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Supporting Information

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Supplementary Information for

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SYNTHETIC AND CHARACTERIZATION METHODS

Materials. The hydroxy-terminated perfluoropolyether (PFPE AL-2, M_w ~ 2000 g/mol, CAS Number: 126066-30-6) was provided by The Chemours Company. Dimethyl 2-hydroxyethylphosphonate was purchased from Acros Organics. Acryloyl chloride was purchased from Merck Schuchardt OHG. 2-(Butylthiocarbonothioylthio)propionic acid (BTPA) was synthesized according to a previously published literature.[1] 2-(Dimethylamino)ethyl acrylate (DMAEA) and oligo(ethylene glycol)methyl ether acrylate (OEGA, M_w = 480 g/mol) were passed through basic alumina columns before use. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized twice from methanol before use. Iron-oleate complex was synthesized using iron chloride and sodium oleate as the reactants and following the same procedure reported previously.[2] Heptafluorobutyric acid (PFBA, 96%, CAS: 375-22-4), perfluoropentanoic acid (PFPeA, 97%, CAS: 2706-90-3) and perfluoroheptanoic acid (PFHpA, 96%, CAS: 375-85-9) were purchased from ThermoFisher Scientific. Undecafluorohexanoic acid (PFHxA, 97%, CAS: 307-24-4) was purchased from FUJIFILM Wako Pure Chemical Corporation. Ammonium perfluoro(2-methyl-3-oxahexanoate) (GenX, 97%, CAS: 62037-80-3) was purchased from Apollo Scientific. Perfluorooctanesulfonic acid (PFOS, CAS: 1763-23-1) was purchased from Synquest Laboratories. Perfluorooctanoic acid (PFOA, 95%, CAS: 335-67-1), perfluorononanoic acid (PFNA, 97%, CAS: 375-95-1), perfluorodecanoic acid (PFDA, 98%, CAS: 335-76-2), nonafluorobutane-1-sulfonic acid (PFBS, 97%, CAS: 375-73-5) and tridecafluorohexane-1-sulfonic acid potassium salt (PFHxS salt, CAS: 3871-99-6) were purchased from Sigma Aldrich. Milli-Q water with a resistivity of 18.2 MΩ·cm was used for preparation of PFAS stock solutions. All other chemicals were purchased from Sigma-Aldrich and used as received.

Synthesis of 2-(Dimethoxyphosphoryl)ethyl Acrylate (PA) Monomer. In a round bottom flask, acryloyl chloride (1.32 g, 14.6 mmol) was added dropwise into a solution of dimethyl (2-hydroxyethyl)phosphonate (1.5 g, 9.73 mmol) and triethylamine (1.97 g, 19.47 mmol) dissolved in anhydrous dichloromethane (DCM, 5 mL) at 0 ℃ with stirring. After complete addition, the solution was reacted at 0 °C for 1 hour and then at room temperature for another 12 hours. The crude mixture was purified by running a silica column using DCM/methanol (19:1, v/v) as the eluent. PA monomer, a pale-yellow liquid, was obtained by evaporating the eluent under high vacuum at room temperature using an oil pump for 3 hours.

Synthesis of BTPA-PFPE Macro-reversible Addition−fragmentation Chain-transfer (RAFT) Agent. The BTPA-PFPE macro-RAFT agent was synthesized by N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride/4-(dimethylamino)pyridine (EDCl/DMAP) coupling reaction. Typically, a solution of EDCl (958.5 mg, 5 mmol) dissolved in 20 mL of anhydrous DCM was dropwise added into a solution of PFPE (5 g, 2.5 mmol), BTPA (1.19 g, 5 mmol) and DMAP (183.26 mg, 1.5 mmol) dissolved in 40 mL of α,α,α-trifluorotoluene (TFT) at 0 °C with stirring. After complete addition, the solution mixture was reacted at room temperature for 48 hours, followed by precipitation into large excess of methanol solution five times for purification. The product, BTPA-PFPE macro—RAFT agent, was obtained by evaporation of the excess solvent under high vacuum at room temperature using an oil pump for overnight.

Synthesis of Poly(PA)$_4$-PFPE. Poly(PA)$_4$-PFPE was synthesized via RAFT polymerization. The PFPE macro-RAFT agent (2 g, 0.901 mmol), PA (0.844 g, 4.056 mmol) and AIBN (29.55 mg, 0.180 mmol) were dissolved in 6 mL of TFT solution in a glass round bottom flask fitted with a magnetic stirring bar. The solution mixture was deoxygenated using argon for 15 mins on an ice bath and then reacted in an oil bath at 70 °C for 11 h. The reaction was stopped by placing the reaction mixture on an ice bath and exposing to air. The solution was concentrated and precipitated into a large excess of cold hexane/diethyl ether (1:1, v/v) mixed solution. After centrifugation, the precipitated polymer was redissolved in tetrahydrofuran (THF) and reprecipitated again into the cold hexane/diethyl ether mixed solution. The precipitation cycle was repeated three times and the product, poly(PA)$_4$-PFPE was obtained by evaporating excess solvent under high vacuum using an oil pump at 40 °C for overnight.

Chain Extension Using DMAEA and OEGA as Monomers to Produce Poly(PA$_4$-*b*-OEGA$_2$-DMAEA$_9$)-PFPE (P2-9). Typically, the above synthesized poly(PA)$_4$-PFPE (0.5 g, 0.159 mmol), DMAEA (0.217 g, 1.515 mmol), OEGA (0.161 g, 0.335 mmol) and AIBN (5.23 mg, 0.032 mmol) were dissolved in a 3 mL solution of TFT/dimethylformamide (DMF) (5:1, v/v) in a glass round-bottom flask with a magnetic stirring bar. Argon was used to deoxygenate the solution mixture for 15 mins on an ice bath, followed by reacting in an oil bath at 70 °C for 14 h. Upon completed reaction, the solution was placed on an ice bath and exposed to air. The solution mixture was concentrated and precipitated into a large excess solution of cold hexane/diethyl ether (4:1, v/v), followed by centrifugation. THF was used to redissolve the polymer and the purification was repeated three times. P2-9, the final product was obtained by evaporating excess solvent under high vacuum using an oil pump at room temperature for overnight.

Synthesis of Poly(PA$_4$-*b*-OEGA$_4$-DMAEA$_6$)-PFPE (P4-6). P4-6 was synthesized via RAFT polymerization. Typically, poly(PA)$_4$-PFPE (0.5 g, 0.159 mmol), DMAEA (0.137 g, 0.957 mmol), OEGA (0.306 g, 0.638 mmol) and AIBN (5.23 mg, 0.032 mmol) were dissolved in a 3 mL solution of TFT/DMF (5:1, v/v) in a glass round-bottom flask with a magnetic stirring bar and sealed. Argon was used to deoxygenate the solution mixture for 15 minutes at 0 °C and reacted at 70 °C for 14 hours. The reaction was stopped by placing the reaction mixture on an ice bath and exposing to air. The polymer was purified by precipitating the solution mixture into a large excess of cold hexane/diethyl ether (4:1, v/v) three times, followed by centrifugation. The clean product, P4-6 was obtained by drying under high vacuum at room temperature using an oil pump for overnight to remove the excess solvent.

Synthesis of Poly(PA$_4$-*b*-OEGA$_6$-DMAEA$_3$)-PFPE (P6-3). P6-3 was synthesized via RAFT polymerization. For a typical polymerization, a solution of TFT/DMF (3 mL, 5:1, v/v) containing poly(PA)$_4$-PFPE (0.5 g, 0.159 mmol), DMAEA (68.5 mg, 0.478 mmol), OEGA (0.459 g, 0.957 mmol) and AIBN (5.23 mg, 0.032 mmol) was sealed in a glass round-bottom flask with a magnetic stirring bar. The solution mixture was deoxygenated using argon at 0 °C for 15 minutes, followed by reacting at 70 °C for 14 hours. The reaction was terminated by placing the round bottom flask on an ice bath and exposing the solution to air. The solution mixture was precipitated into a large excess of cold hexane/diethyl ether (4:1, v/v), followed by centrifugation. The precipitation cycle was repeated 3 times

and the purified product, P6-3, was obtained by evaporating the excess solvent under high vacuum at room temperature using an oil pump for overnight.

Synthesis of Poly(PA_4-*b*-$OEGA_8$)-PFPE (P8-0). P8-0 was synthesized via RAFT polymerization. In a typical experiment, poly$(PA)_4$-PFPE (0.5 g, 0.159 mmol), OEGA (0.589 g, 1.228 mmol) and AIBN (5.23 mg, 0.032 mmol) were dissolved in a solution of TFT and sealed in a glass round-bottom flask with a magnetic stirring bar. The solution mixture was deoxygenated using the argon at 0 °C for 15 minutes and then placed in an oil bath at 70 °C reacting for 14 hours. Upon completed reaction, the round bottom flask was placed on an ice bath and the solution mixture was exposed to air. Purification of the polymer was performed by precipitating the reaction mixture into a large excess of cold hexane/diethyl ether (4:1, v/v) for three times, followed by centrifugation. The product, P8-0 was obtained by evaporating the excess solvent under high vacuum at room temperature using an oil pump for overnight.

Quaternization of P2-9 to Produce P2-9+. 500 mg of P2-9 was dissolved in 5 mL DMF in a 20 mL glass vial with a magnetic stirring bar. Excess iodomethane (0.237 g, 1.672 mmol) was added and the solution was reacted at 50 °C for 24 h in darkness. The polymer was precipitated into a large excess of cold solution of hexane/diethyl ether (1:1, v/v), followed by dialysis against Milli-Q water for 24 h. The purified product, P2-9+, was obtained by freeze-drying. Same procedure was applied on quaternization of P6-3 and P4-6 to produce P6-3+ and P4-6+.

Deprotection of P2-9+. Typically, 450 mg of P2-9+ was dissolved in 5 mL of DCM solution in a 20 mL glass vial with a magnetic stirring bar. The polymer solution was put on an ice bath and deoxygenated using argon for 5 mins, followed by slow addition of 0.106 g (0.692 mmol) of bromotrimethylsilane (TMBS) dissolved in 2 mL of DCM solution. After complete addition, the deoxygenation was kept for another 5 mins and the solution mixture was reacted at room temperature for 24 h. Rotary evaporation was used to remove the solvent and excess TMBS. Methanol (5 mL) was added to dissolve the polymer and the solution was reacted at room temperature for 3 h. Large excess of cold hexane/diethyl ether (1:1, v/v) was used for precipitation of the deprotected polymer. The product was dried under high vacuum using an oil pump at room temperature for overnight. Same deprotection procedure was used for P8-0, P6-3+ and P4-6+.

Synthesis of Oleic Acid Coated Magnetic Iron Oxide Nanoparticles (OA@IONPs). The IONPs used in this study was prepared by thermal decomposition method using a heating mantle (MS-DMS631). In a typical experiment, 9 g (10 mmol) of the iron-oleate complex and 1.41 g of oleic acid (5 mmol) were dissolved in 50 g of trioctylamine in a three-neck round-bottom flask at room temperature with a magnetic stirring bar. Nitrogen was used to purge the solution mixture throughout the whole reaction process by using two needles, with the inert gas going in from the long needle and purging out from the short needle. A condenser tube was used to condense the vaporized solvent during the reaction. The solution mixture was heated to 90 °C and the temperature was kept for 1 h to remove any of the moisture in the solution. The solution mixture was heated to 340 °C and maintained at the temperature for 2 h, followed by cooling down to the room temperature and precipitating into ethanol three times for purification. The IONPs were dispersed in chloroform and store at 4 °C for further use.

Preparation of P2-9+ Grafted IONPs (P2-9@IONPs). P2-9+@IONPs was produced via ligand exchange reaction. Typically, 200 mg of the deprotected P2-9+ polymer was dissolved in 2.5 mL of the chloroform solution in a 20 mL glass vial fitted with a magnetic stirring bar. 2.5 mL of 10 mg/mL of the above solution of IONPs dispersed in chloroform was added to the deprotected polymer solution. The solution mixture was reacted at 50 °C for 24 h and precipitated into large excess of hexane. Excess/ungrafted polymer was removed by washing the polymer-IONPs crude mixture three times using Milli-Q water and recovering the polymer grafted IONPs via magnetic separation. The purified P2-9+@IONPs were obtained by freeze drying. The preparation procedure for P8-0 grafted IONPs (P8-0@IONPs), P6-3+ grafted IONPs (P6-3+@IONPs) and P4-6+ grafted IONPs (P4-6+@IONPs) was the same as the procedure for preparation of P2-9+@IONPs.

Equilibrium Sorption Studies. Four different polymer grafted IONPs, P8-0@IONPs, P6-3+@IONPs, P4-6+@IONPs and P2-9+@IONPs as prepared above, along with two commercially available sorbents, activated carbon and anion exchange resin (Amberlite IRA-410), were used for equilibrium studies. 11 different PFAS, including PFBA, PFPeA, PFHxA, GenX, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS and PFOS were spiked into Milli-Q water with presence of 200 mg/L (ppm) of sodium chloride and 20 ppm of humic acid (HA), to create an initial concentration of 100 µg/L (ppb) for each of the PFAS. For each sorbent, 5 mL of the above prepared PFAS stock solution was added into a polypropylene vial with 2.5 mg (excluding weight of IONPs for polymer grafted IONPs, based on TGA results) of the polymer to create a final concentration of polymer of 0.5 mg/mL. The total weight of four polymer grafted IONPs were 2.91 mg for P8-0@IONPs, 3.42 mg for P6-3+@IONPs, 3.57 mg for P4-6+@IONPs and 3.38 mg for P2-9@IONPs. Each solution mixture was shaken on a shaker for 24 h. A large magnet was attached to the polypropylene vials of four magnetic polymer grafted IONPs for 10 mins for sorbent recovery. For each sorption experiment, 1.5 mL of the supernatant was collected and centrifuged for 15 mins at 12000 revolution per min (rpm) to remove undissolved HA. The two commercially available sorbents were directly spun down by centrifugation under the same conditions, followed by collection of the supernatant. The collected liquids were taken for measurement of residue PFAS concentrations using liquid chromatography with tandem mass spectrometry (LC-MS/MS). Control experiments of measuring the concentration of initial PFAS stock solution were also conducted. The experiments were repeated three times.

Stability Test of Magnetic Polymer Sorbents in Aqueous Solution. Typically, 400 µL of residue liquid from the above Equilibrium Sorption Studies after treatment by P2-9+@IONPs and magnetic separation was collected, followed by ^{19}F NMR spectroscopy analysis using a coaxial insert filled with D_2O for locking in NMR.

Sorption Kinetics of GenX. Sorption kinetics of GenX at initial concentration of 100 ppb was studied using P2-9+@IONPs as the sorbent. In a polypropylene bottle, 3.38 mg of P2-9+@IONPs (2.5 mg of P2-9+) was dispersed in 24.375 mL of Milli-Q water on a shaker for 3 h, followed by addition of 0.625 mL of 4000 ppb of GenX solution in Milli-Q water. The final concentration of the polymer was 0.1 mg/mL and the concentration of GenX was 100 ppb. At each predetermined time of 0.5 min, 1 min, 3 min, 5 min, 10 min, 30 min, 1 h, 2 h, 4 h and 24 h, 2 mL of the solution mixture was collected and directly

centrifuged at 12000 ppm for 15 mins. For each sample, 1.5 mL of the supernatant was collected for LC-MS/MS analysis. Control experiments without presence of P2-9+@IONPs were also performed under identical conditions. The experiments were repeated three times.

Sorption Isotherms of GenX. The sorption isotherm of GenX was studied using P2-9+@IONPs as the sorbent. A series concentrations of GenX stock solutions, with the initial concentrations of 0.2 ppm, 1 ppm, 5 ppm, 10 ppm, 20 ppm, 40 ppm and 100 ppm were prepared in Milli-Q water. In a polypropylene vial, 16 mL of Milli-Q water was added to disperse 4.32 mg (3.2 mg of P2-9+ polymer) of P2-9+@IONPs on a shaker for 3 h. Aliquots of 2 mL of the dispersed P2-9+@IONPs solution was added to mix with another 2 mL of the prepared GenX stock solutions. The final concentration of the polymer was 0.1 mg/mL for each solution and the concentrations of the GenX solutions were 0.1 ppm, 0.5 ppm, 2.5 ppm, 5 ppm, 10 ppm, 20 ppm and 50 ppm respectively. The solution mixtures were placed on a shaker for 24 h, followed by magnetic separation for 10 mins. For each sample, 1.5 mL of the supernatant was collected for LC-MS/MS analysis. Serial dilutions were conducted to dilute all of the samples to a final concentration of GenX to 50 ppb, with 0.1 ppm diluted two times, 0.5 ppm diluted ten times, 2.5 ppm diluted 50 times, 5 ppm diluted 100 times, 10 ppm diluted 200 times, 20 ppm diluted 400 times and 50 ppm diluted 1000 times. Control experiments without addition of P2-9+@IONPs were conducted under identical conditions. The experiments were repeated three times.

Regeneration Ability of P2-9+@IONPs. Methanolic ammonium acetate (400 mM) solution was used for desorption of GenX from the sorbent. The regeneration of P2-9+@IONPs was tested for four cycles. In a typical cycle, 1.5 mL of 10 ppm of GenX solution dissolved in Milli-Q water was directly added into an Eppendorf tube (polypropylene, 1.5 mL maximum capacity) with 2.02 mg (1.5 mg of P2-9+ polymer) of P2-9+@IONPs. The solution mixture was shaken on a shaker for 10 mins and then centrifuged at 12000 rpm for 15 mins to fully recover the sorbent at the bottom of the Eppendorf tube. 1 mL of the supernatant was collected, diluted ten times using Milli-Q water for LC-MS/MS analysis. Rest of 0.5 mL of the residue liquid was thoroughly removed using a pipette and 1.5 mL of the above prepared methanolic ammonium acetate solution was added to redisperse the sorbent on the shaker for 10 mins, followed by 5 mins of centrifugation at 12000 rpm. 1 mL of the supernatant of methanolic ammonium solution was collected, diluted 100 times using Milli-Q water and taken for LC-MS/MS analysis. The residue 0.5 mL of methanolic ammonium acetate solution was carefully removed again using a pipette. The cycle was repeated four times and the experiment was conducted in triplicates. The initial GenX stock solution was also collected, centrifuged under identical conditions and diluted 100 times using Milli-Q water for LC-MS/MS analysis.

Multiple PFAS Removal in Ground Water Matrices. The experiments were conducted using 2 different ground wastewater (GWW) matrices, namely 1) GWW1 and 2) GWW2. The sample solution GWW1 was extracted from a shallow freshwater unconfined aquifer. The groundwater well is situated at a conventional activated sludge wastewater treatment plant that was constructed in the late 1970s and treats approximately 20 mL/day wastewater from a predominately residential catchment. The other ground water sample GWW2 was taken from an effluent lagoon of a conventional activated sludge wastewater treatment plant (100,000 population equivalent) that receives domestic wastewater in

Australia (97%). 11 different PFAS, as has been described above in the section of Equilibrium Sorption Studies, were respectively spiked into each of the above two ground water solutions and created an initial concentration of 1 ppb for each of the PFAS. 30 mL of each type of the above prepared ground water solution was individually mixed with 20.27 mg of P2-9+@IONPs (15 mg of P2-9+ polymer) in a polypropylene vial. After shaking for predetermined time of 30 mins and 2 h on a shaker, 14 mL of each of the solution mixture was collected and the sorbent was recovered via magnetic separation for 10 mins. Solid-phase extraction (SPE) was performed to concentrate the solution by weak anion exchange based on US Environmental Protection Agency (EPA) methods 537.1 and 533, followed by LC-MS/MS analysis.

Characterization Methods. *Nuclear Magnetic Resonance (NMR).* All NMR experiments were conducted on a Bruker AVANCE 400 MHz (9.4 T) spectrometer at 25 °C. ^{1}H NMR spectra of the polymer solutions were acquired in either $CDCl_3$ or DMSO-d_6: a 90° pulse width of 14 μs, relaxation delay of 1 s, acquisition time of 4.1 s, and 32 scans were used in all measurements. ^{19}F NMR spectra were acquired using $CDCl_3$, DMSO-d_6 or H_2O as the solvent. Spectra were measured under the following conditions: 90° pulse width 15 μs, relaxation delay 2 s, acquisition time 0.73 s, and 128 (in $CDCl_3$ or DMSO-d_6) or 400 (in H_2O) scans. A coaxial insert filled with D_2O was used for the measurement of sample dissolved in H_2O. ^{31}P spectra were acquired in $CDCl_3$: 90° pulse width 14 μs, relaxation delay of 2 s, acquisition time of 0.4 s, and 2048 scans.

Size Exclusion Chromatography (SEC). Molecular weights and molecular weight distributions of the polymers were measured by SEC using a Polymer Laboratories GPC50 Plus equipped with a differential refractive index detector. HPLC grade *N,N*-dimethylacetamide (DMAc) containing 0.03 wt% LiCl was used as the mobile phase at a flow rate of 1 mL/min. InfinityLab EasiVial polystyrene standards were used for the column calibration. Two PLGel Mixed B (7.8 × 300 mm^2) columns connected in series were held at a constant temperature of 50 °C for separations. Samples were prepared in DMAc + 0.03 wt% LiCl at a concentration of 5 mg/mL and passed through 0.45 μm PTFE filters before measurement.

Dynamic Light Scattering (DLS) Size Measurement. The hydrodynamic diameters of the polymers were measured using BRAND semi-microcuvettes made of polystyrene on a Nanoseries Zetasizer (Malvern, UK) instrument with a 2 mW He−Ne laser operating at a wavelength of 633 nm. The scattering angle was 173°. The number of runs per measurement was set as automatic and the number of measurements for each sample was 3.

Zeta Potential (ζ) Measurement. The ζ was measured on the Nanoseries Zetasizer (Malvern, UK) instrument using a DTS1070 folded capillary zeta cell. For each test, 800 μL of the sample solution was used for the measurement. The number of runs per measurement ranged from 20 to 50. Four repeated measurements were conducted in each test.

Transmission Electron Microscopy (TEM). The morphology of either OA@IONPs or polymer grafted IONPs were observed by TEM using a Hitachi HT7700 (Hitachi Ltd., Tokyo, Japan) operated at 100 kV.

Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Thermo Scientific Nicolet 5700 FTIR spectrometer equipped with a smart orbit diamond ATR unit. The wavenumber range was 4000-525 cm^{-1} and the resolution was 4 cm^{-1}. The number of scans was set as 64.

Thermogravimetric analysis (TGA). Weight percentage of either oleic acid from OA@IONPs or polymer from polymer grafted IONPs were determined using a STARe thermogravimetric analyzer (Mettler-Toledo, LLC, Columbus, OH). Samples were heated from 30 to 600 °C at a rate of 10 °C min^{-1}.

Liquid chromatography with tandem mass spectrometry (LC-MS/MS). The samples were analysed in Shimadzu Nexera LC-40 coupled to a SCIEX Triple Quad 7500 system. Before analysing, all the samples are spiked with mass labelled internal standards at final concentration of 4 ng/mL. Chromatographic separation was achieved at 50 °C on a Phenomenex Kinetex EVO C18 2.6 µm, 100 x 2.1 m column (Part number 00D-4725-AN) equipped with a guard cartridge (Part number AJ0-9298) using gradient elution of mobile phase A (1% methanol/ 8mM ammonium acetate in water) and mobile phase B (95% methanol/ 8mM ammonium acetate in water). The flow rate was set at 0.4 mL/min with an injection volume of 5 µL. To mitigate interference from PFASs contamination in the UHPLC solvents and instrument system, a delay column Kinetex EVO C18, 5 µm, 30 x 2.1 mm) was installed between the solvent mixer and autosampler. The mass spectrometer was operated in multiple reaction monitoring (MRM) mode in negative ion mode and details of the MRM used for both analytes and internal standards are presented in **Table S3**. The Optiflow ion source with an electrospray ionisation was used. The source and MS parameters were as follows: source temperature = 450 °C, curtain gas = 42 psi, ion source gas 1 = 50 psi, ion source gas 2 = 70 psi, spray voltage = 1500 V, CAD gas = 9.

The removal efficiency was calculated as RE (%) = $[(C_0 - Cs)/C_0] \times 100\%$, where C_0 and Cs are the concentration of PFAS before and after treatment by sorbents, respectively.

Limits of detection (LODs) of PFAS by direction injection were: 0.01 ppb for PFBA, PFBS, PFHpA, and PFOS, 0.5 ppb for GenX, 0.05 ppb for PFPeA, PFHxA, PFOA, PFNA, PFDA, and PFHxS. The method of direction injection was applied for the following experiments as described above: Equilibrium Sorption Studies, Sorption Kinetics of GenX, Sorption Isotherm of GenX and Regeneration Ability of P2-9+@IONPs. For PFAS concentrations below the LODs after treatment by sorbents, LODs were used for calculations of removal efficiency values of PFAS.

Solid-phase extraction (SPE) was performed to concentrate the PFAS-containing ground wastewater after treatment by P2-9+@IONPs based on USEPA 537.1 and 533 prior to LC-MS/MS analysis. Quantifiable signals were observed for all of the 11 PFAS in the solutions after being concentrated.

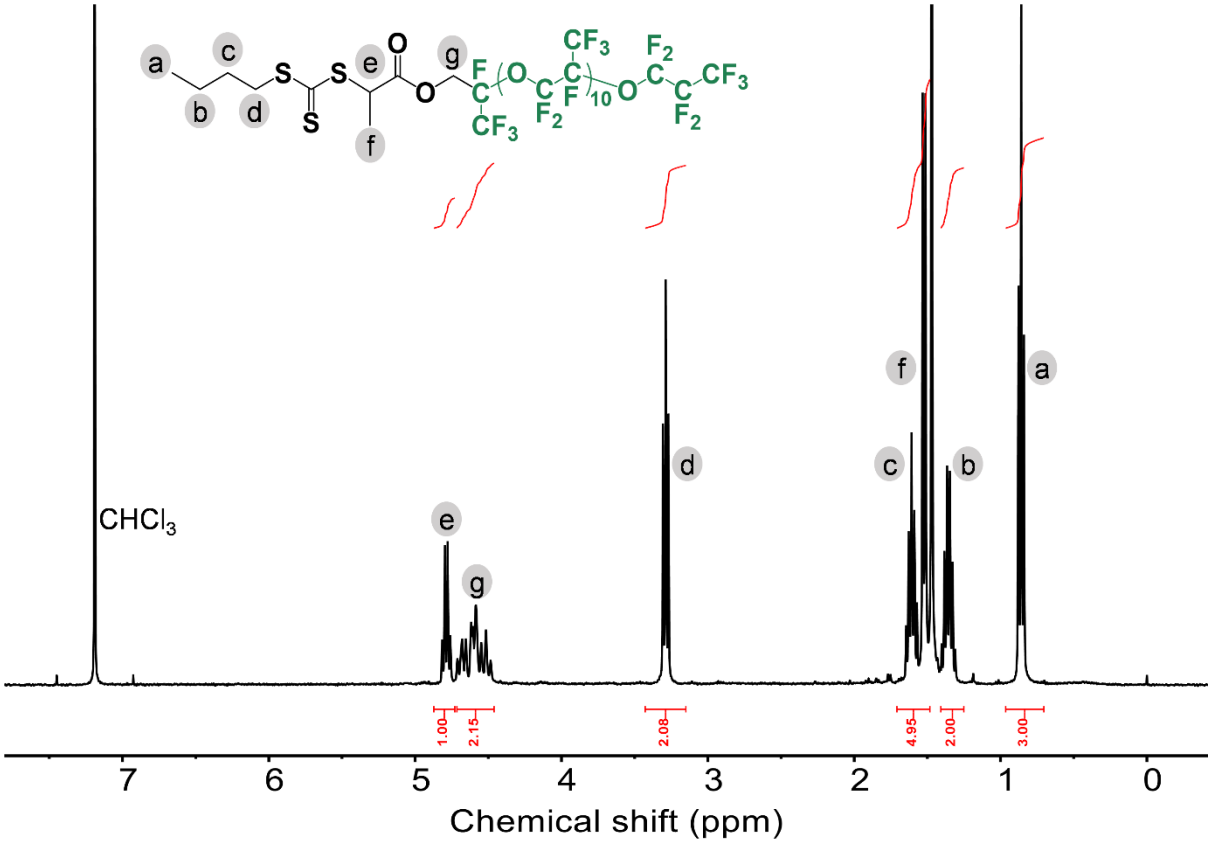


Figure S1. ^{1}H NMR spectrum of PFPE macro-RAFT agent in $CDCl_3$.

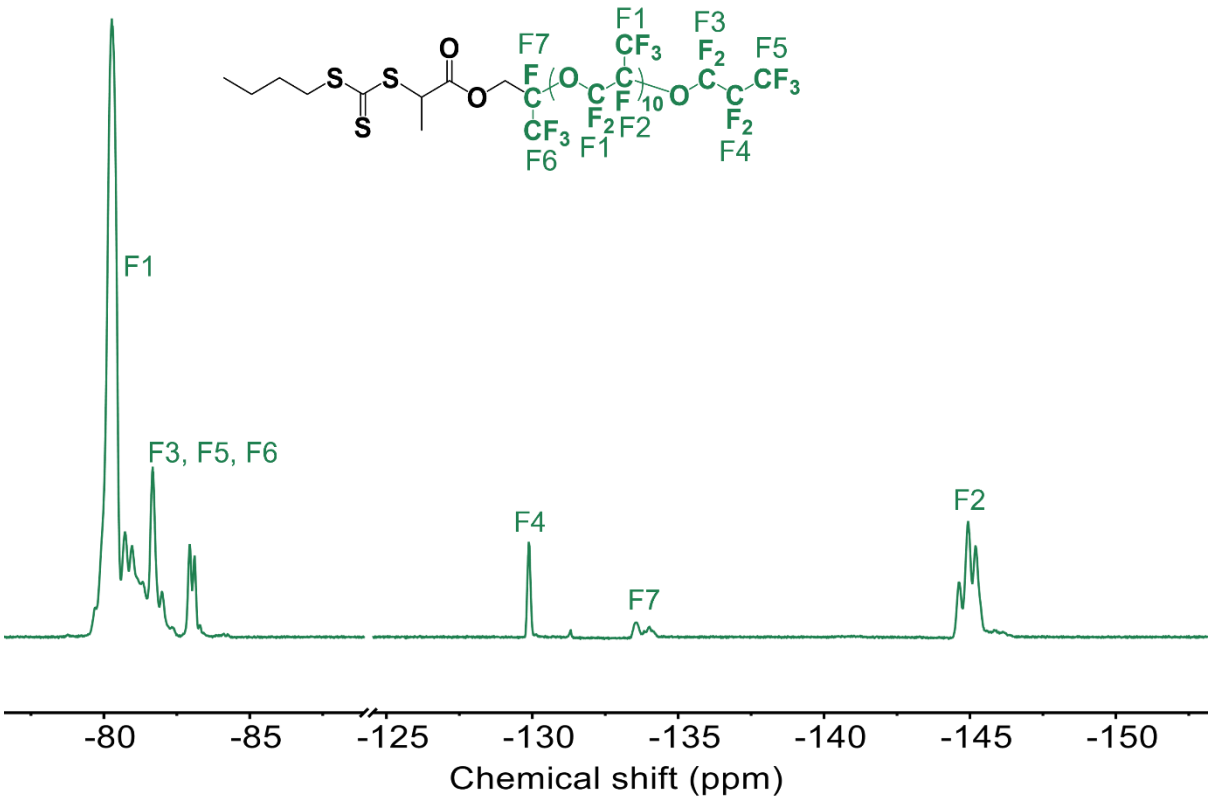


Figure S2. ^{19}F NMR spectrum of PFPE macro-RAFT agent in $CDCl_3$.

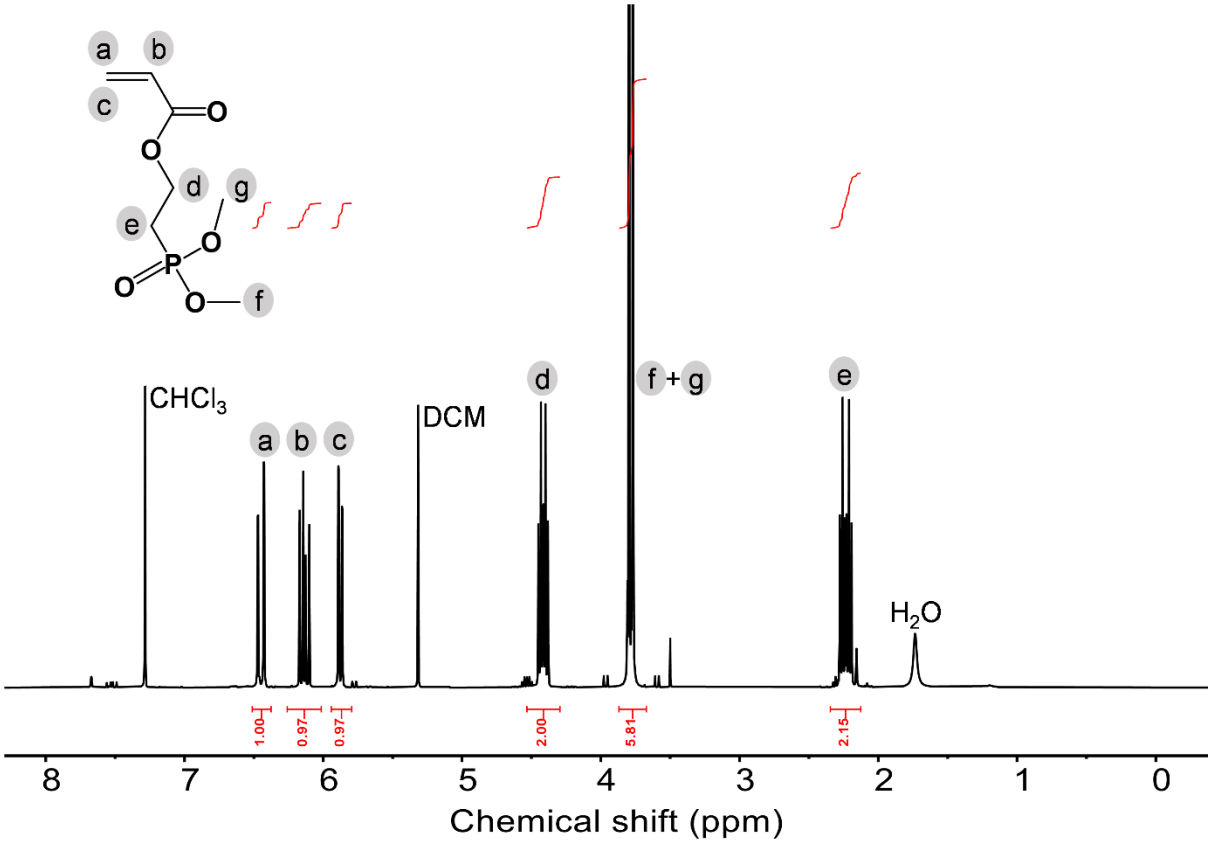


Figure S3. ^{1}H NMR spectrum of PA monomer in $CDCl_3$.

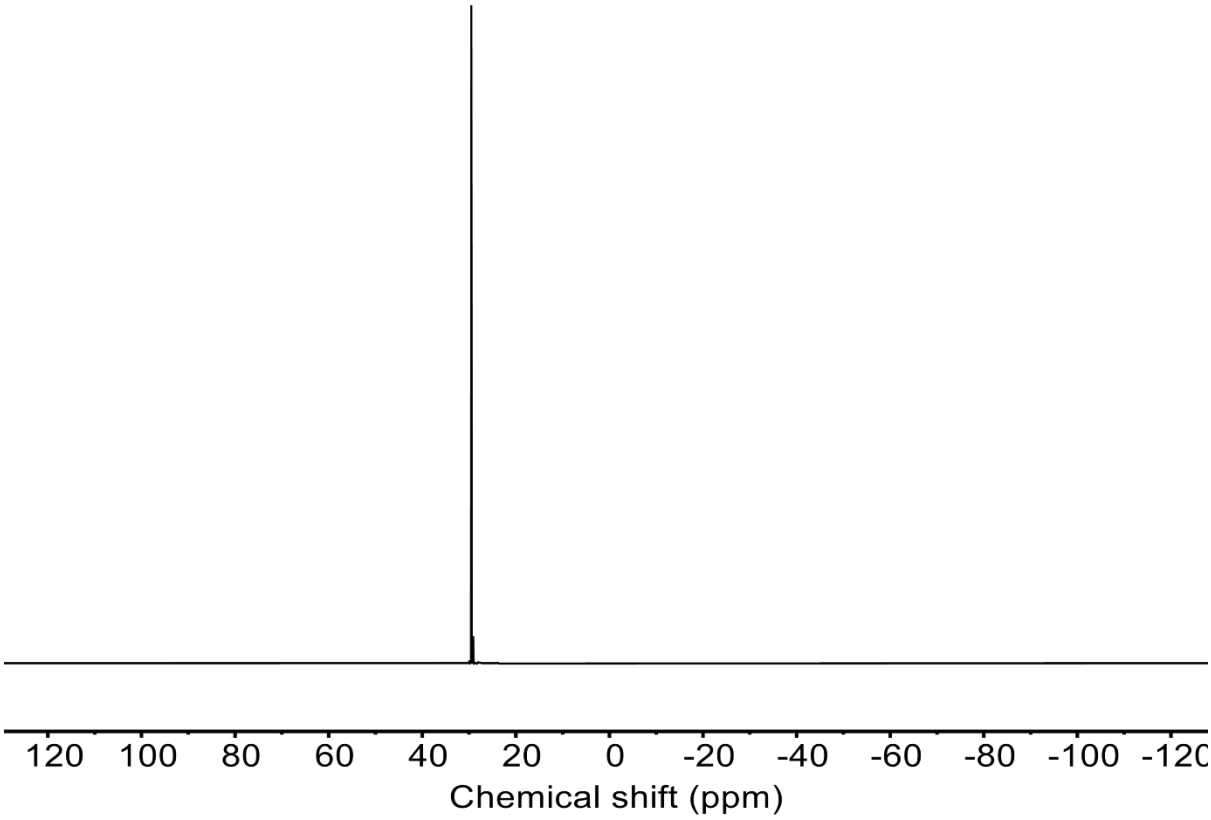


Figure S4. ^{31}P NMR spectrum of PA monomer in $CDCl_3$

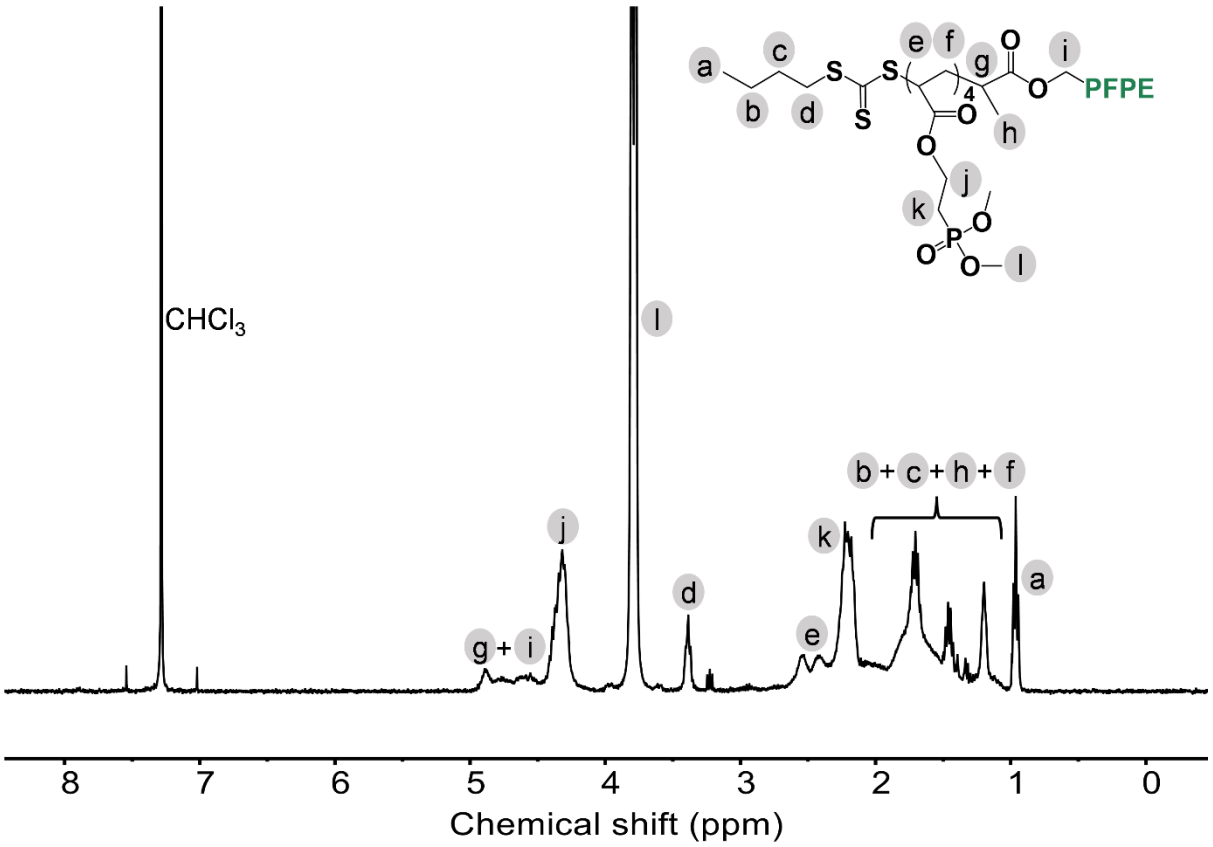


Figure S5. ^{1}H NMR spectrum of poly$(PA)_4$-PFPE in $CDCl_3$.

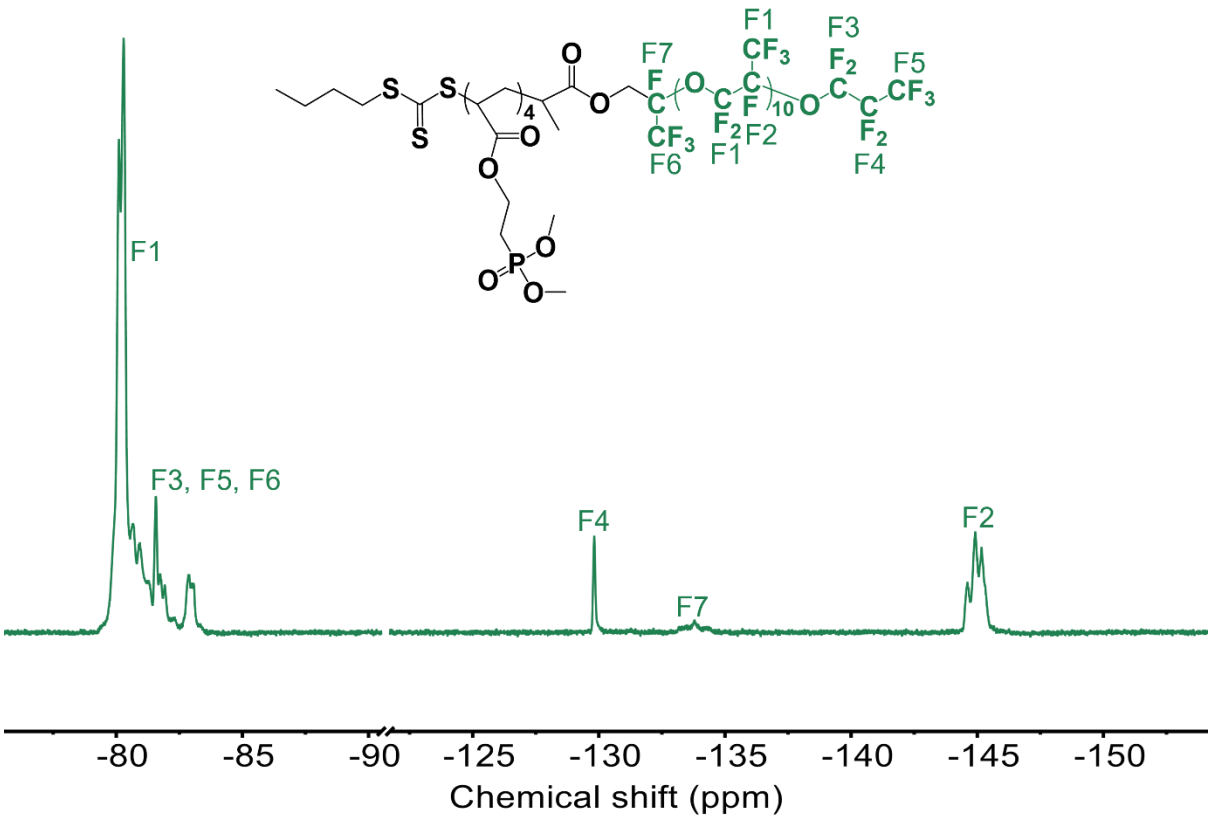


Figure S6. ^{19}F NMR spectrum of poly(PA)$_4$-PFPE in $CDCl_3$.

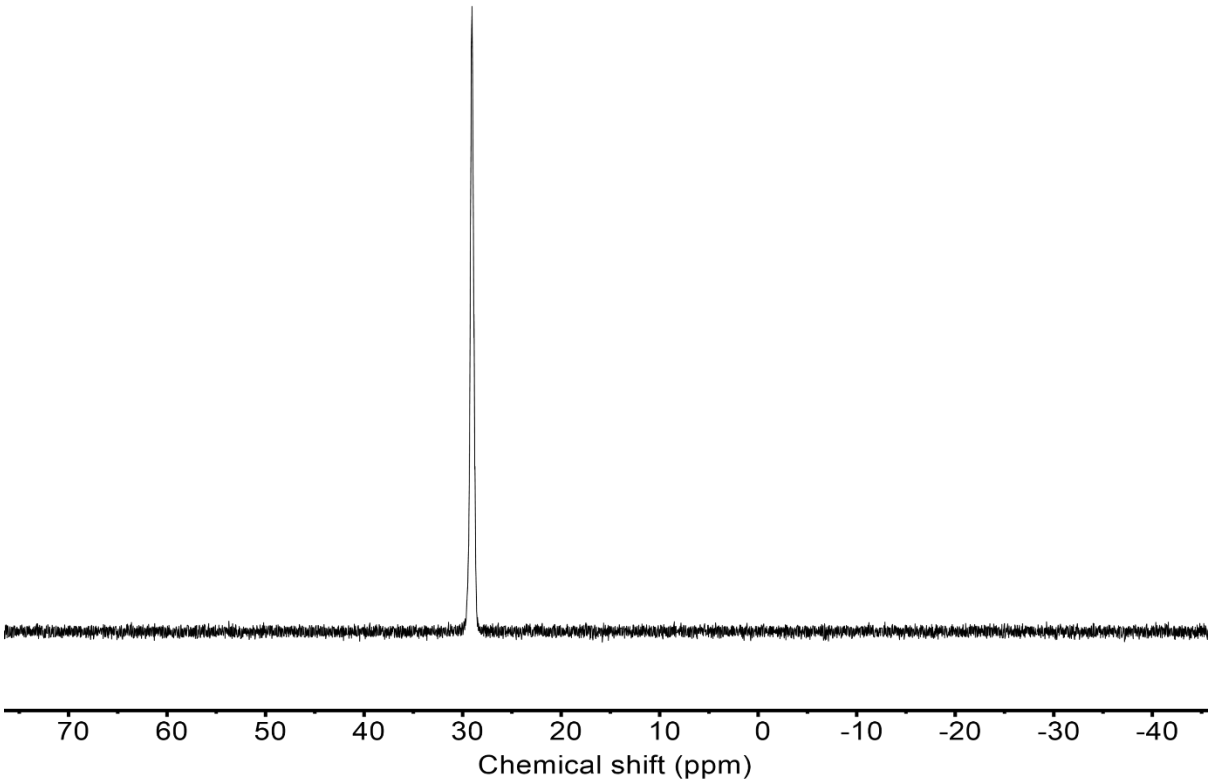


Figure S7. ^{31}P NMR spectrum of poly$(PA)_4$-PFPE in $CDCl_3$.

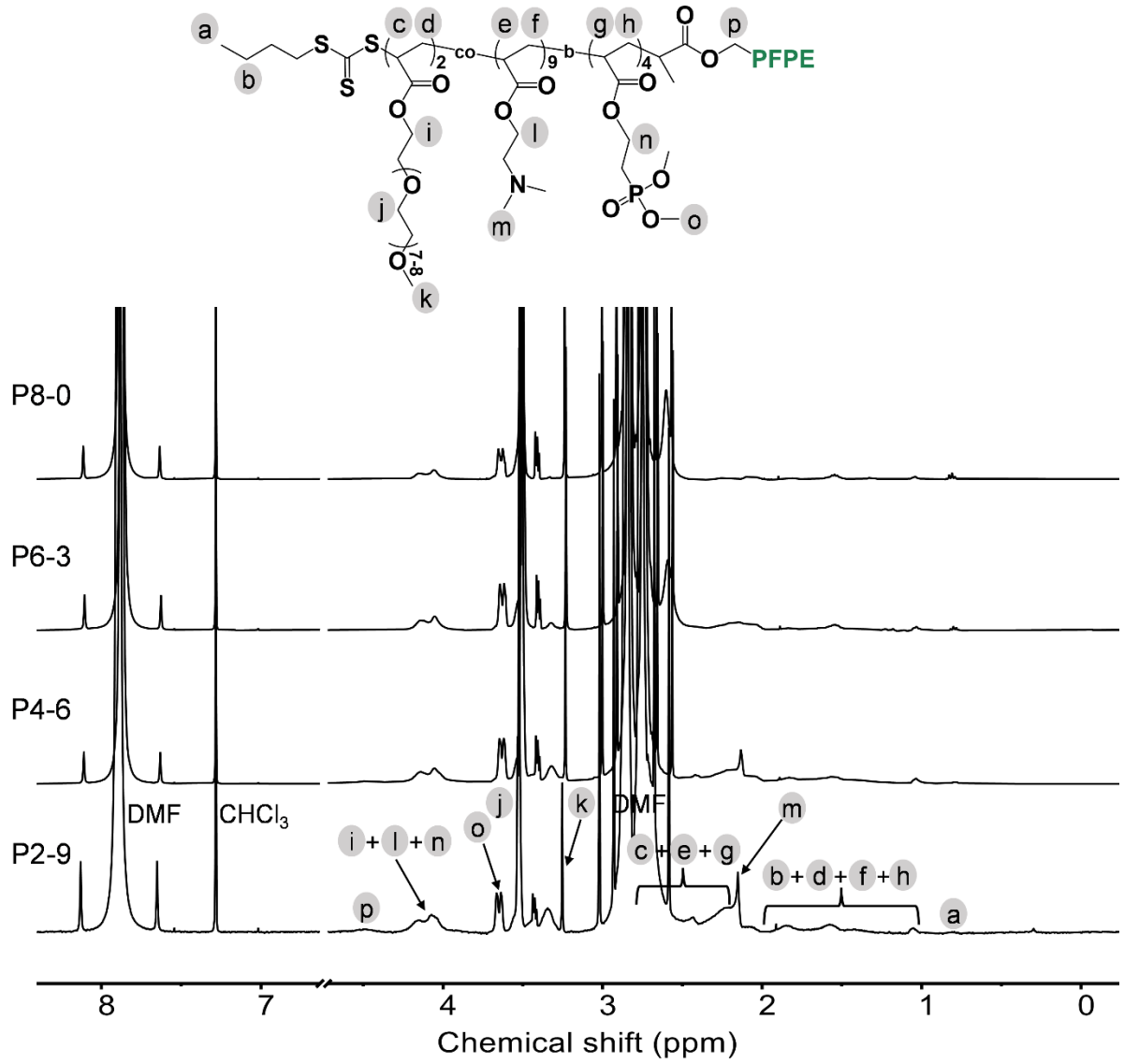


Figure S8. ^{1}H NMR spectra of four polymers before quaternization in $CDCl_3$/DMF (9:1, v/v).

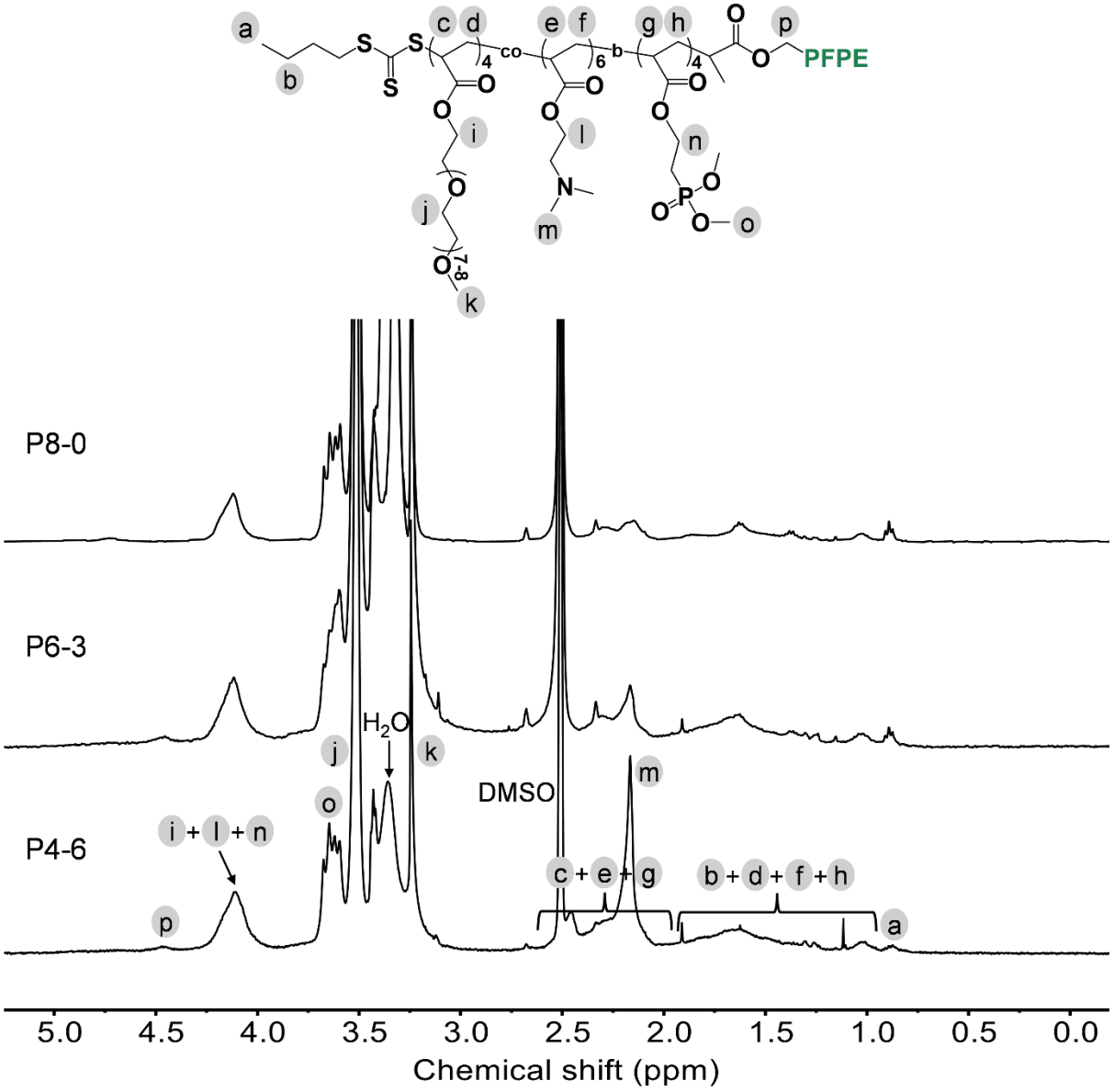


Figure S9. ^{1}H NMR spectra of P8-0, P6-3 and P4-6 polymers before quaternization in DMSO-d_6.

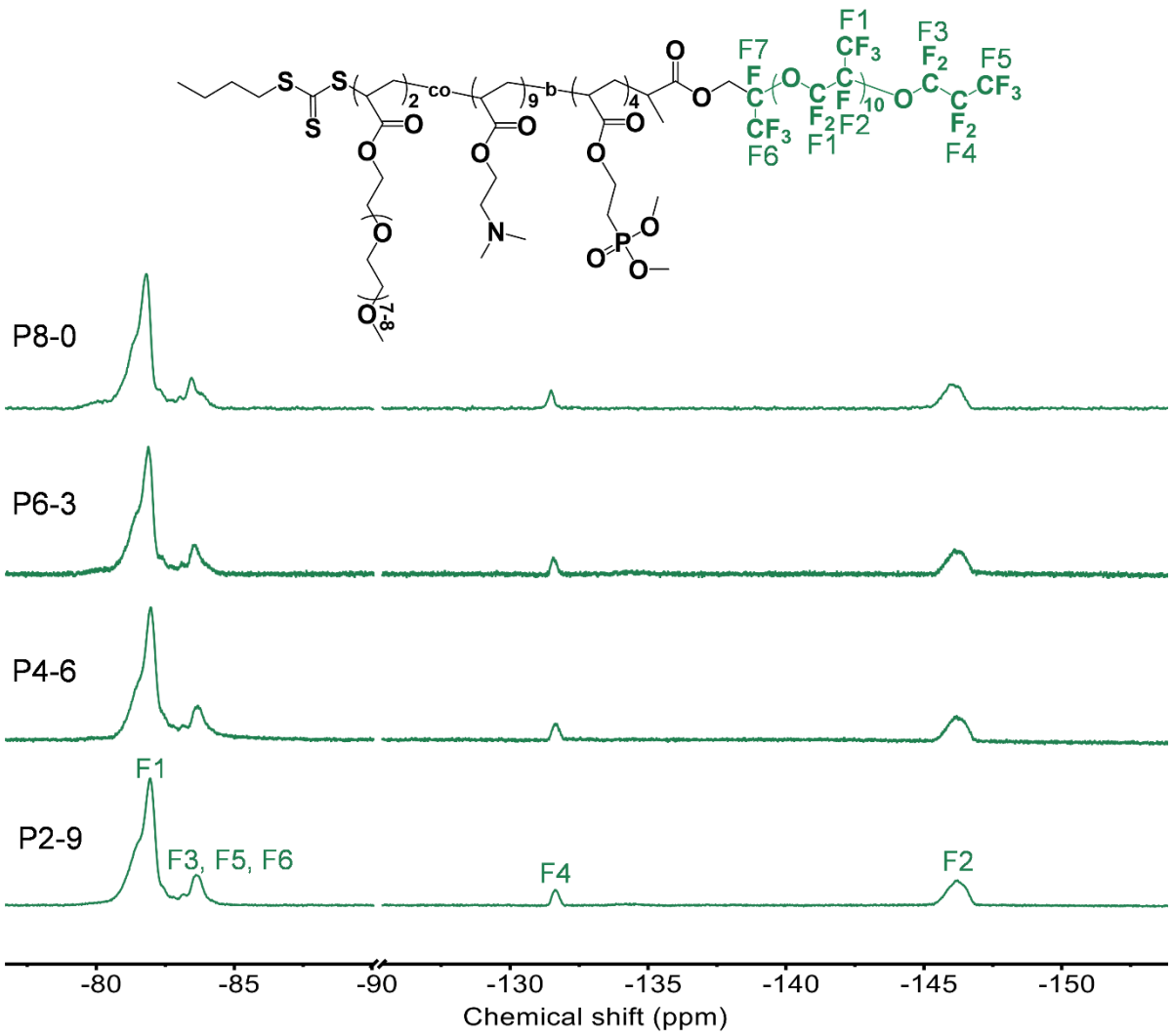


Figure S10. ^{19}F NMR spectra of four polymers before quaternization in DMSO-d_6.

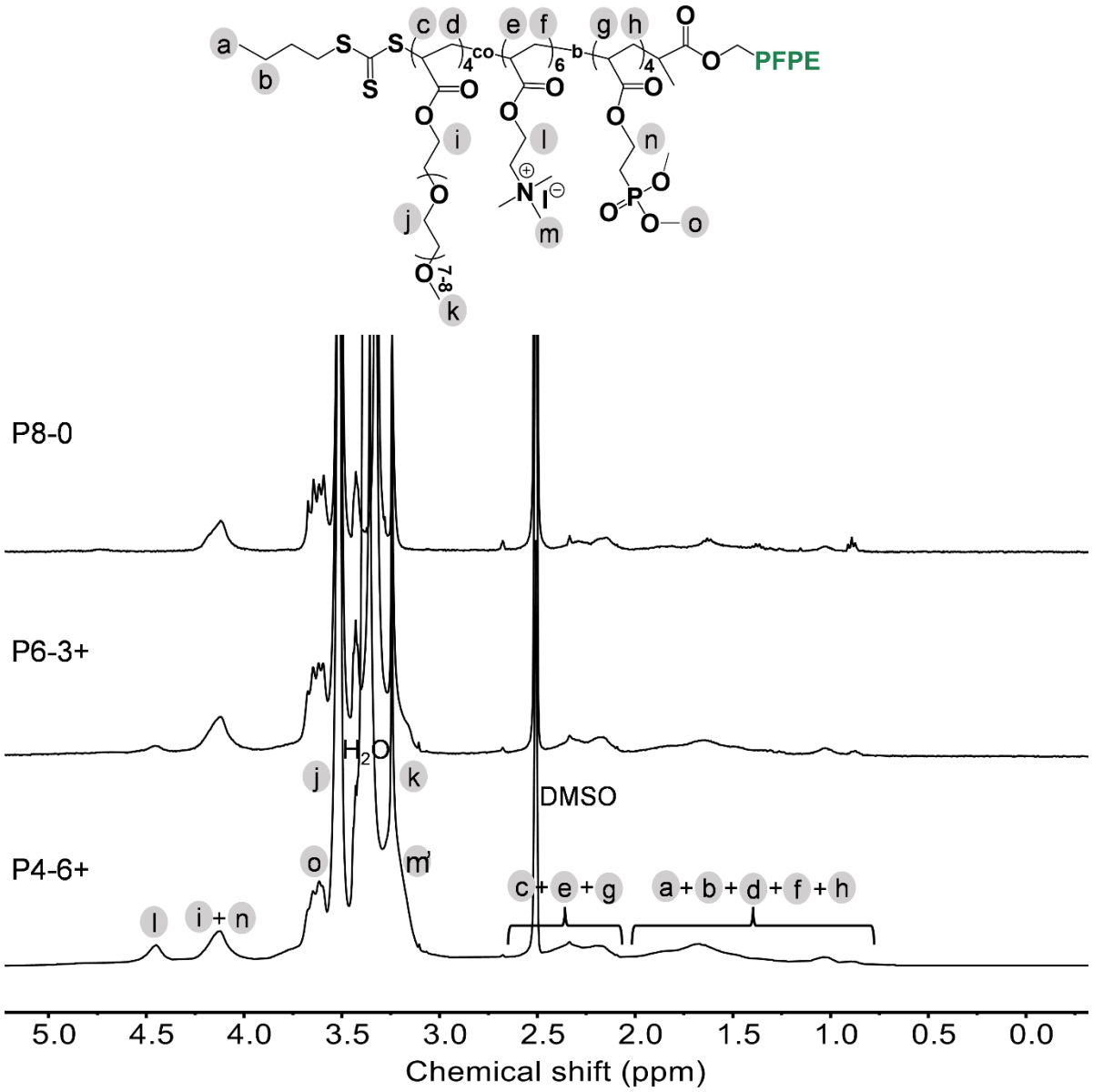


Figure S11. ^{1}H NMR spectra of P8-0, P6-3+ and P4-6+ polymers after quaternization in DMSO-d_6.

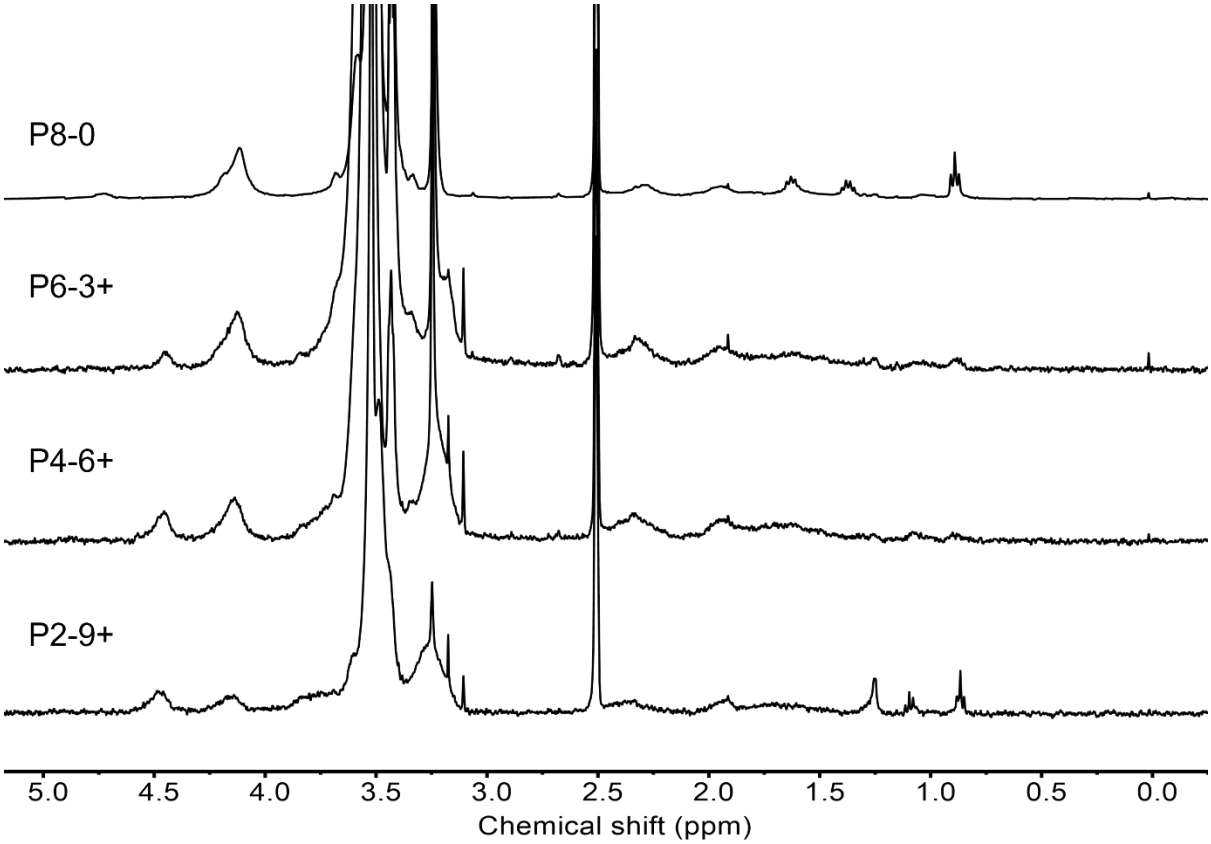


Figure S12. ^{1}H NMR spectra of four polymers after phosphonate deprotection in DMSO-d_6.

Table S1. Hydrodynamic diameters (D_h) of four PFPE-containing polymers after phosphonate deprotection in Milli-Q water. The values are the average of three measurements with standard deviations.

	D_h (nm, number-based)
P8-0	4.4 ± 0.7
P6-3+	19.3 ± 3.3
P4-6+	18.3 ± 2.1
P2-9+	28.5 ± 3.2

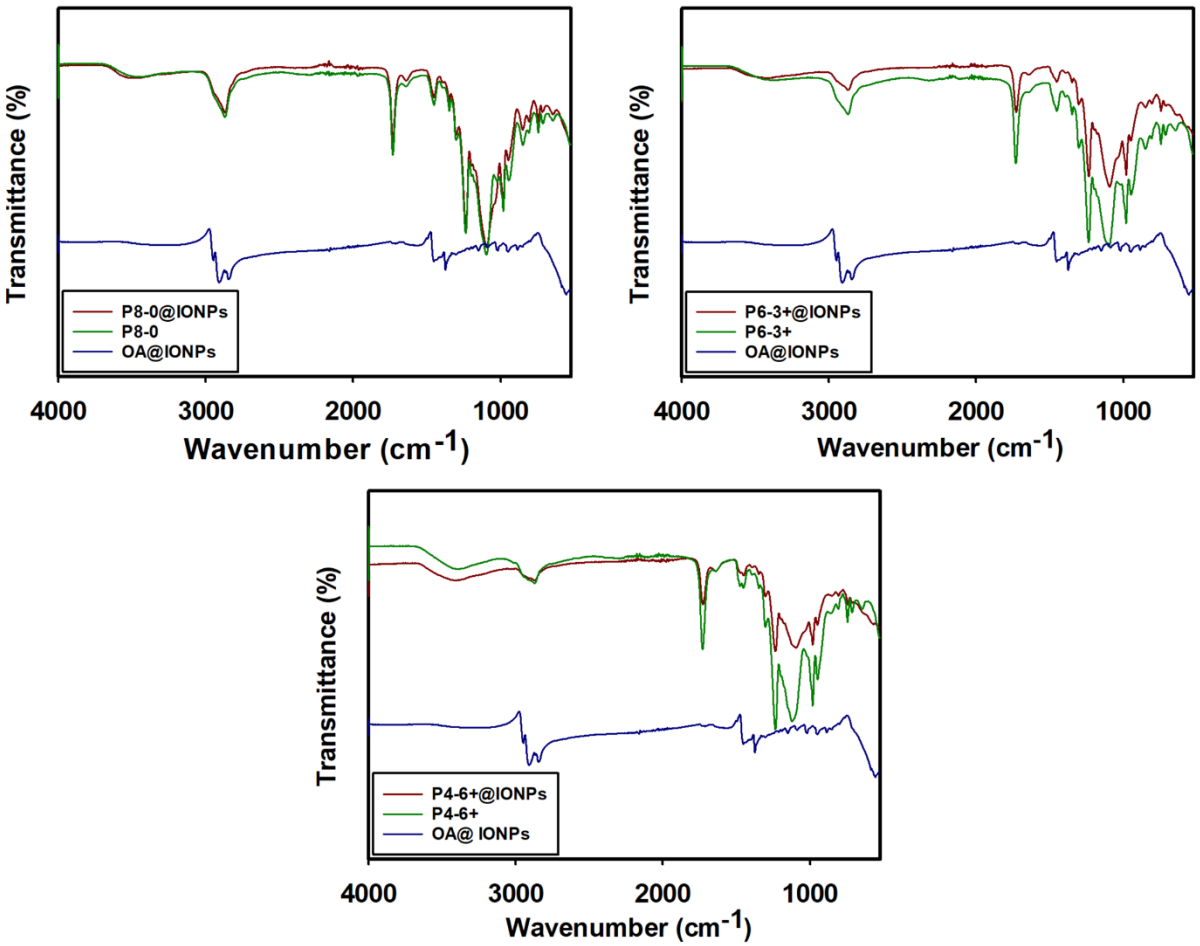


Figure S13. FTIR spectra of oleic acid coated IONPs and three polymers P8-0, P6-3+ and P4-6+ before and after grafting IONPs.

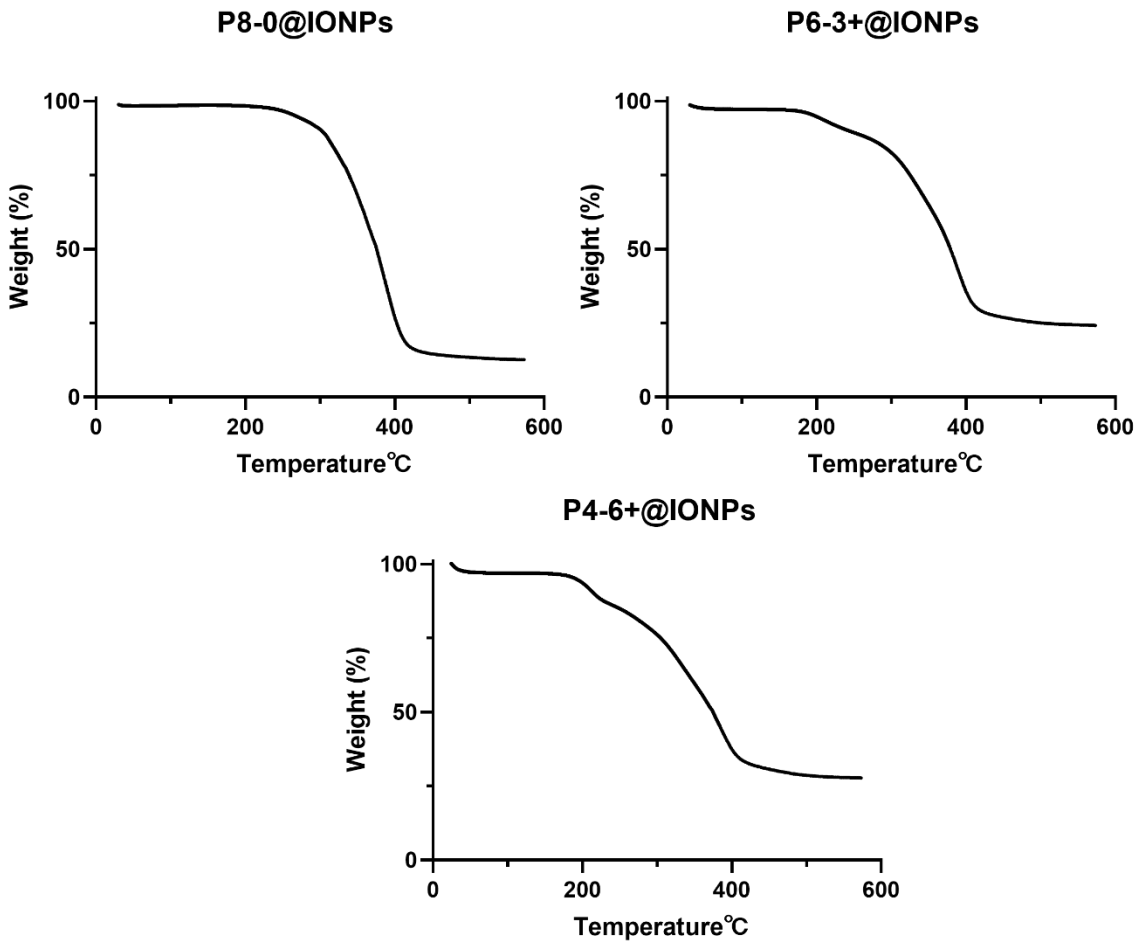


Figure S14. TGA of P8-0, P6-3+ and P4-6+ grafted IONPs.

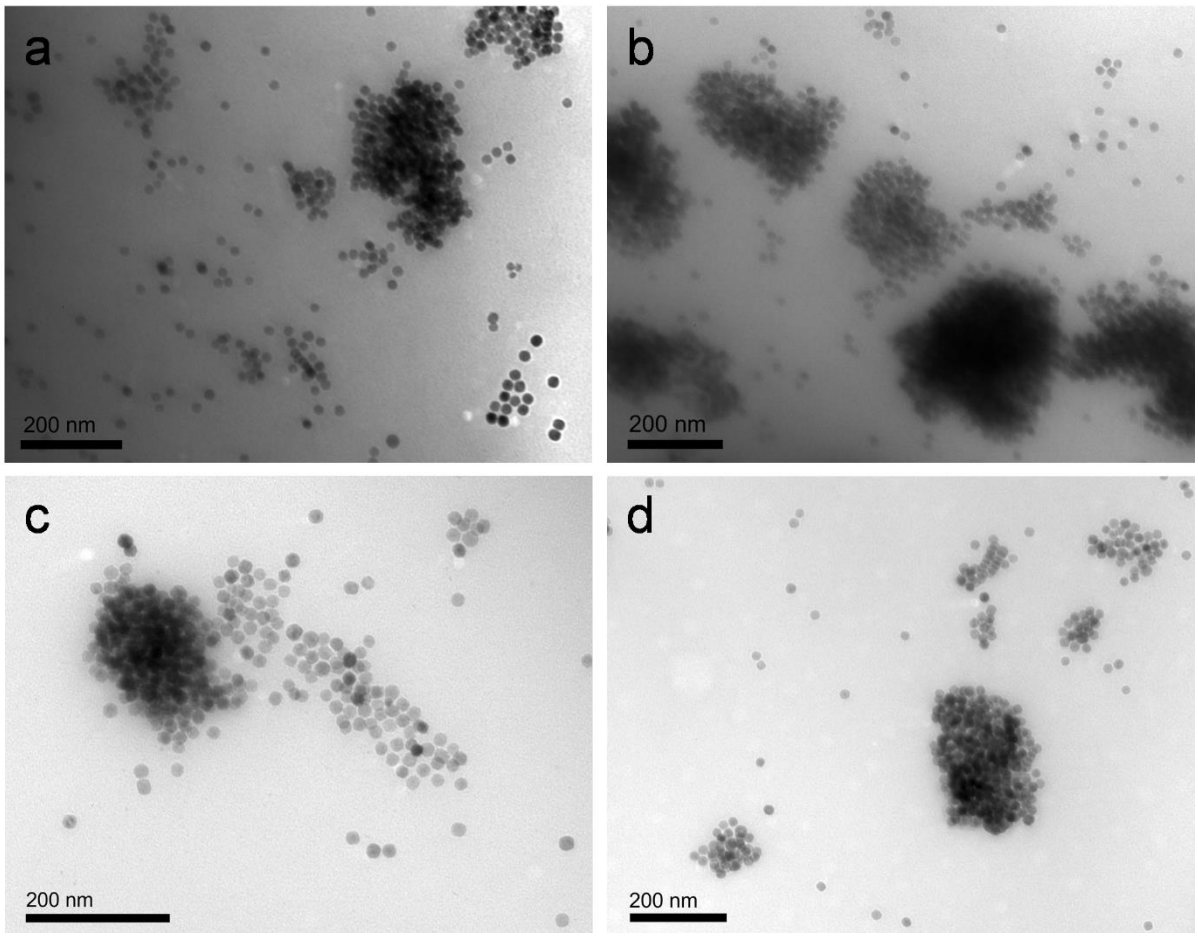
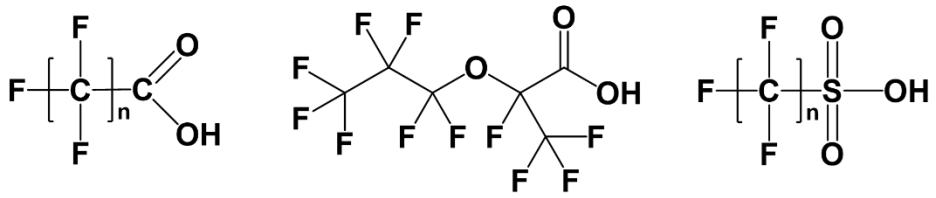


Figure S15. TEM of the four polymer grafted IONPs. a, P8-0@IONPs; b, P6-3+@IONPs; c, P4-6+@IONPs; d, P2-9+@IONPs.



PFCA **GenX** **PFSA**

n= 3 **PFBA**
n= 4 **PFPeA**
n= 5 **PFHxA**
n= 6 **PFHpA**
n= 7 **PFOA**
n= 8 **PFNA**
n= 9 **PFDA**

n= 3 **PFBS**
n= 6 **PFHxS**
n= 8 **PFOS**

PFBA: perfluorobutanoic acid
PFPeA: perfluoropentanoic acid
PFHxA: perfluorohexanoic acid
PFHpA: perfluoroheptanoic acid
PFOA: perfluorooctanoic acid
PFNA: perfluorononanoic acid
PFDA: perfluorodecanoic acid

PFBS: perfluorobutanesulfonic acid
PFHxS: perfluorohexanesulfonic acid
PFOS: perfluorooctanesulfonic acid

Figure S16. Chemical structures of the 11 PFAS used in this project.

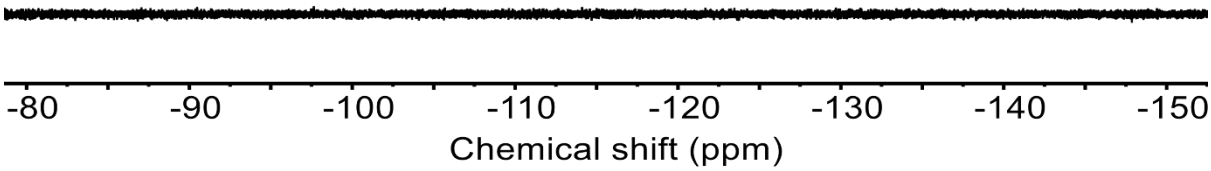


Figure S17. ^{19}F NMR spectrum of residue liquid after treatment by P2-9+@IONPs and magnetic separation.

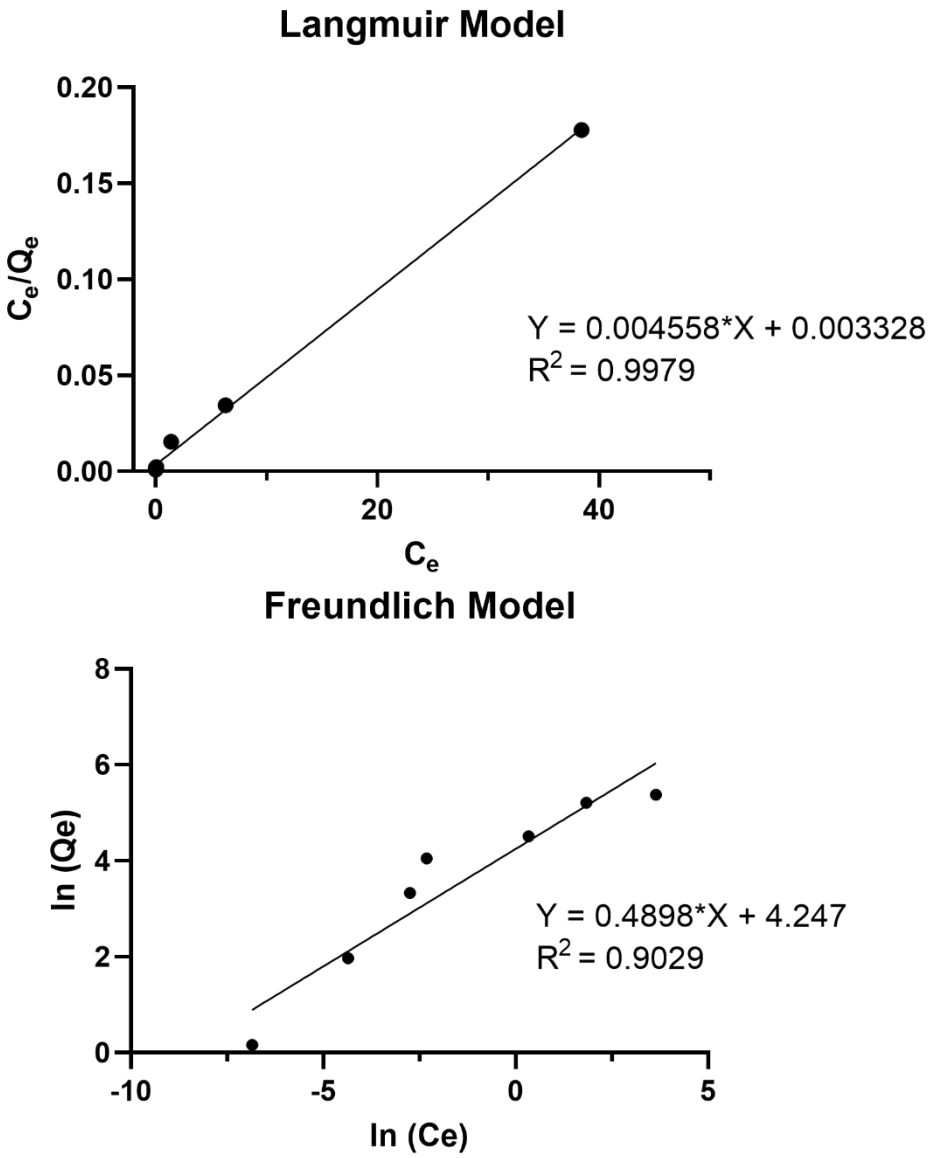


Figure S18. Sorption isotherm of GenX by P2-9+@IONPs fitted to linearized form of Langmuir model (top) and Freundlich model (bottom).

Table S2. Comparison of binding parameters between GenX and different types of sorbents reported from previous works.

Sorbent	GenX		Ref.
	Q_m (mg/g)	K_L (M^{-1})	
Ionic perfluoroalkane-containing hydrogel	34	-	[3]
Covalent organic framework	200	6.3×10^4	[4]
β-cyclodextrin-containing polymer	222	8.8×10^4	[5]
Ionic PFPE-containing fluorogel	217	1.5×10^7	[6]

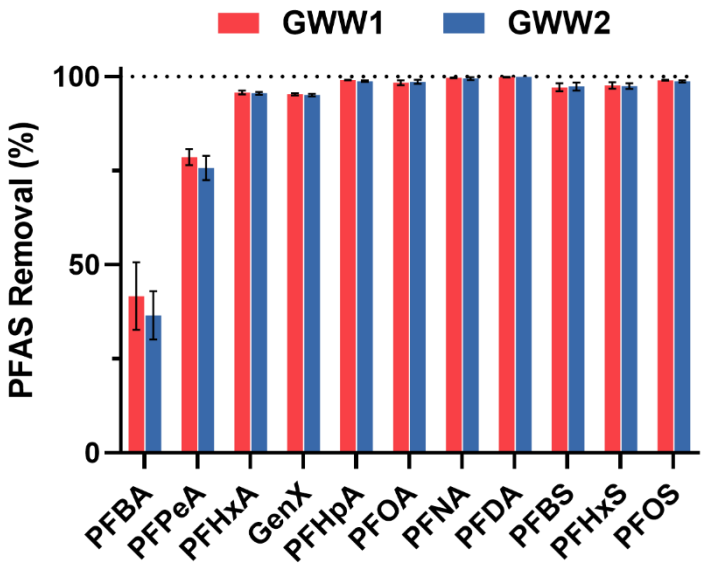


Figure S19. Multiple PFAS removal by P2-9+@IONPs in two different ground wastewater matrices. TOC: GWW1, 5.6 mg/L; GWW2, 8.1 mg/L. pH: GWW1, 7.4; GWW2, 7.3. Polymer concentration, 0.5 mg/mL (excluding IONPs). PFAS initial concentration, 1 ppb each. Sorption duration, 2 h. The results are the average of triplicates, and standard deviation is shown.

Table S3. Multiple reaction monitoring details for analytes shown in bold font, and internal standards used are shown in italic font.

Compound ID	Q1 mass	Q3 mass	EP	CE	CXP	Retention time
PFBA 1	212.8	169.0	-8	-13	-18	1.4
PFPeA 1	262.8	219.0	-8	-12	-25	1.73
PFPeA 2	262.8	69.0	-8	-58	-8	1.73
PFBS 1	298.9	80.0	-10	-65	-12	1.77
PFBS 2	298.9	99.0	-10	-36	-9	1.77
PFHxA 1	312.8	269.0	-8	-12	-25	2.02
PFHxA 2	312.8	119.0	-8	-24	-12	2.02
GenX 1	328.9	185.0	-10	-32	-16	2.14
GenX 2	328.9	119.0	-10	-49	-10	2.14
PFHpA 1	362.8	319.0	-8	-14	-25	2.39
PFHpA 2	362.8	169.0	-8	-23	-18	2.39
PFHxS 1	398.8	80.0	-10	-90	-12	2.4
PFHxS 2	398.8	99.0	-10	-75	-9	2.4
PFOA 1	412.8	369.0	-9	-14	-15	2.81
PFOA 2	412.8	169.0	-9	-23	-15	2.81
PFNA 1	462.8	419.0	-9	-15	-35	3.27
PFNA 2	462.8	169.0	-9	-26	-18	3.27
PFOS 1	498.8	80.0	-10	-100	-11	3.27
PFOS 2	498.8	99.0	-10	-95	-13	3.27
PFDA 1	512.8	469.0	-10	-18	-35	3.73
PFDA 2	512.8	269.0	-10	-23	-25	3.73
$^{13}C_4$-PFBA	216.8	172.0	-8	-12	-14	1.39
$^{13}C_4$-PFPeA	265.9	222.0	-9	-13	-20	1.72
$^{13}C_3$-PFBS	301.8	80.0	-10	-70	-12	1.76
$^{13}C_2$-PFHxA	314.9	270.0	-8	-13	-25	2.01
$^{13}C_3$-GenX	332	185.0	-10	-32	-15	2.18

Compound ID	Q1 mass	Q3 mass	EP	CE	CXP	Retention time
$^{13}C_3$-*PFHpA*	366.8	322.0	-9	-14	-28	2.37
$^{18}O_2$-*PFHxS*	402.8	103.0	-8	-80	-10	2.39
$^{13}C_4$-*PFOA*	416.9	372.0	-10	-13	-28	2.81
$^{13}C_5$-*PFNA*	467.8	423.0	-9	-14	-30	3.27
$^{13}C_4$-*PFOS*	502.9	80.0	-9	-115	-10	3.27
$^{13}C_2$-*PFDA*	514.8	470.0	-10	-15	-35	3.72

EP=Entrance potential, CE=Collision energy, CXP=Collision exit potential

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