged for 1 min to separate the solids. The solids were collocated and the precipitation process was repeated once in benzene and twice in pentane, respectively, and dried in a drying tube at 50 °C for 40 h to yield polyelectrolyte **7b** as a yellow powder. Yield = 0.32 g, 79%. ¹H NMR (599.4 MHz, CDCl₃): δ 3.40–5.00 (broad, C₅H₅, C₅H₄R and CH₂CH₂O), 0.50–3.10 (broad, saturated polymer backbone CH₂, C₅H₄CH₂, C₅H₄CH₂CH₂, PCH₂CH₂CH₂, CH₃, PCH₂CH₂CH₂). ¹⁹F NMR (376.4 MHz, CDCl₃): δ –77.2. ³¹P NMR (242.7 MHz, CDCl₃): δ 31.8 (s). FT-IR (KBr): 638 (m), 827 (w), 1031 (m), 1159 (m), 1267 (s), 1656 (br, w), 1730 (br, m), 2937 (br, w), 3099 (br, w) cm^{–1}. UV-vis (CH₂Cl₂): λ_{max} 438 nm (ε = 310 M^{–1} cm^{–1}). Anal. Calcd. (%) for (C₄₄H₅₀PFe₃O₅SF₃)_n: C, 55.84; H, 5.32; S, 3.39. Found: C, 56.96; H, 5.56; S, 3.50.

Preparation of polyelectrolyte **7c**

In a 20 mL grease-free Schlenk flask, monomer **6** (0.400 mg, 0.423 mmol) was dissolved in 0.800 mL of a tetrahydrofuran solution containing AIBN (0.232 mg, 0.00141 mmol). The resulting solution was degassed using 3 freeze-pump-thaw cycles before it was allowed to stir at 75 °C for 32 h. The solution was concentrated *in vacuo* to yield a dark orange residue before it was dissolved in a minimum amount of dichloromethane, precipitated in benzene, and centrifuged for 1 min to separate the solids. The solids were collocated and the precipitation process was repeated once in benzene and twice in pentane, respectively, and dried in a drying tube at 50 °C for 40 h to yield polyelectrolyte **7c** as a yellow powder. Yield = 0.30 g, 75%. ¹H NMR (599.4 MHz, CDCl₃): δ 3.50–5.50 (broad, C₅H₅, C₅H₄R and CH₂CH₂O), 0.50–3.20, (broad, saturated polymer backbone CH₂, C₅H₄CH₂, C₅H₄CH₂CH₂, PCH₂CH₂CH₂, CH₃, PCH₂CH₂CH₂). ¹⁹F NMR (376.4 MHz, CDCl₃): δ –77.2. ³¹P NMR (242.7 MHz, CDCl₃): δ 31.9 (s). FT-IR (KBr): 638 (m), 827 (w), 1032 (m), 1161 (m), 1265 (s), 1651 (br, m), 1732 (br, m), 2935 (br, w), 3101 (br, w) cm^{–1}. UV-vis (CH₂Cl₂): λ_{max} 440 nm (ε = 323 M^{–1} cm^{–1}). Anal. Calcd. (%) for (C₄₄H₅₀PFe₃O₅SF₃)_n: C, 55.84; H, 5.32; S, 3.39. Found: C, 55.86; H, 5.54; S, 3.58.

Additional Figures

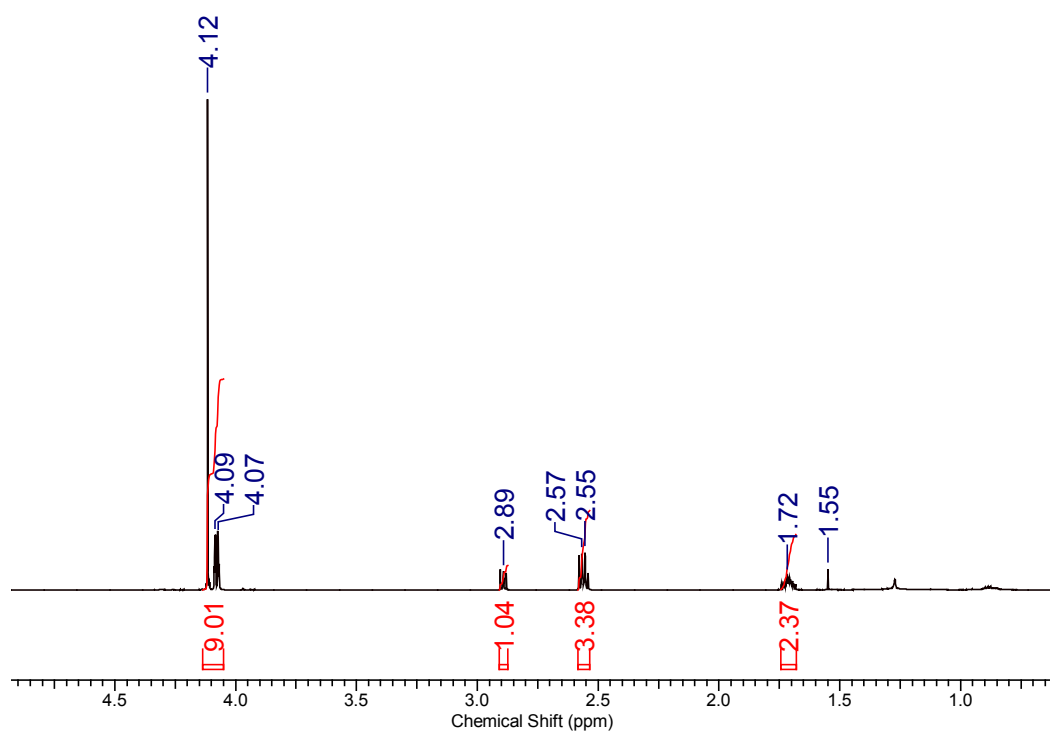


Fig. S1 ^1H NMR spectrum of primary phosphine **4a** in CDCl_3 .

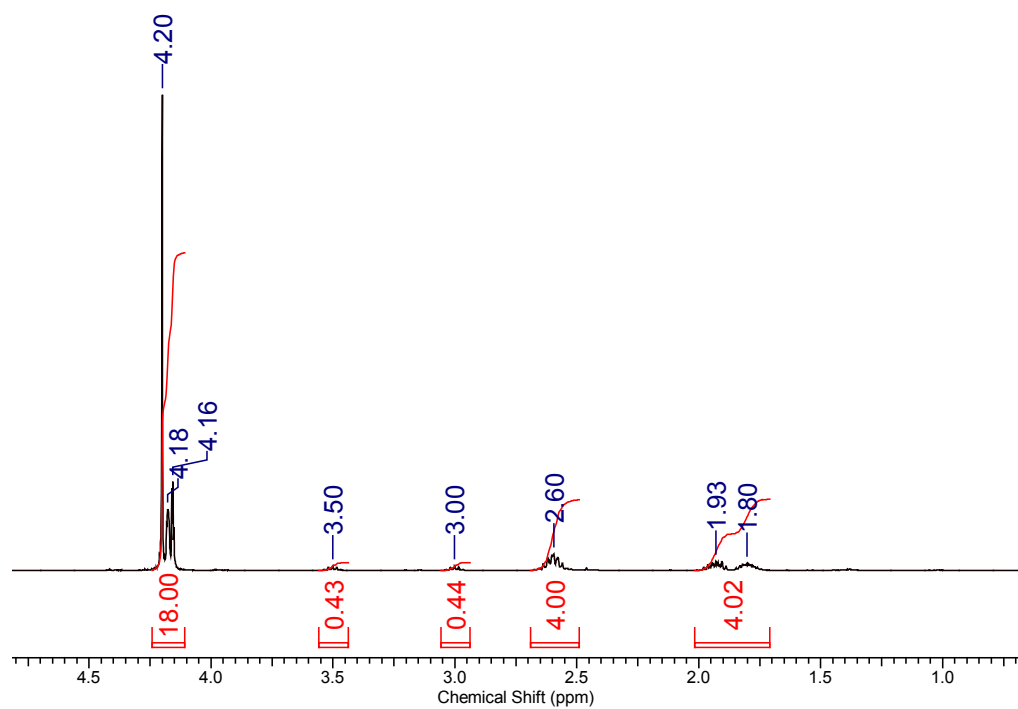


Fig. S2 ^1H NMR spectrum of secondary phosphine **4b** in CDCl_3 .

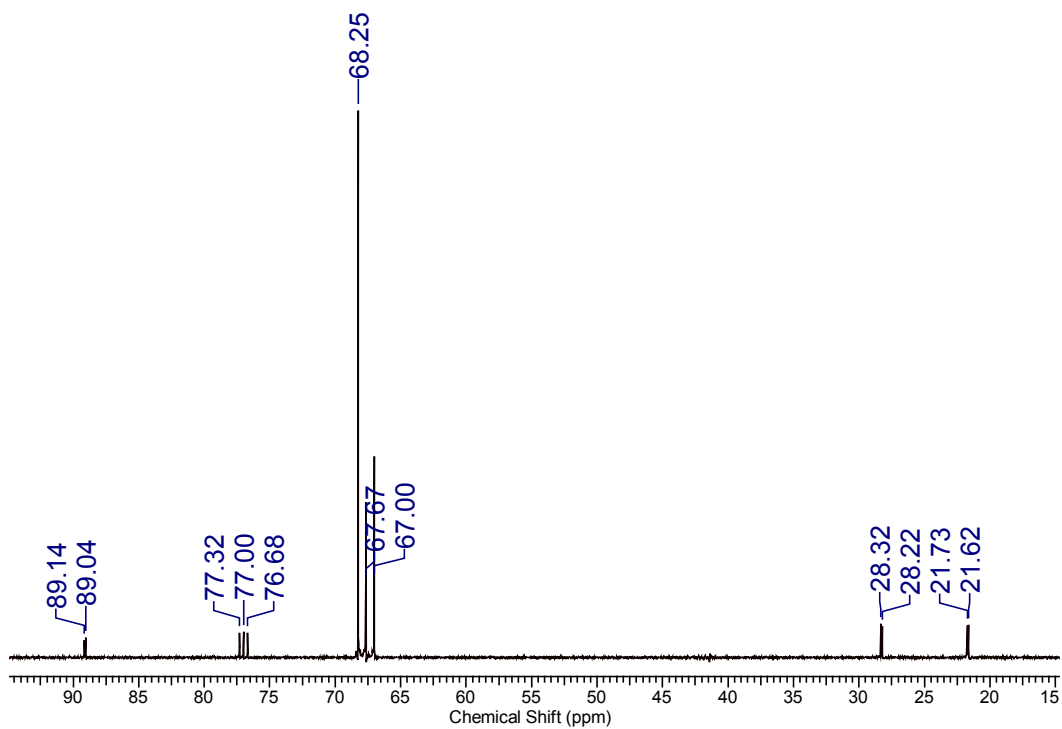


Fig. S3 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of secondary phosphine **4b** in CDCl_3 .

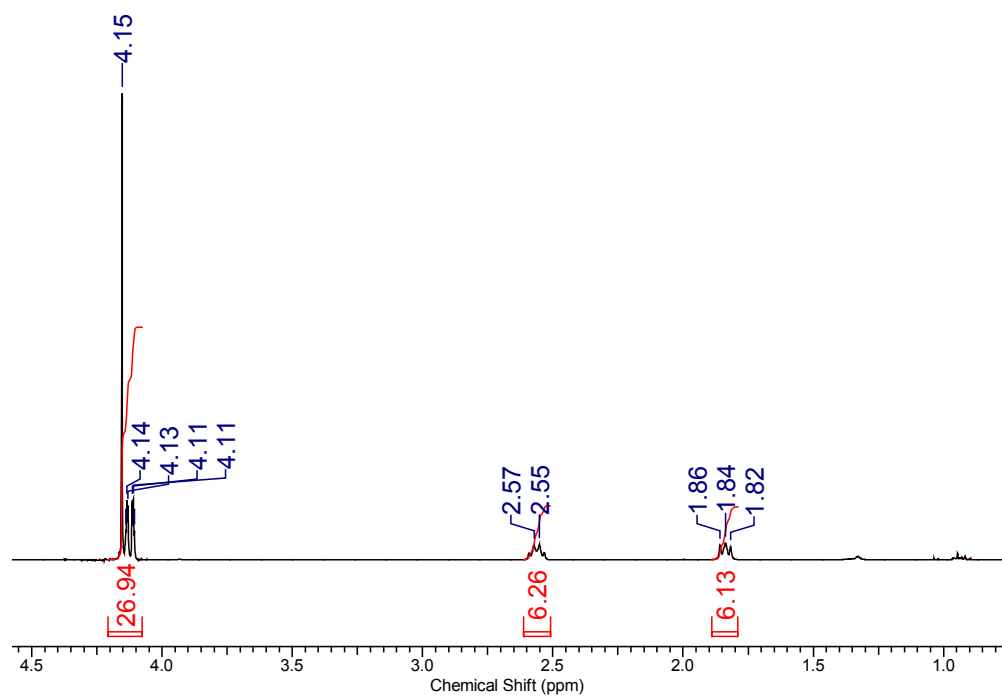


Fig. S4 ^1H NMR spectrum of tertiary phosphine **4c** in CDCl_3 .

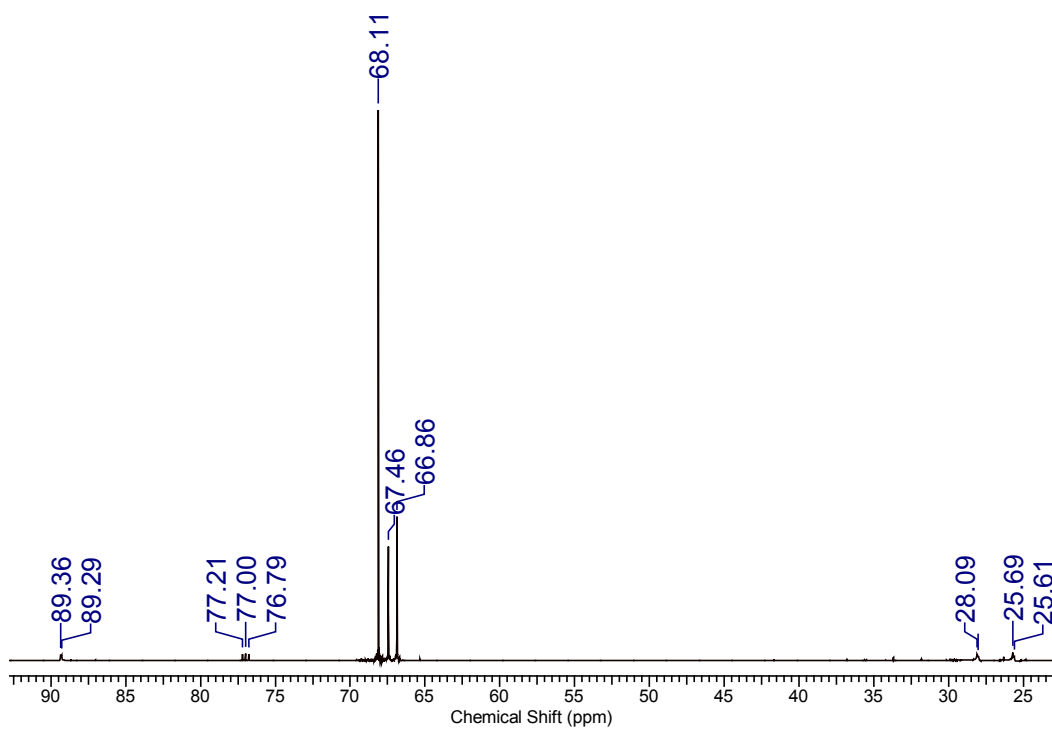


Fig. S5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of tertiary phosphine **4c** in CDCl_3 .

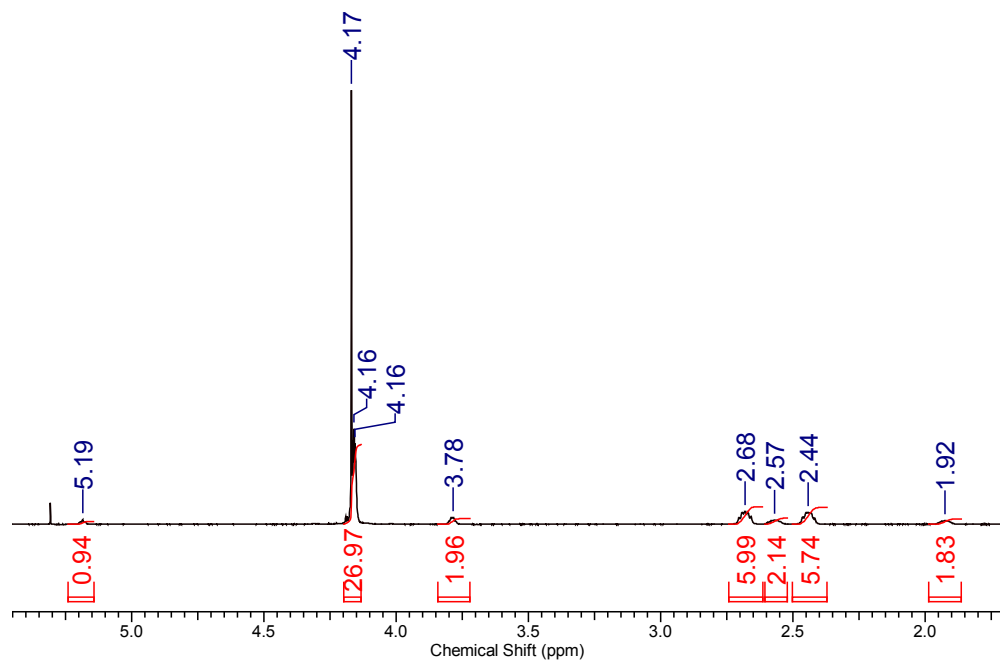


Fig. S6 ¹H NMR spectrum of phosphonium chloride salt **5a** in CDCl₃.

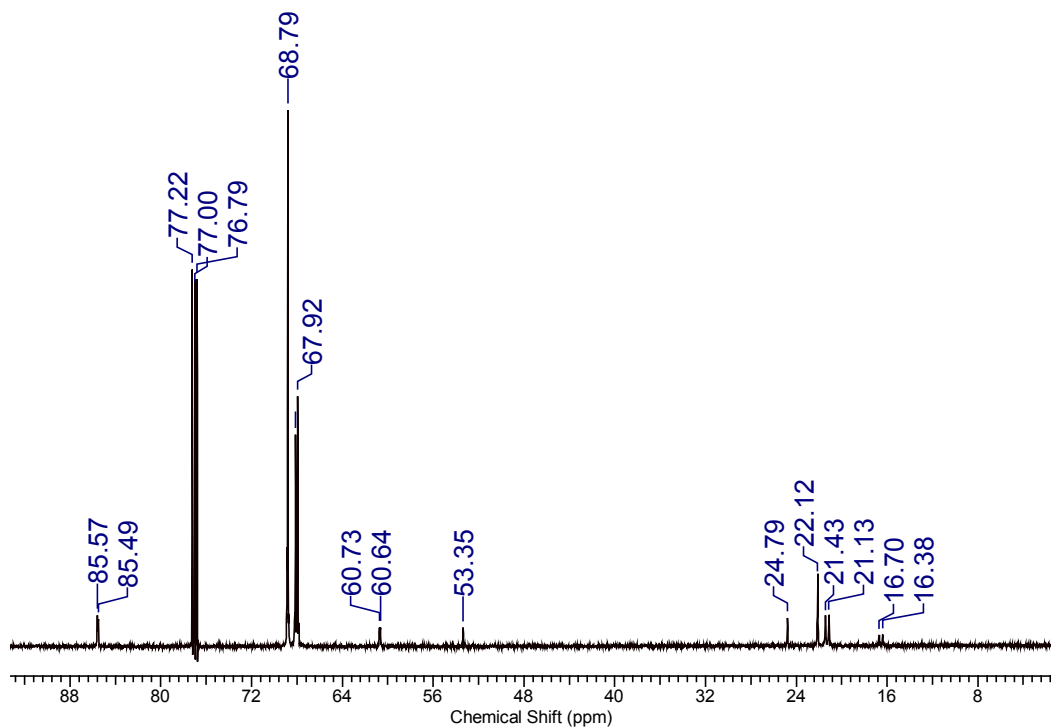


Fig. S7 ¹³C{¹H} NMR spectrum of phosphonium chloride salt **5a** in CDCl₃.

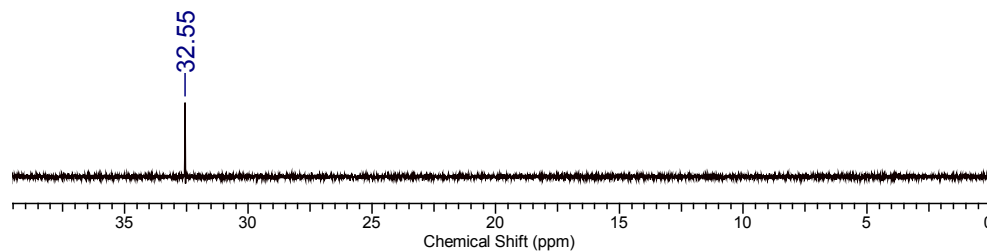


Fig. S8 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphonium chloride salt **5a** in CDCl_3 .

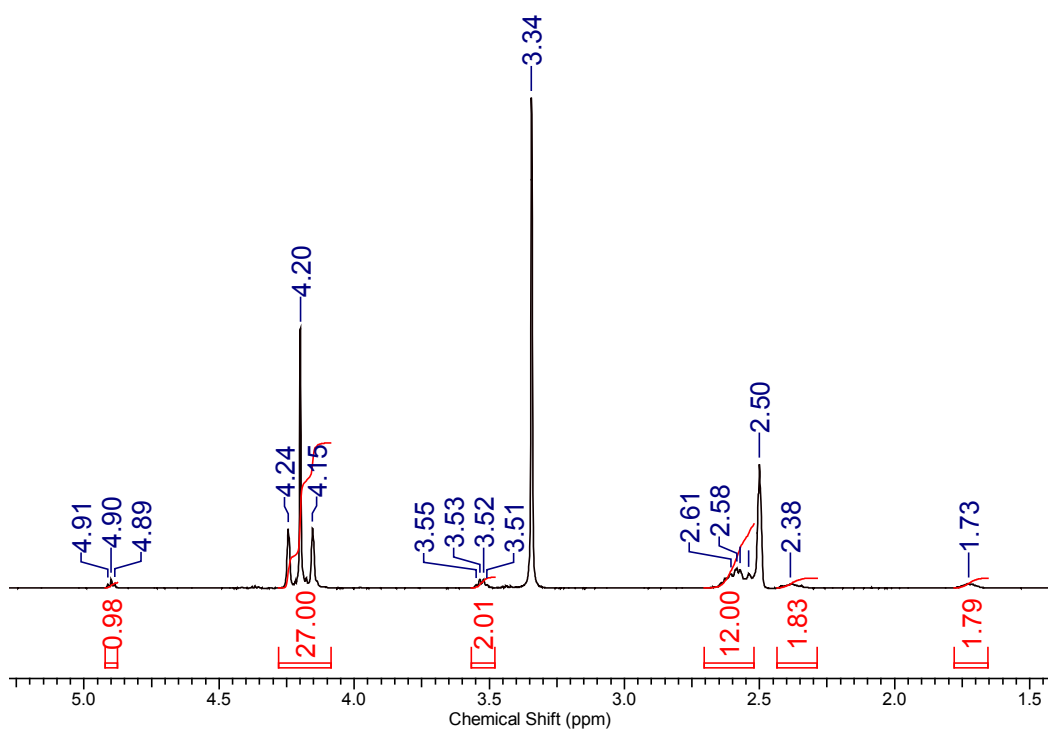


Fig. S9 ^1H NMR spectrum of phosphonium tetrafluoroborate salt **5b** in d_6 -DMSO.

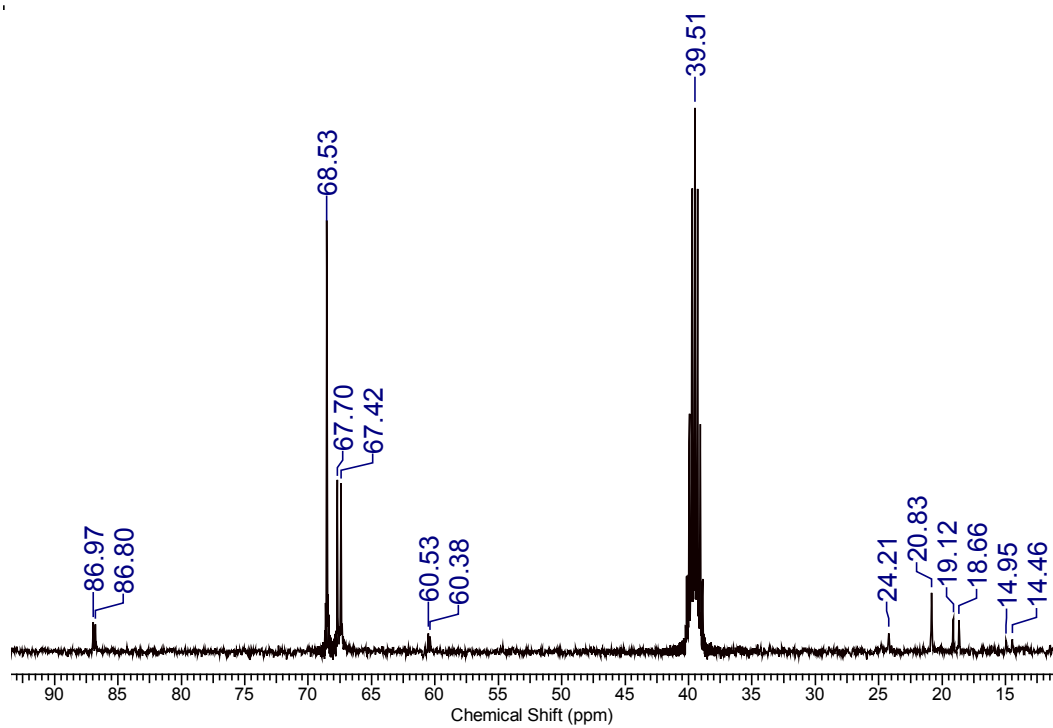


Fig. S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of phosphonium tetrafluoroborate salt **5b** in d_6 -DMSO.

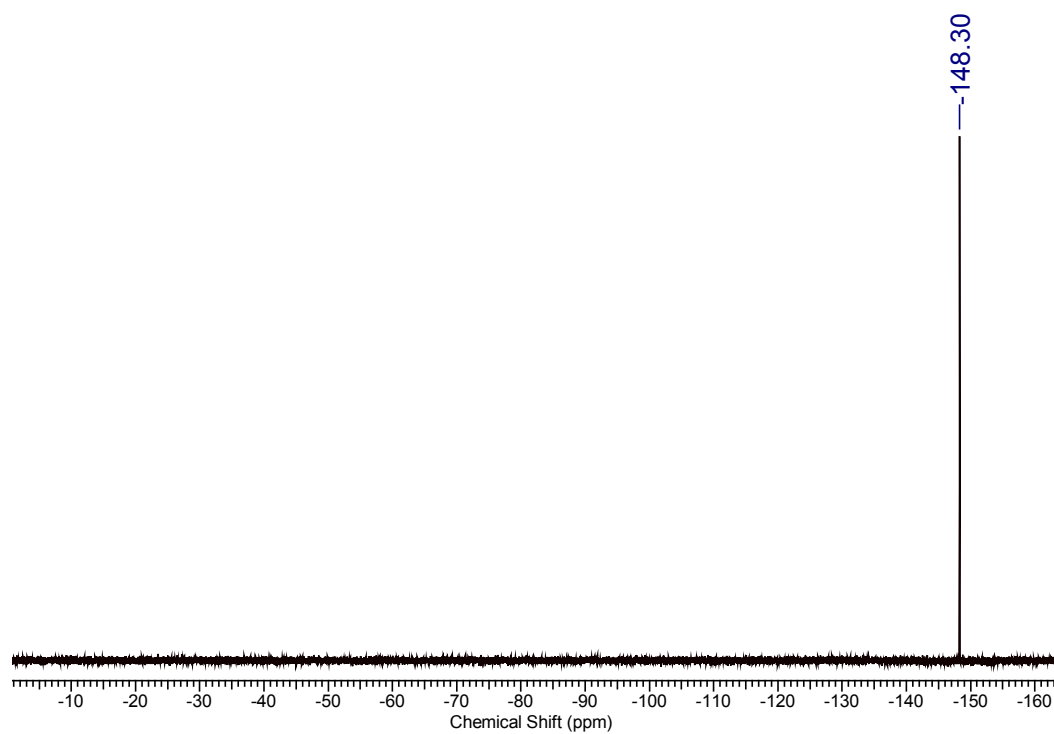


Fig. S11 ^{19}F NMR spectrum of phosphonium tetrafluoroborate salt **5b** in d_6 -DMSO.

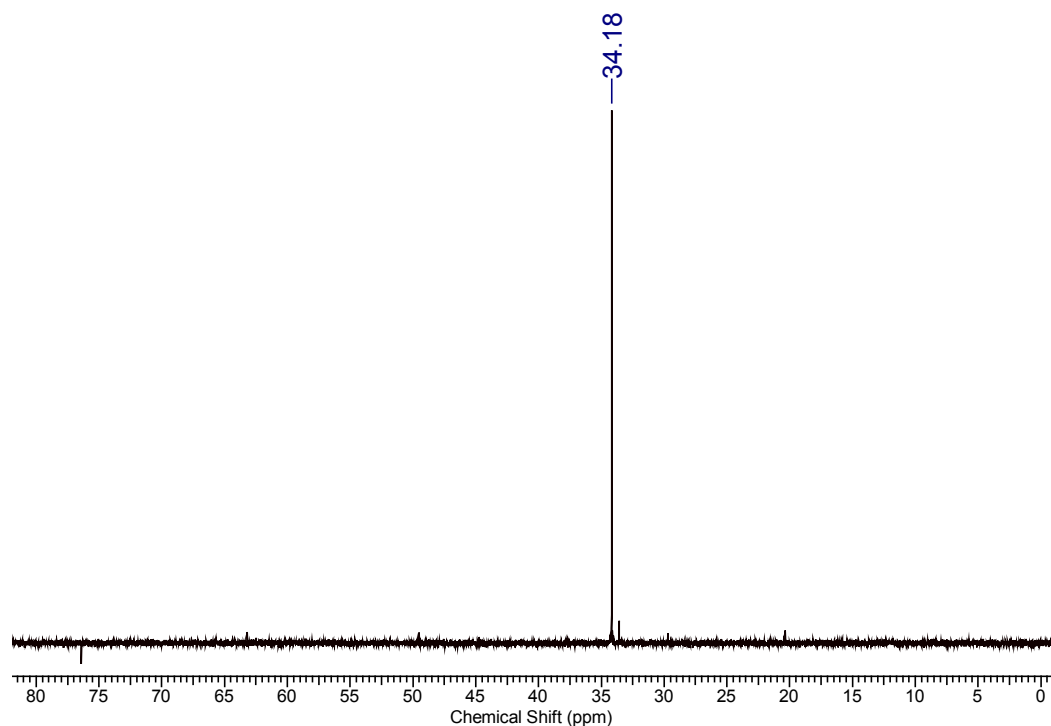


Fig. S12 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of phosphonium tetrafluoroborate salt **5b** in d_6 -DMSO.

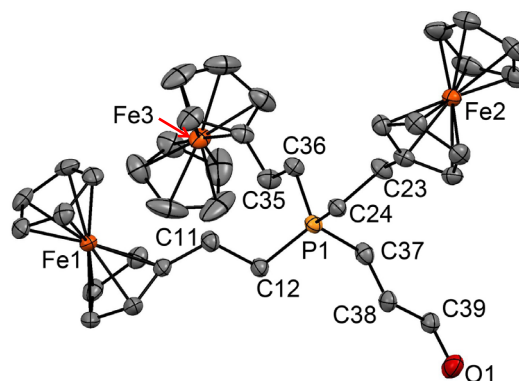


Fig. S13 Solid-state structure of phosphonium alcohol **5b**. Thermal ellipsoids shown at 50% probability level. Hydrogen atoms and BF_4^- counter anion have been removed for clarity. Selected bond lengths (Å) and angles (°): P1-C12 1.806(4), P1-C24 1.809(4), P1-C36 1.802(4), P1-C37 1.808(4), C11-C12 1.550(6), C23-C24 1.545(5), C35-C36 1.548(6), C37-C38 1.522(6); C12-P1-C24 110.9(2), C12-P1-C36 109.1(2), C12-P1-C37 109.4(2), C24-P1-C36 110.2(2), C24-P1-C37 109.6(2), C36-P1-C37 107.6(2).

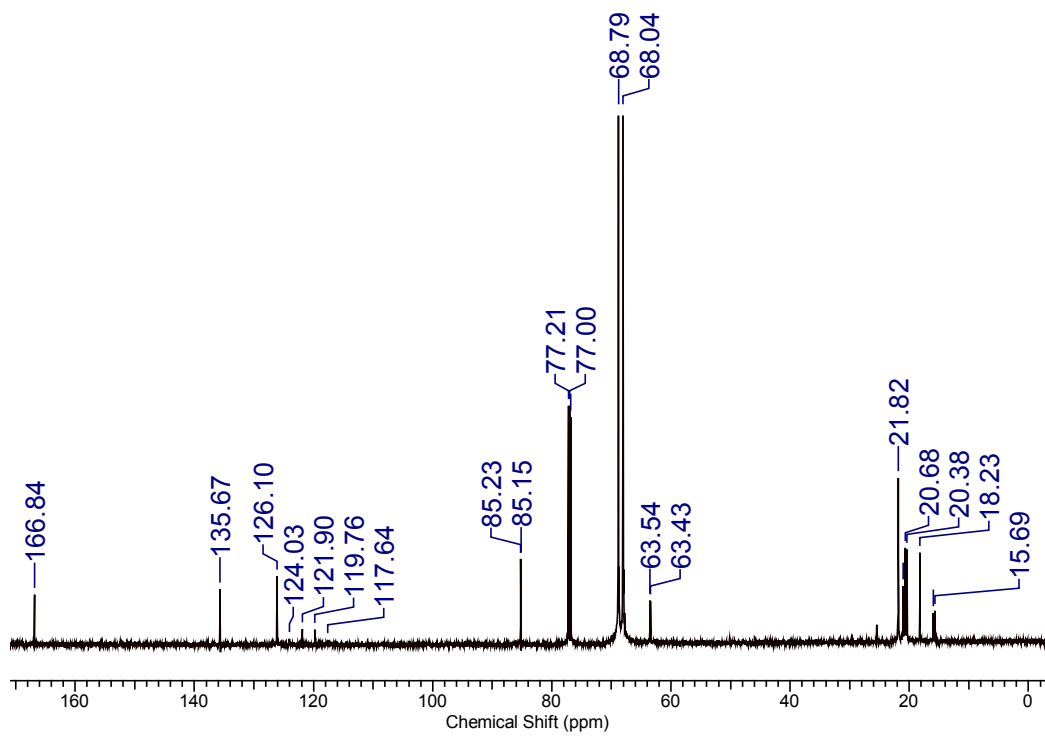


Fig. S14 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of phosphonium monomer **6** in CDCl_3 .

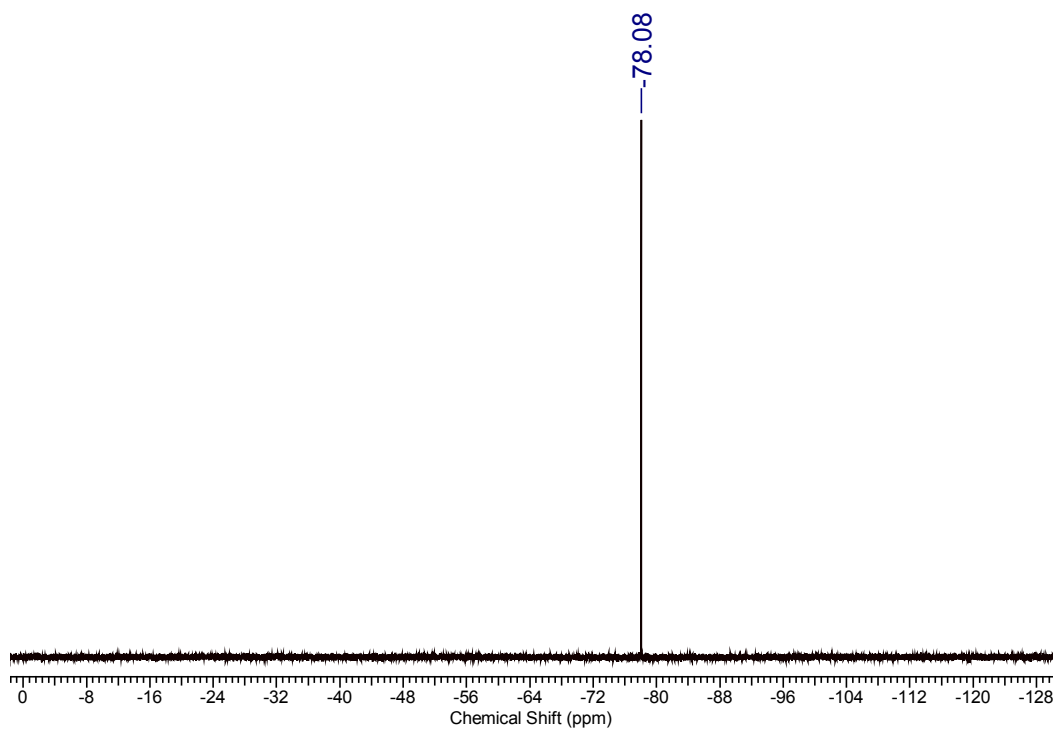


Fig. S15 ^{19}F NMR spectrum of monomer **6** in CDCl_3 .

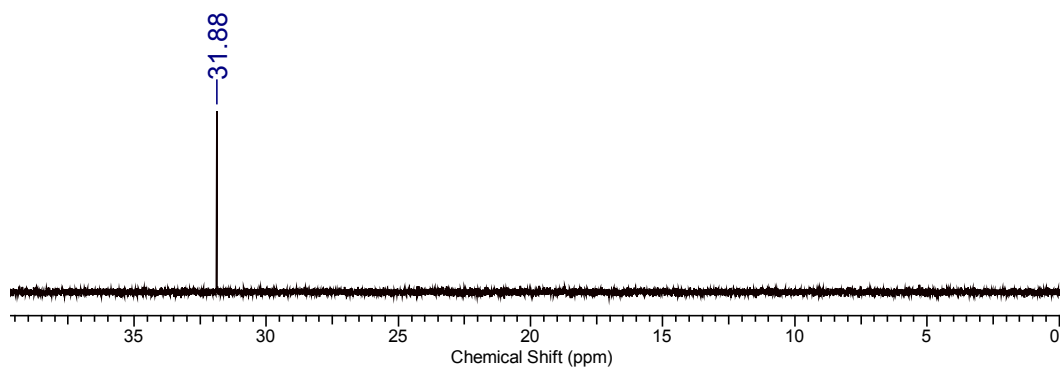


Fig. S16 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of monomer **6** in CDCl_3 .

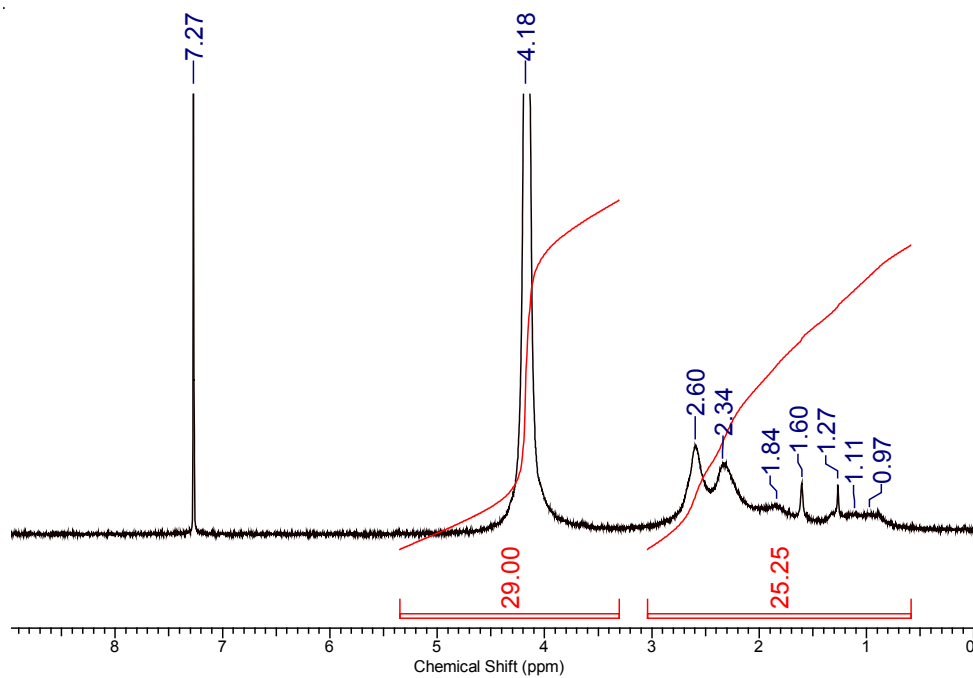


Fig. S17 ^1H NMR spectrum of polyelectrolyte **7a** in CDCl_3 .

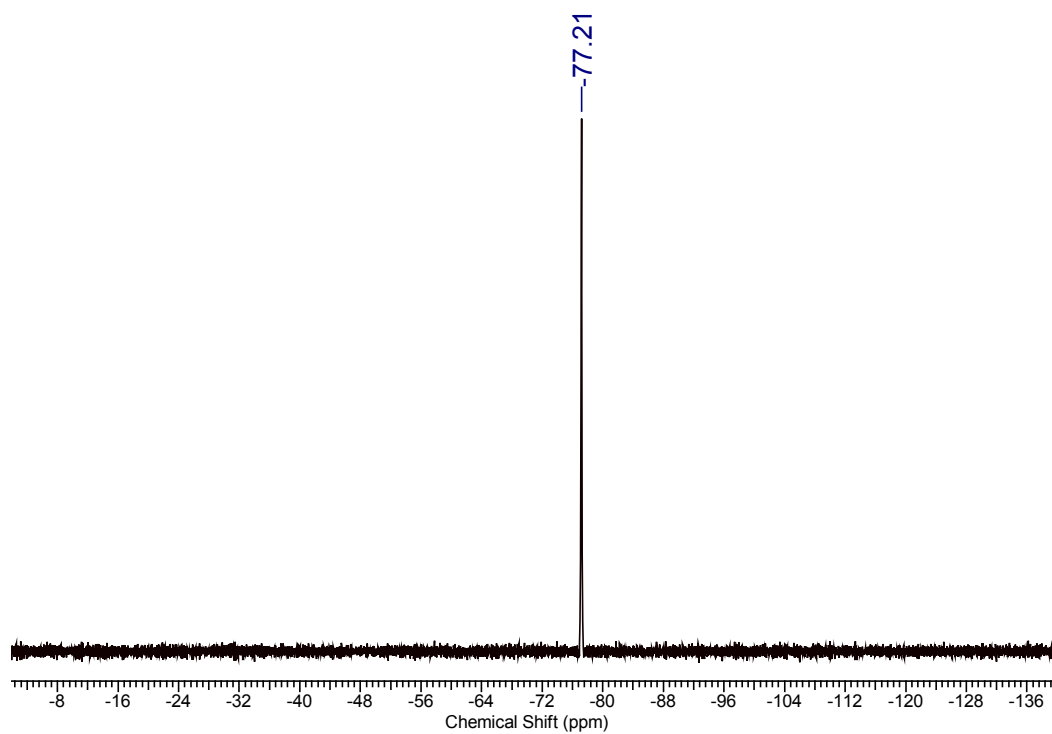


Fig. S18 ^{19}F NMR spectrum of polyelectrolyte **7a** in CDCl_3 .

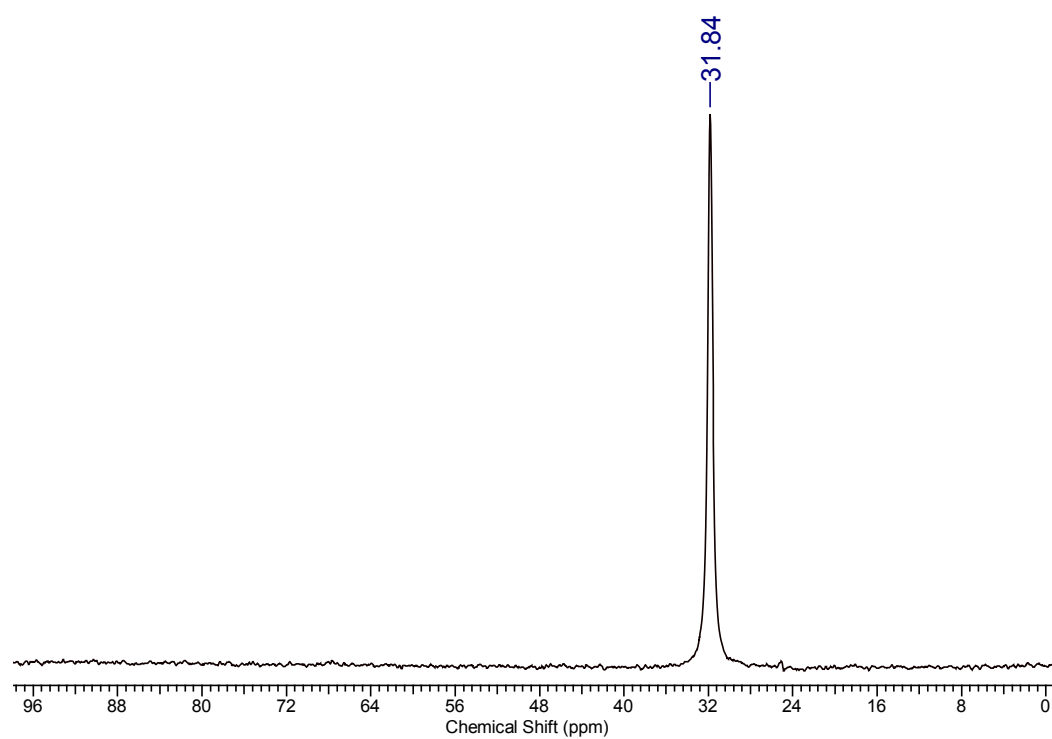


Fig. S19 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of polyelectrolyte **7a** in CDCl_3 .

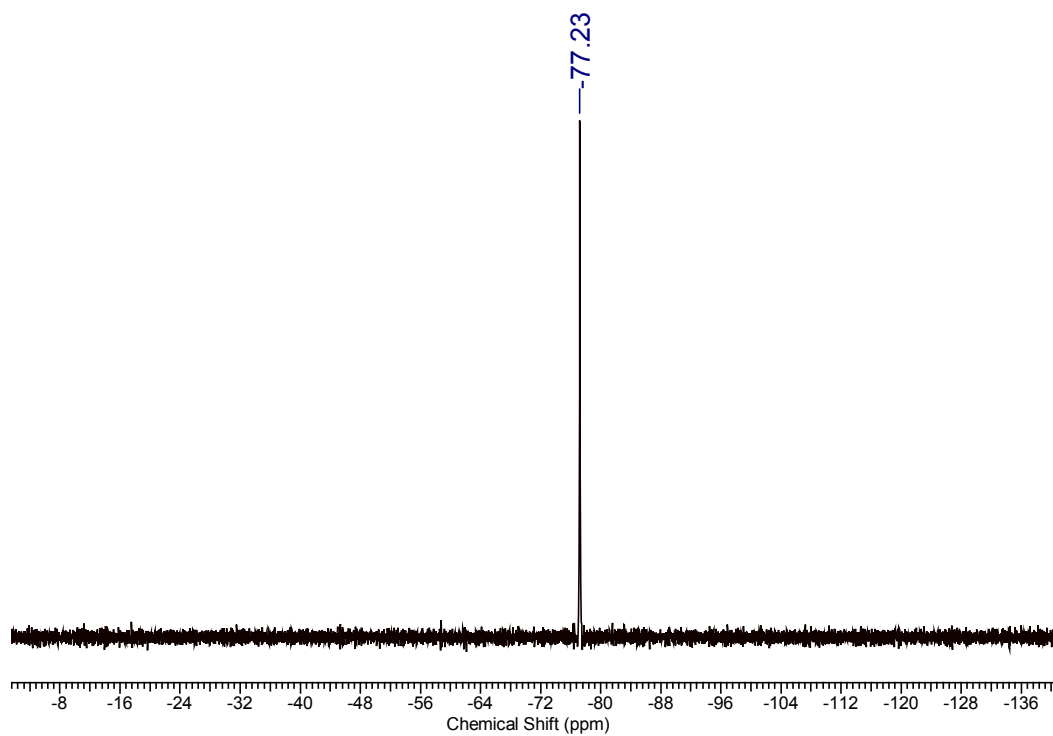


Fig. S20 ^{19}F NMR spectrum of polyelectrolyte **7b** in CDCl_3 .

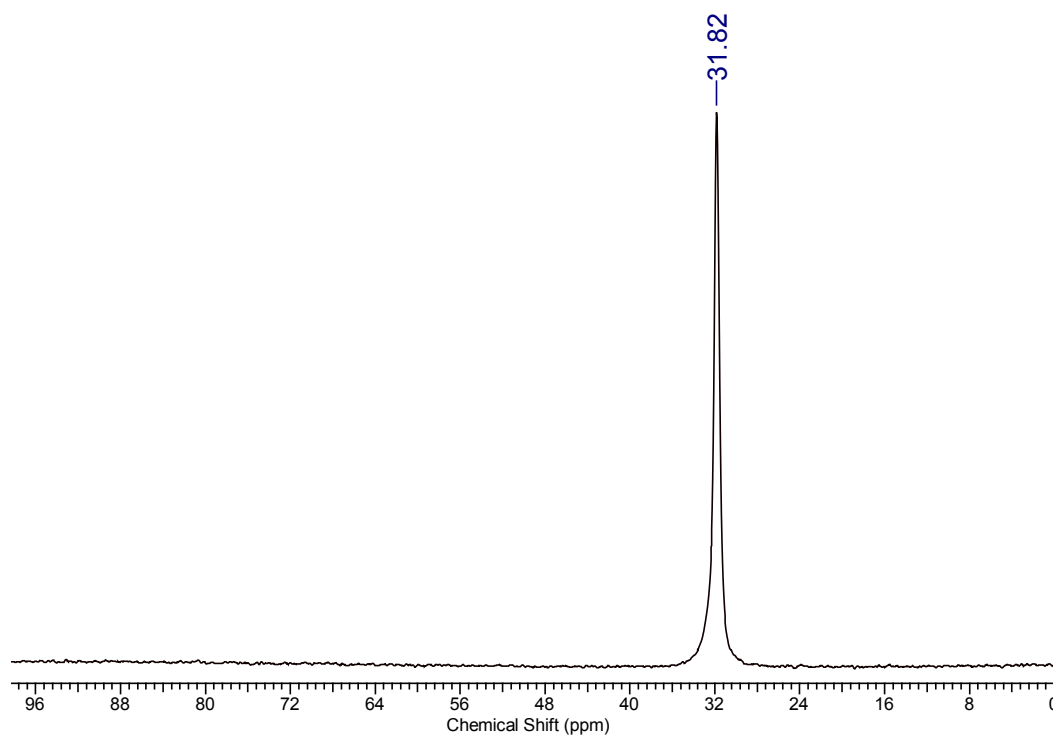


Fig. S21 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of polyelectrolyte **7b** in CDCl_3 .

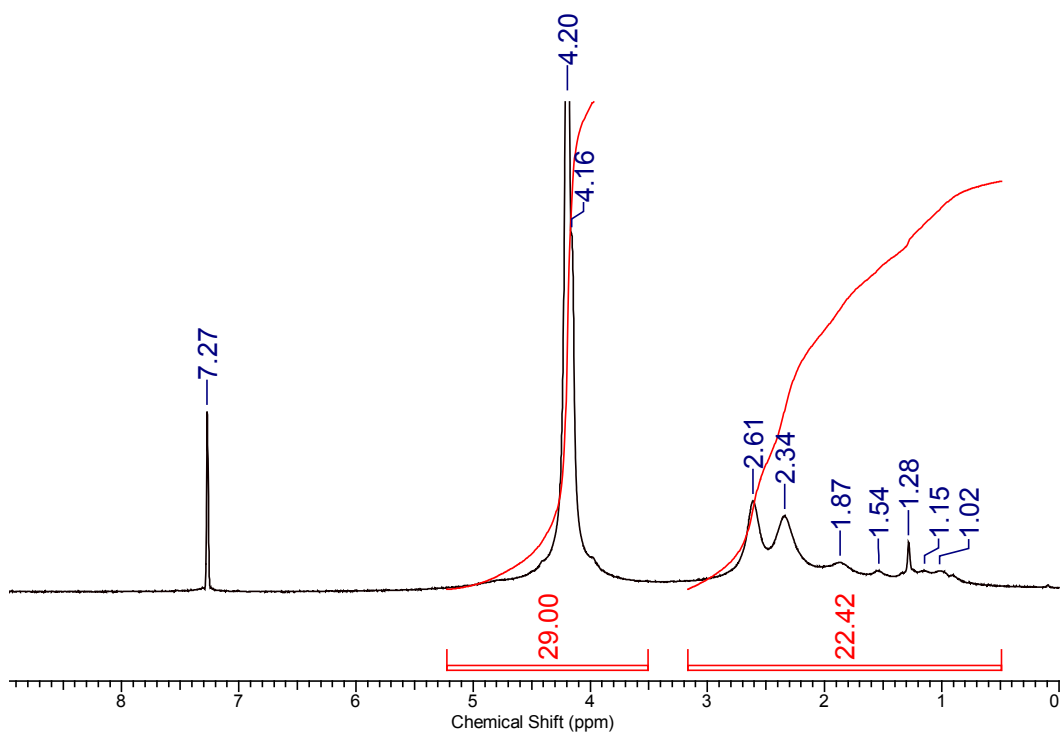


Fig. S22 ¹H NMR spectrum of polyelectrolyte **7c** in CDCl₃.

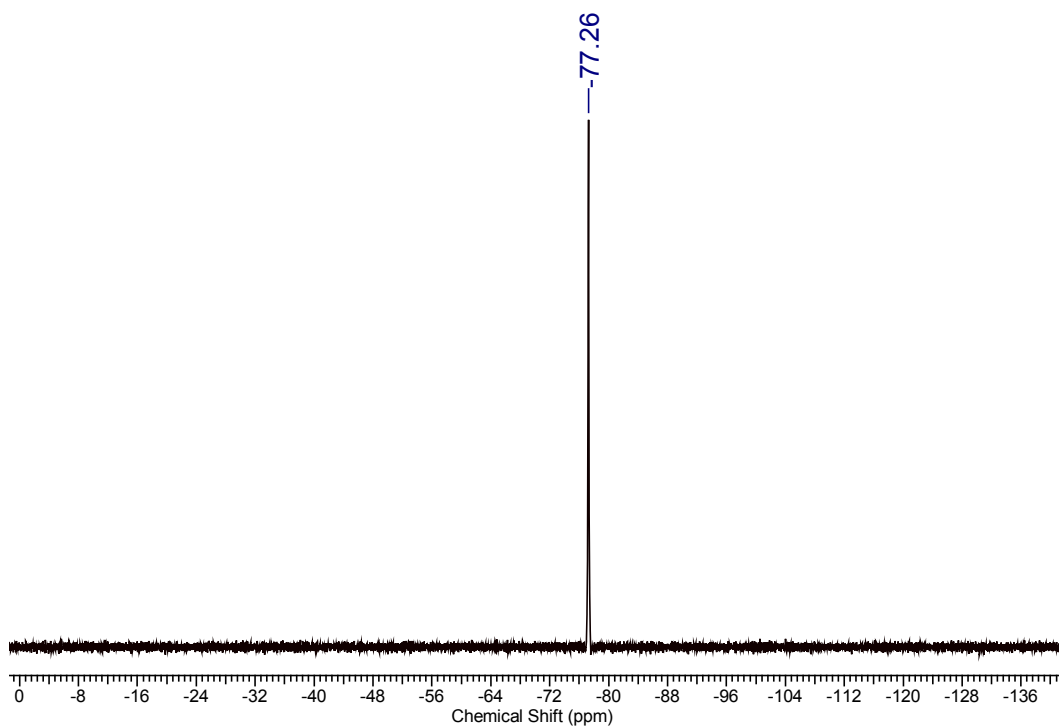


Fig. S23 ¹⁹F NMR spectrum of polyelectrolyte **7c** in CDCl₃.

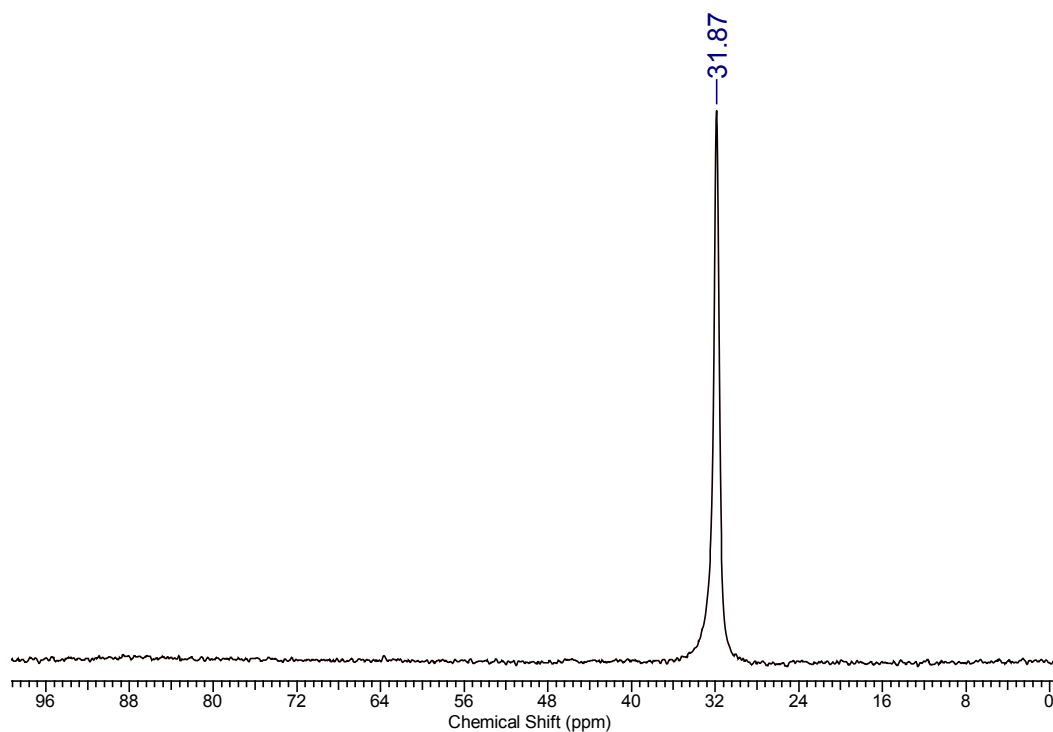


Fig. S24 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of polyelectrolyte **7c** in CDCl_3 .

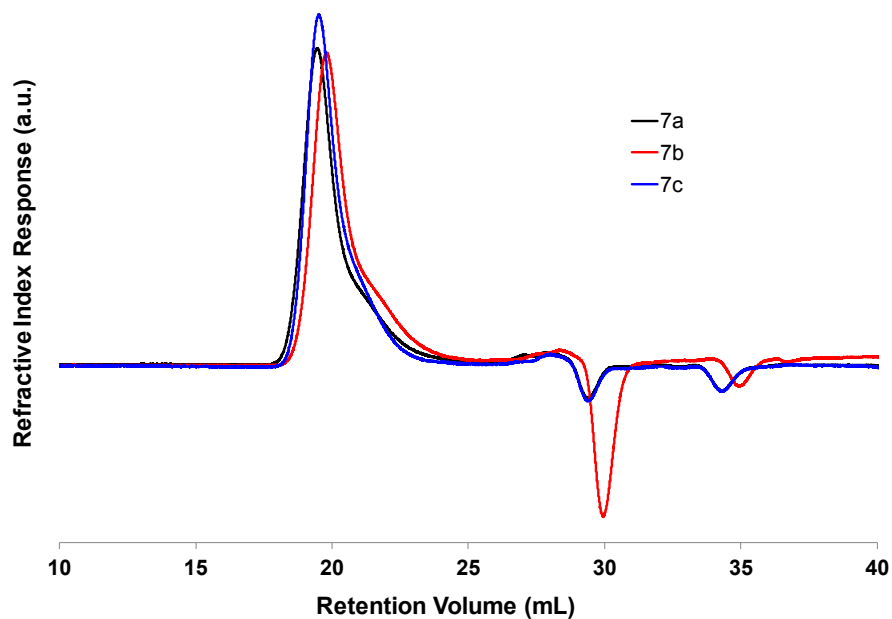


Fig. S25 GPC traces (RI response) for phosphonium polyelectrolytes **7a–c** in DMF containing 0.02 M tetrabutylammonium trifluoromethanesulfonate at 60 °C. The fluctuations from 27–37 mL arise due to changes in RI associated with sample injections.

Table S2. Processed conventional calibration GPC data for phosphonium polyelectrolytes **7a–c**.

Sample	Injection	Max RI Response (mL)	M _n (Da)	M _w (Da)	M _w /M _n
7a	1	19.45	43,045	117,420	2.73
	2	19.45	44,343	118,607	2.68
	3	19.44	41,977	118,645	2.83
	Average	19.45	43,122	118,224	2.74
	Std. Dev.	0.004	967	569	0.063
	%RSD	0.02%	2.24%	0.48%	2.28%
7b	1	19.79	31,220	76,774	2.46
	2	19.80	32,602	77,052	2.366
	3	19.74	33,287	83,142	2.50
	Average	19.78	32,370	78,989	2.44
	Std. Dev.	0.028	860	2,939	0.057
	%RSD	0.14%	2.66%	3.72%	2.32%
7c	1	19.51	45,022	104,760	2.33
	2	19.51	44,623	105,486	2.36
	3	19.50	45,765	106,803	2.33
	Average	19.51	45,137	105,683	2.34
	Std. Dev.	0.005	473	846	0.016
	%RSD	0.03%	1.05%	0.80%	0.69%

Table S3. Processed triple detection GPC (right-angle light scattering) data for phosphonium polyelectrolytes **7a–c**.

Sample	Injection	Max RI Response (mL)	M _n (Da)	M _w (Da)	M _w /M _n	dn/dc (mL g ⁻¹)	IV (dL g ⁻¹)	R _h (nm)
7a	1	19.45	294,695	421,274	1.43	0.133 (fixed)	0.116	8.8
	2	19.45	304,058	429,502	1.41		0.117	9.0
	3	19.44	297,232	426,401	1.42		0.155	8.9
	Avg.	19.45	298,662	425,726	1.43		0.129	8.9
	Std. Dev.	0.004	4,842	4,155	0.01		0.02	0.06
	%RSD	0.02%	1.62%	0.98%	0.81%		17.30%	0.72%
7b	1	19.79	266,434	373,866	1.40	0.133	0.115	8.5
	2	19.80	275,087	379,379	1.38	0.132	0.108	8.3
	3	19.74	275,793	380,991	1.38	0.133	0.116	8.6
	Avg.	19.78	272,438	378,079	1.39	0.133	0.113	8.5
	Std. Dev.	0.028	5,212	3,736	0.01	0.00	0.00	0.15
	%RSD	0.14%	1.91%	0.99%	0.96%	0.38%	3.88%	1.76%
7c	1	19.51	285,807	366,321	1.28	0.133 (fixed)	0.113	8.5
	2	19.51	282,975	364,615	1.29		0.116	8.6
	3	19.50	282,326	365,010	1.29		0.118	8.6
	Avg.	19.51	283,703	365,315	1.29		0.115	8.6
	Std. Dev.	0.005	1,851	893	0.01		0.00	0.07
	%RSD	0.03%	0.65%	0.24%	0.43%		2.33%	0.79%

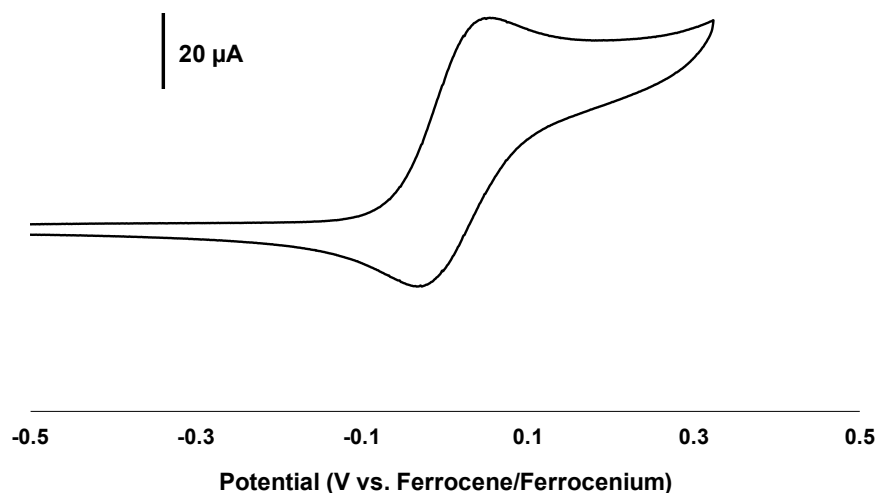


Fig. S26 Cyclic voltammogram of primary phosphine **4a** recorded at 250 mV s^{-1} recorded for a 1 mM solution of 2:1 dichloromethane:acetonitrile containing 0.1 M tetrabutylammonium trifluoromethanesulfonate as supporting electrolyte.

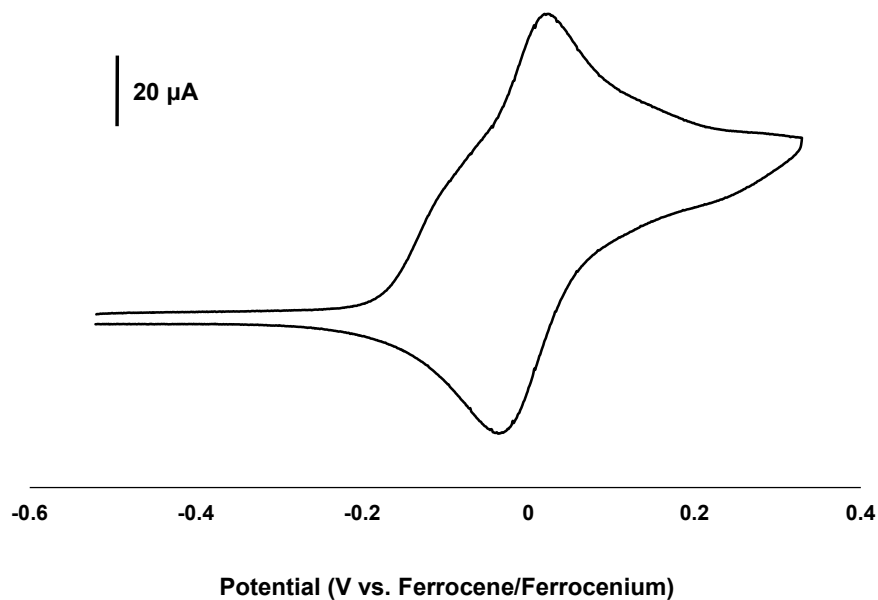


Fig. S27 Cyclic voltammogram of secondary phosphine **4b** recorded at 250 mV s^{-1} recorded for a 1 mM solution of 2:1 dichloromethane:acetonitrile containing 0.1 M tetrabutylammonium trifluoromethanesulfonate as supporting electrolyte.

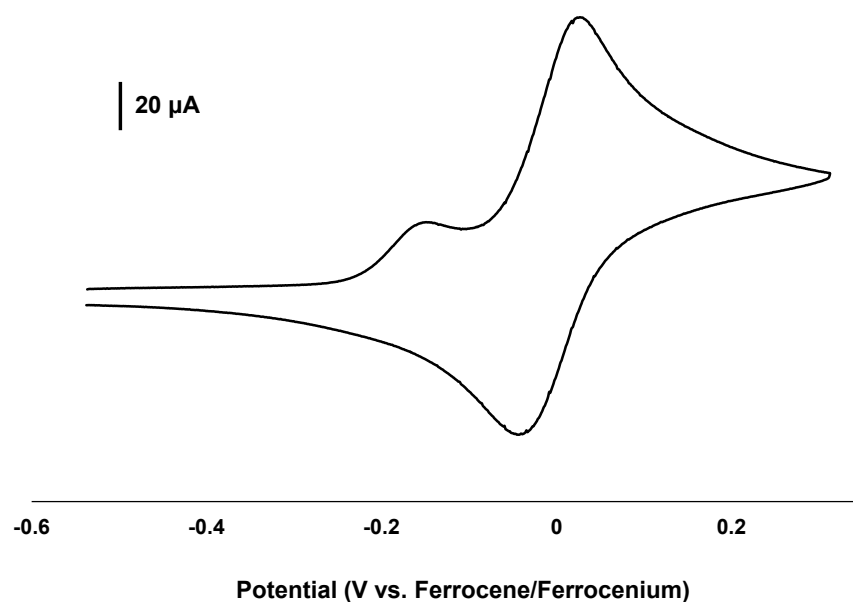


Fig. S28 Cyclic voltammogram of tertiary phosphine **4c** recorded at 250 mV s^{-1} recorded for a 1 mM solution of 2:1 dichloromethane:acetonitrile containing 0.1 M tetrabutylammonium trifluoromethanesulfonate as supporting electrolyte.

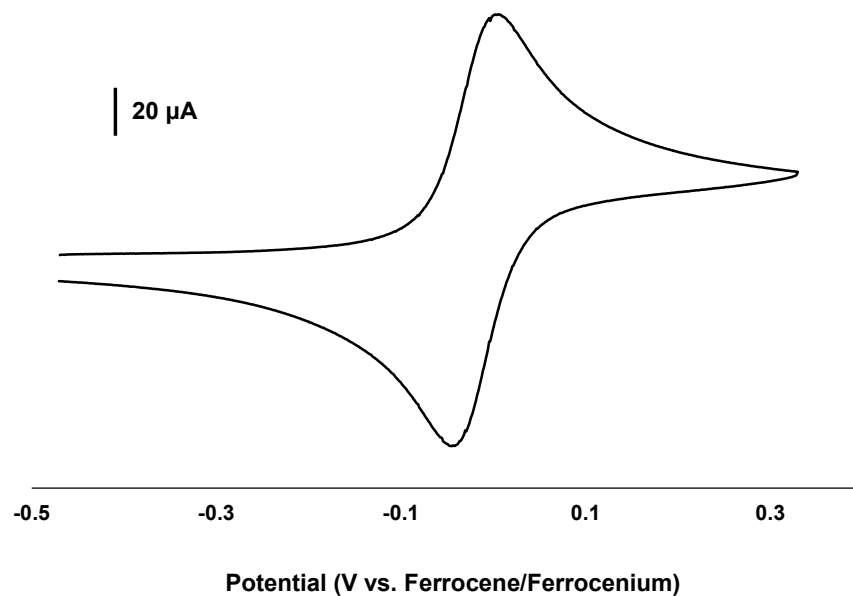


Fig. S29 Cyclic voltammogram of phosphonium chloride salt **5a** recorded at 250 mV s^{-1} recorded for a 1 mM solution of 2:1 dichloromethane:acetonitrile containing 0.1 M tetrabutylammonium trifluoromethanesulfonate as supporting electrolyte.

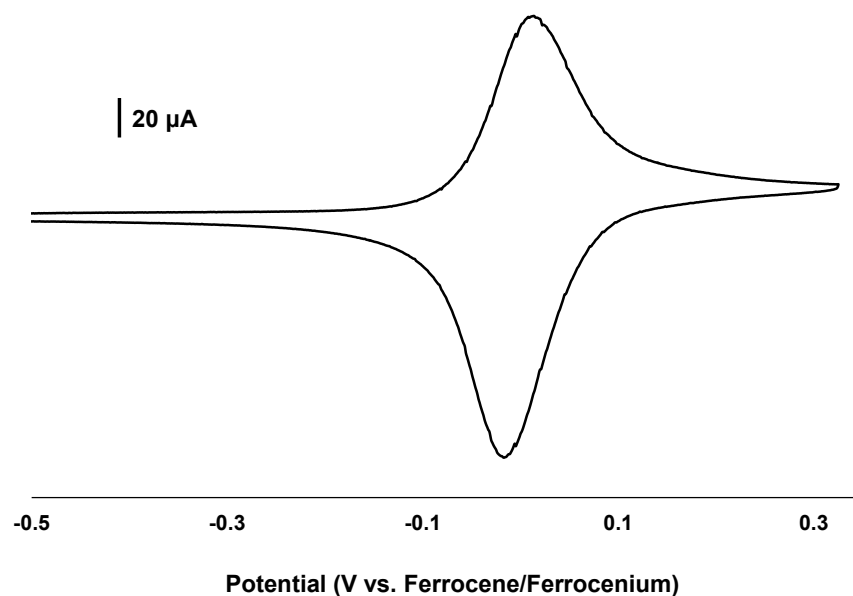


Fig. S30 Cyclic voltammogram of polyelectrolyte **7a** recorded at 250 mV s^{-1} recorded for a 1 mM solution of 2:1 dichloromethane:acetonitrile containing 0.1 M tetrabutylammonium trifluoromethanesulfonate as supporting electrolyte.

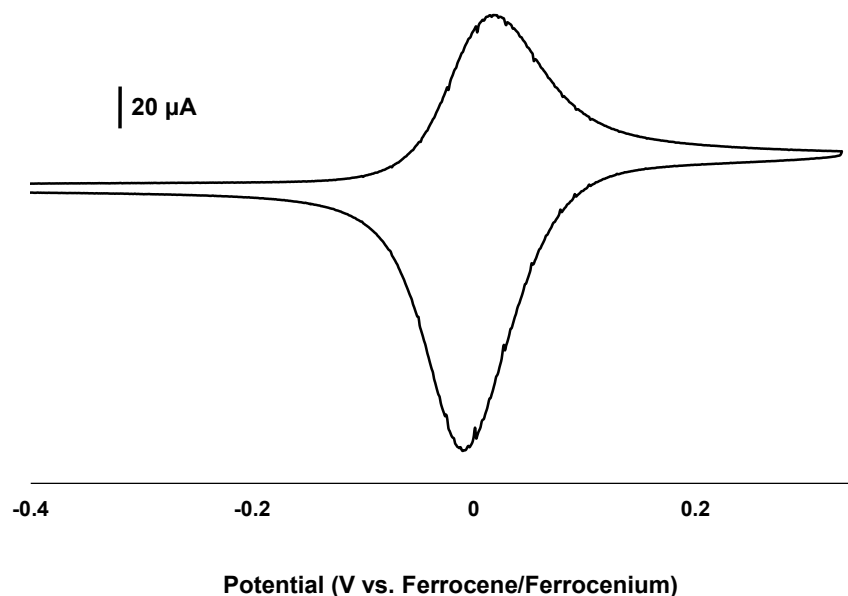


Fig. S31 Cyclic voltammogram of polyelectrolyte **7c** recorded at 250 mV s^{-1} recorded for a 1 mM solution of 2:1 dichloromethane:acetonitrile containing 0.1 M tetrabutylammonium trifluoromethanesulfonate as supporting electrolyte.

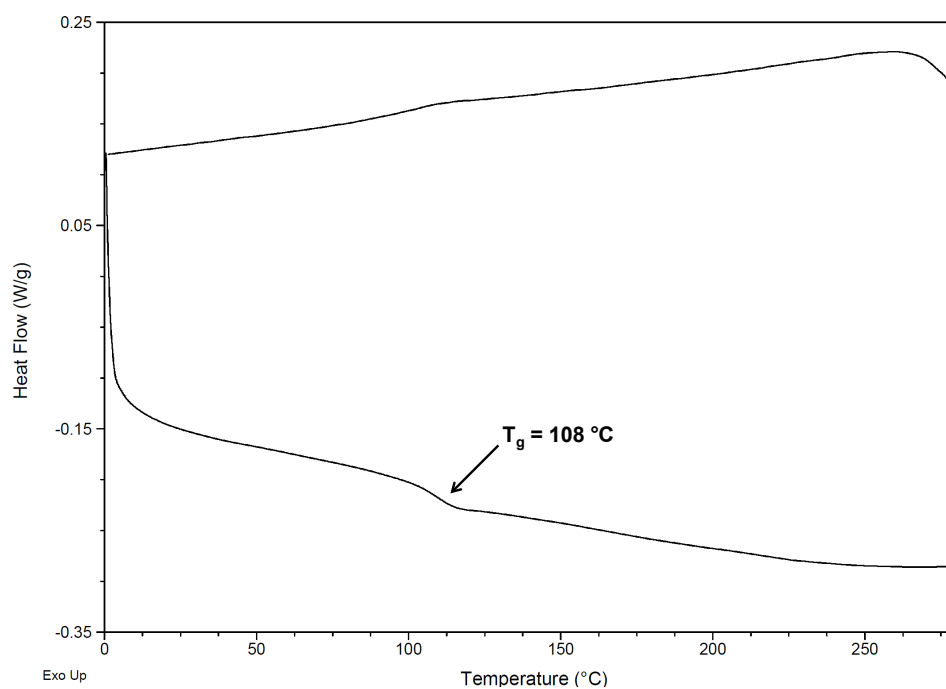


Fig. S32 DSC thermogram of polyelectrolyte **7a**.

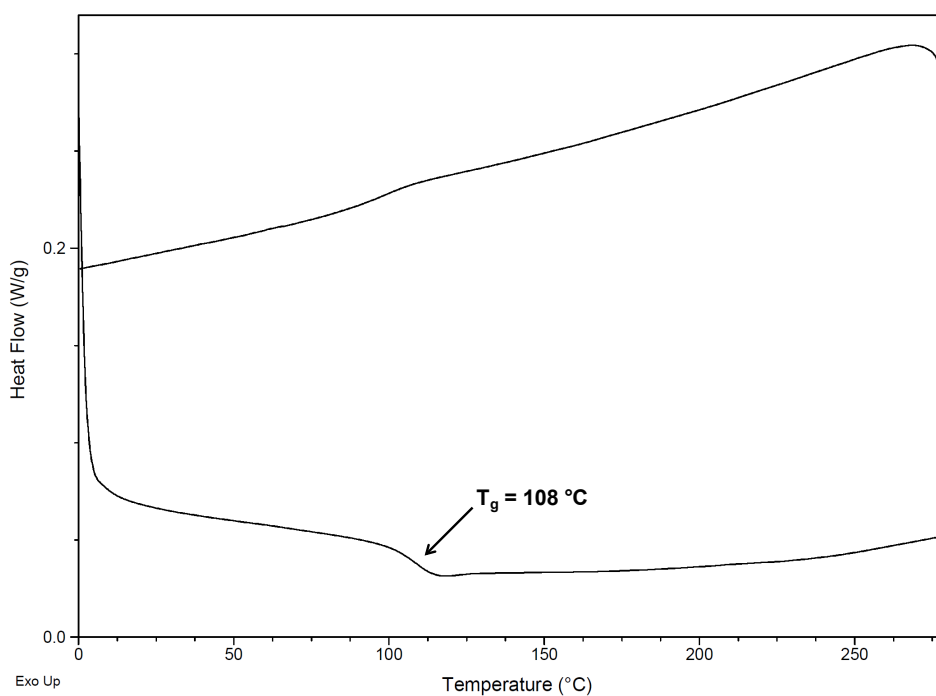


Fig. S33 DSC thermogram of polyelectrolyte **7b**.

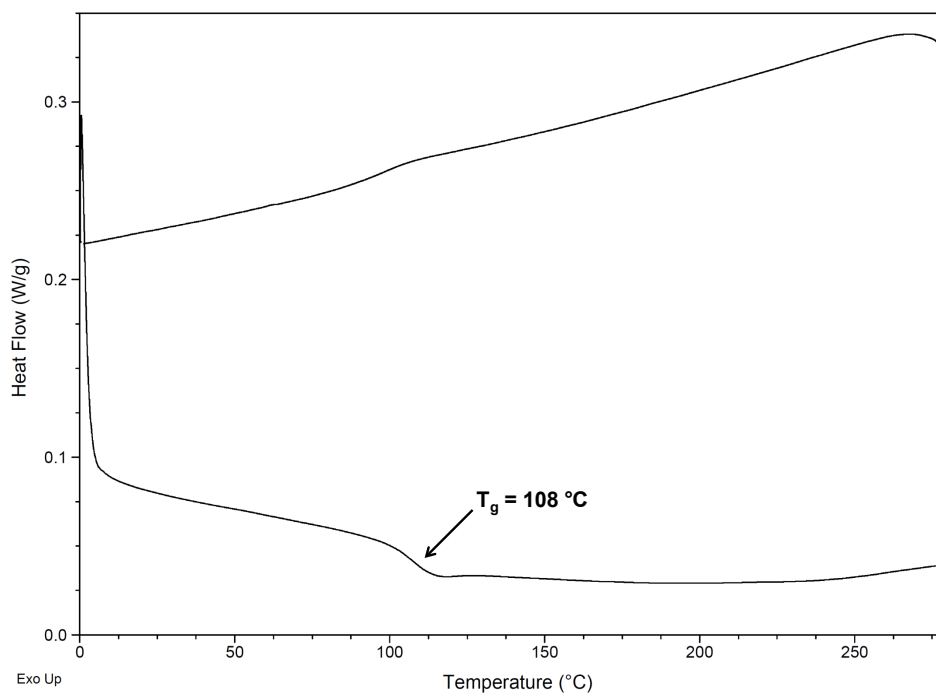


Fig. S34 DSC thermogram of polyelectrolyte **7c**.

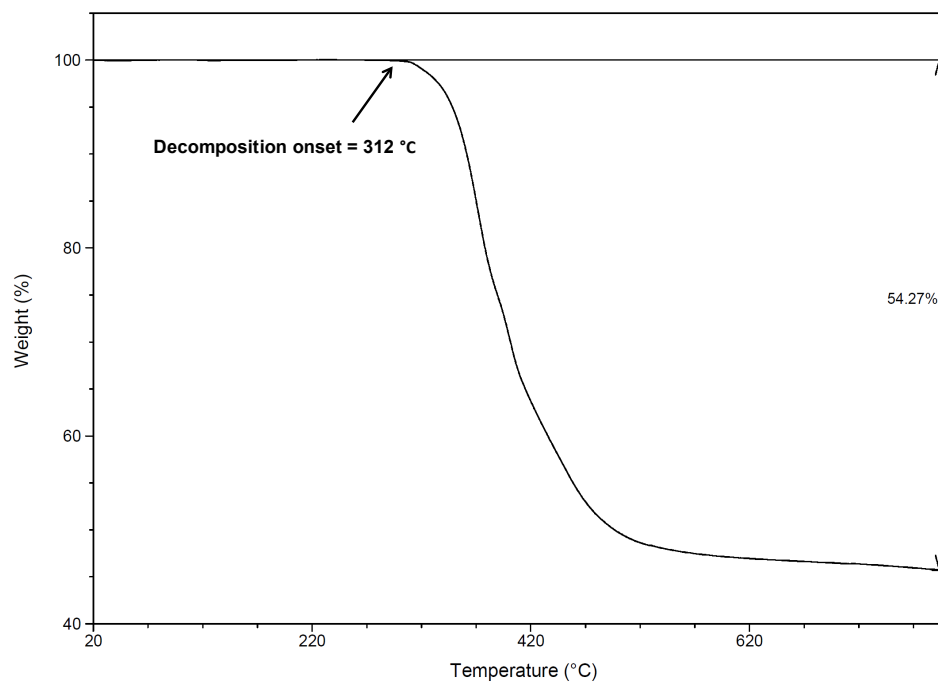


Fig. S35 TGA trace for polyelectrolyte **7a**.

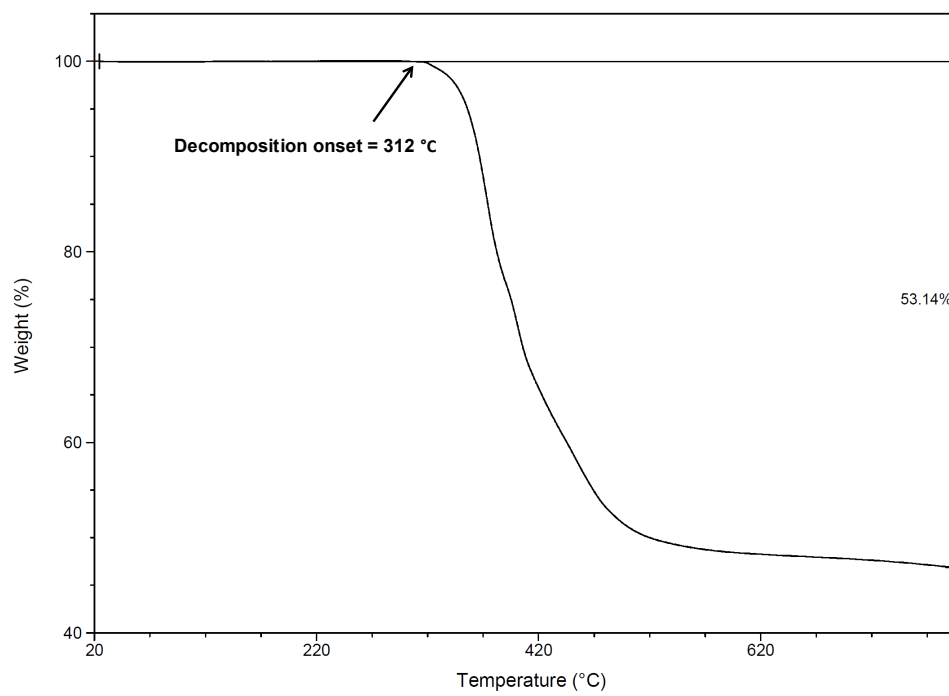


Fig. S36 TGA trace for polyelectrolyte **7c**.

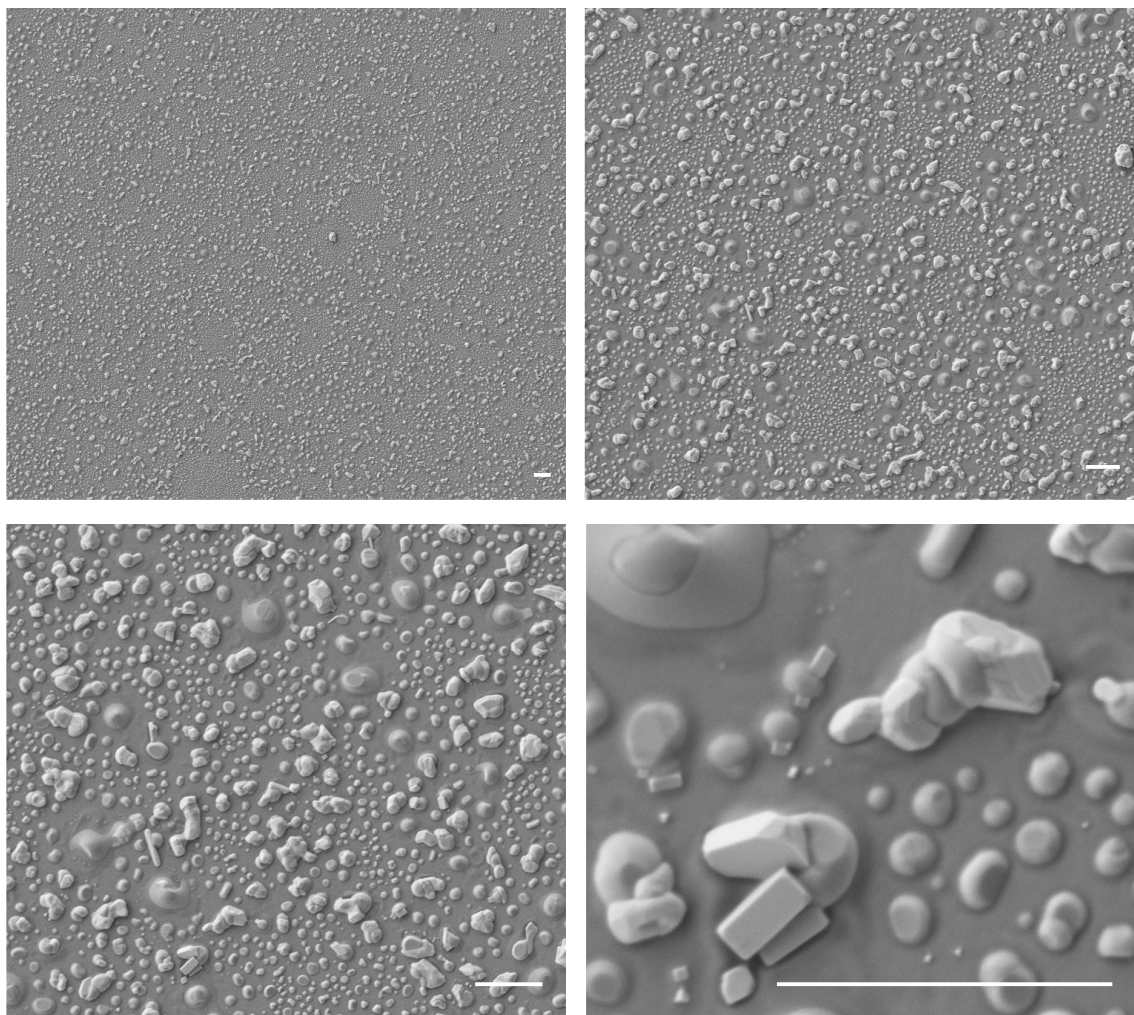


Fig. S37 SEM images of the nanostructures produced by heating a thin film of polyelectrolyte **7b** at 800 °C for 2 h under a flow of N₂ gas. Scale bars = 1 μm.

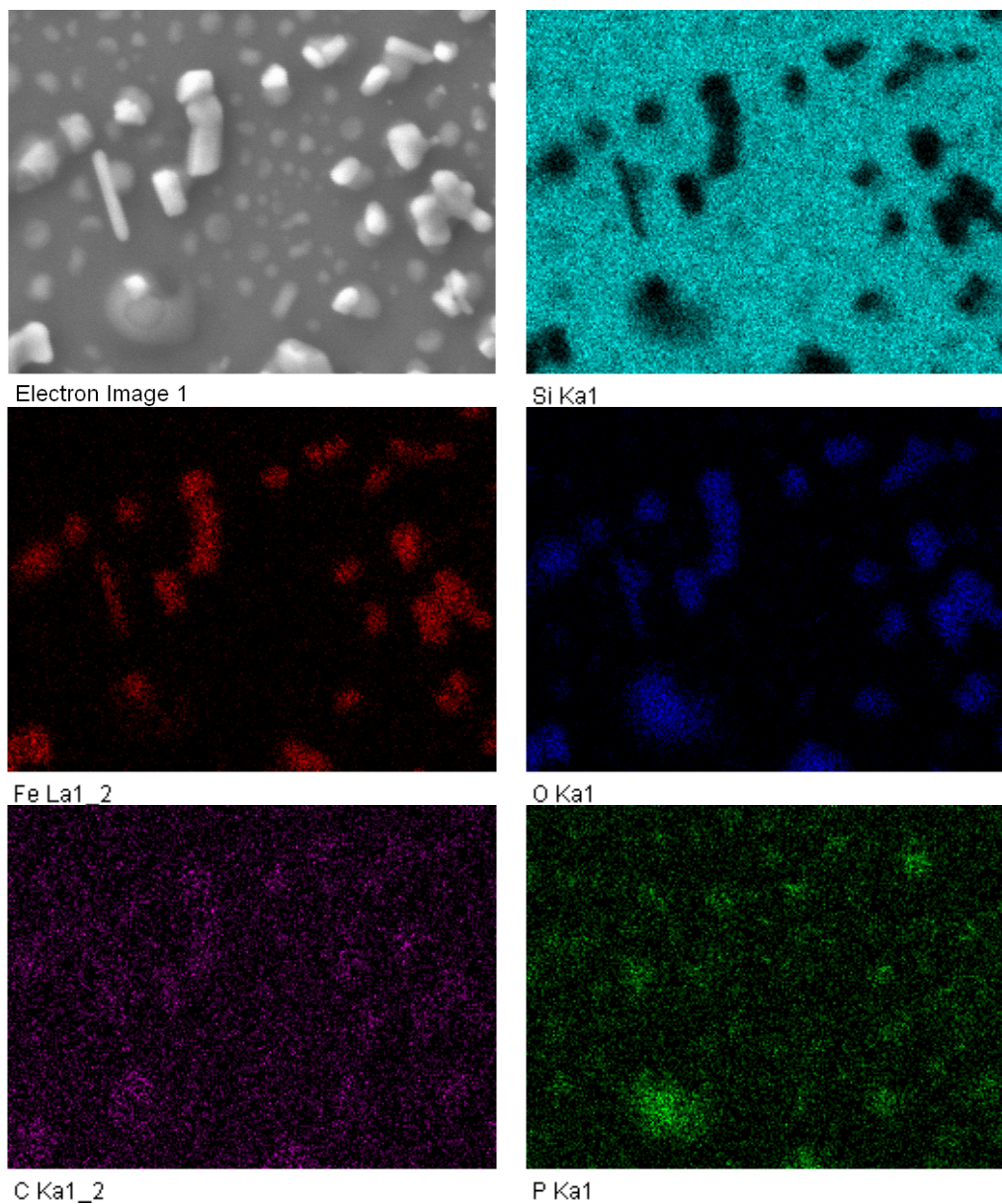


Fig. S38 SEM image and elemental mapping (Si, Fe, O, C, P) for the nanostructured films produced by heating a thin film of polyelectrolyte **7b** at 800 °C for 2 h under a flow of N₂ gas.

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalized)

Number of iterations = 4

Standard :

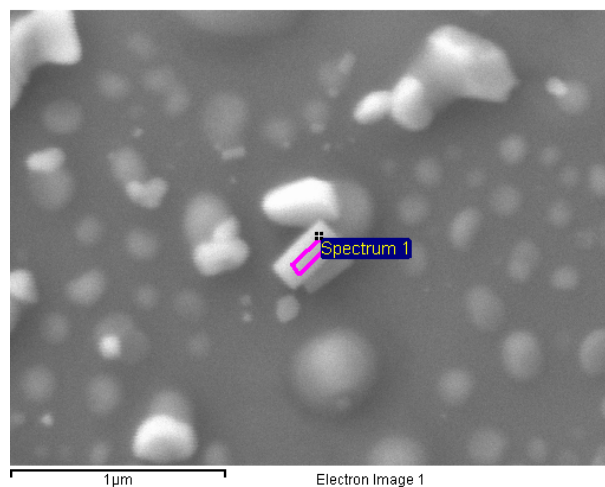
C CaCO₃ 1-Jun-1999 12:00 AM

O SiO₂ 1-Jun-1999 12:00 AM

Si SiO₂ 1-Jun-1999 12:00 AM

P GaP 1-Jun-1999 12:00 AM

Fe Fe 1-Jun-1999 12:00 AM



Element	Weight%	Atomic%
C K	1.74	4.53
O K	20.65	40.23
Si K	21.00	23.31
P K	0.75	0.75
Fe L	55.86	31.18
Totals	100.00	

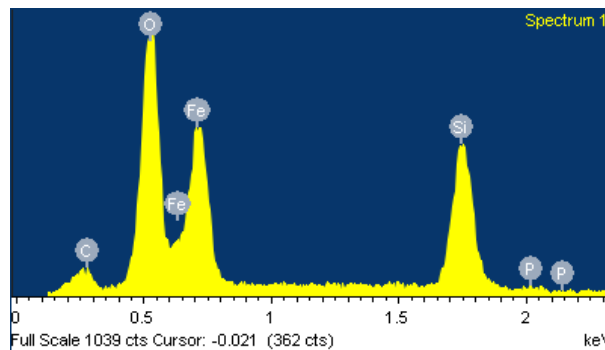


Fig. S39 SEM image and elemental analysis for a crystallite produced by heating a thin film of polyelectrolyte **7b** at 800 °C for 2 h under a flow of N₂ gas. The analyzed area is indicated by the purple box and the ratio of Fe:O is consistent with formation of Fe₃O₄.

References

- 1 (a) R. Sanders and U. T. Mueller-Westerhoff, *J. Organomet. Chem.*, 1996, **512**, 219–224;
(b) M. Gallei, R. Klein and M. Rehahn, *Macromolecules*, 2010, **43**, 1844–1854.
- 2 W. Henderson and S. R. Alley, *J. Organomet. Chem.*, 2002, **656**, 120–128.
- 3 Bruker-AXS, SAINT version 2013.8, 2013, Bruker-AXS, Madison, WI 53711, USA.
- 4 Bruker-AXS, SADABS version 2012.1, 2012, Bruker-AXS, Madison, WI 53711, USA.
- 5 beta version, G. M. Sheldrick, 2014, University of Göttingen.
- 6 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* 1994, **27**, 435–436.
- 7 G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.