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Proton Conductivity

Tetrafluoroaryl Phosphonic Acid Functionalized Polyphosphazenes – Synthesis, Characterization, and Evaluation of Proton Conductivity

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Abstract: A convergent approach for the incorporation of tetrafluoroaryl phosphonate moieties into cyclic triphosphazenes and linear phosphazene resins is described. Our high yield procedure is based on the treatment of chlorinated poly- and cyclotriphosphazenes with *p*-HO(C_6F_4)P(O)$(OR)_2$ (R = Me, Et) in the presence of potassium carbonate. Characterization of the modified cyclotriphosphazenes was accomplished by NMR and IR spectroscopy as well as by mass spectrometry. Similarly, a phosphazene resin decorated with phosphonic esters is characterized by NMR and IR spectra and GPC. Exchange of the ethyl group by a trimethylsilyl group in the novel phosphazene derivatives was effected by the reaction with trimethylsilyl bromide. The resulting silyl phosphonates were converted into the corresponding phosphonic acids by exposure to an excess of methanol. Proton conductivities of the novel phosphonic acid derivatives of poly- and cyclotriphosphazenes were studied by electrochemical impedance spectroscopy under anhydrous conditions.

Introduction

Polymer-based electrolyte membranes are important components in electrochemical energy conversion and storage devices, functioning as conductors and separators. In fuel cells, the use of polymeric electrolyte membranes could circumvent the frequent nuisance of leakage associated with liquid electrolytes.[1] However, there are several requirements a polymeric material must fulfil prior to use as a membrane in fuel cells. In addition to an efficient proton conductivity the materials should have low diffusion coefficients for the fuel (e.g. H_2 or MeOH) and oxidant (e.g. O_2), and moreover should be mechanically and chemically robust.[2]

The most common materials used in fuel cells are polymeric perfluoroalkyl sulfonic acids, e.g. Nafion®. These materials provide an excellent proton conductivity in the presence of moisture at temperatures up to 80 °C.[3] Despite the broad application of the sulfonic acids in polymer electrolyte fuel cells, these materials suffer from major drawbacks.

At temperatures above 80 °C the proton conductivity decreases rapidly due to evaporation of water from the membrane. This limits the working temperature for fuel cells and requires additive humidification and cooling to provide an efficient power output of the fuel cell.[4] Furthermore, Nafion® is not suitable for the use in methanol fuel cells due to high methanol crossover rates.[5] Overall, the use of Nafion® based membranes restricts the operation of fuel cells to a narrow temperature window (T < 80 °C) and prohibits the use of methanol as an inherently safer fuel than hydrogen gas.[6]

Polyphosphazenes render a promising class of polymers for the design of novel proton exchange membranes that may overcome the mentioned drawbacks. These polymers are defined by an –N=P– backbone bearing two substituents (inorganic, organic) at the phosphorus atoms.[7] They provide durability at high temperatures and severe oxidative stress, due to the thermal and chemical stability of the –N=P– backbone.[7] Furthermore, the properties of polyphosphazenes can be easily tuned by the choice of sidegroups introduced to the polymer. The most common synthetic route to introduce specific sidegroups is by the use of $[P(Cl)_2N]_n$ as polymeric precursor, which can be simply functionalized by nucleophilic substitution.[8]

Several ionomers based on polyphosphazenes have been reported.[7a,9] They feature sulfonic acid groups as well as sulfonamine and phosphonic acid groups as protogenic moieties. Experimental studies on phosphonated and sulfonated phosphazenes reported that these materials are comparable to Nafion regarding their proton conductivity and superior regarding their methanol permeability.[10] However, for the design of a membrane with sufficient conductivity at 120 °C, phosphonic acids seem to be one of the most promising protogenic moieties, as discussed in the literature.[11]

As reported in recent papers by our group, perfluoroaryl phosphonic acid provides an even higher conductivity than its

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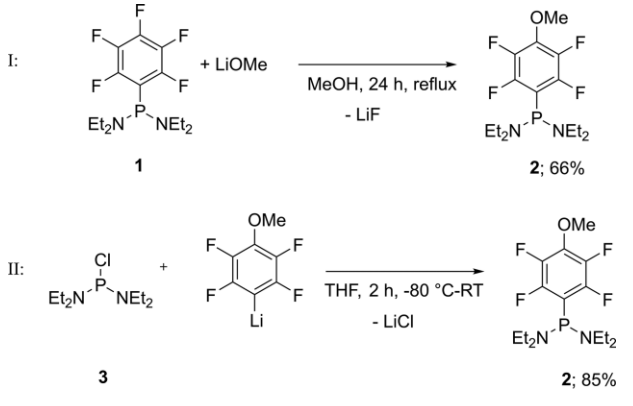
non-fluorinated counterpart at high temperatures and low humid conditions.[12] As shown by, *Desmarteau* et al.[13] fluorinated phosphonic acid also provide a higher conductivity than sulfonic acid derivatives which are currently used in Nafion® based membranes. Polyphosphazenes bearing perfluorinated sulfonic acid groups have already been reported and exhibit higher conductivity and stability than their aliphatic derivative.[14] In view of these observations, polyphosphazenes functionalized with fluorinated phosphonic acids should be promising candidates for membranes in high temperature fuel cells and are, to the best of our knowledge, hitherto unknown.

Here we report on the first examples of cyclotriphosphazenes and polyphosphazenes functionalized with fluorinated 4-oxy-aryl phosphonic acids.

Results and Discussion

Synthesis and Characterization of the Precursor *p*-HO(C_6F_4)P(O)($OR)_2$; R = Me, Et

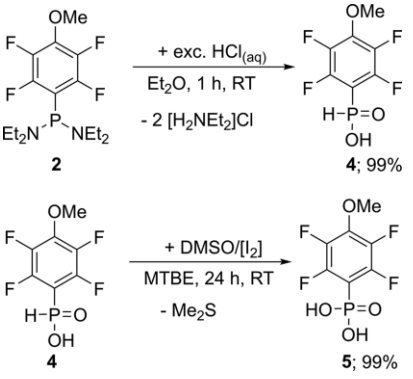
As previously described by our group, bis(diethylamino)pentafluorophenylphosphane (**1**) is readily functionalized with LiOMe to furnish the corresponding phosphane **2** in a 66 % yield (Scheme 1, I).[15] An alternative synthesis makes use of the coupling of lithium tetrafluoroanisole and $ClP(NEt_2)_2$ (**3**) (Scheme 1, II). The employment of this new synthetic route allows the preparation of phosphane **2** in higher yields (85 %) and quantities up to 20 g.



Scheme 1. Synthesis of aminophosphane **2**.

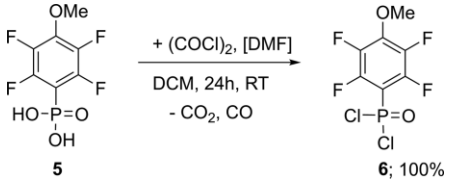
Hydrolysis of aminophosphane **2** with aqueous HCl and subsequent mild oxidation of the obtained phosphinic acid **4** with DMSO/I_2 led to the formation of phosphonic acid **5** (Scheme 2).[15] The analytic data of the described derivatives **1**–**5** are extensively elaborated in our previous report.[15]

Treatment of **5** with oxalyl chloride in the presence of catalytical amounts of DMF in dichloromethane quantitatively furnished phosphonic acid chloride **6** as a yellow solid (Scheme 3).[16] ^{31}P NMR spectroscopic analysis in $CDCl_3$ reveals a resonance at 11.2 ppm. Signals assigned to the fluorine atoms



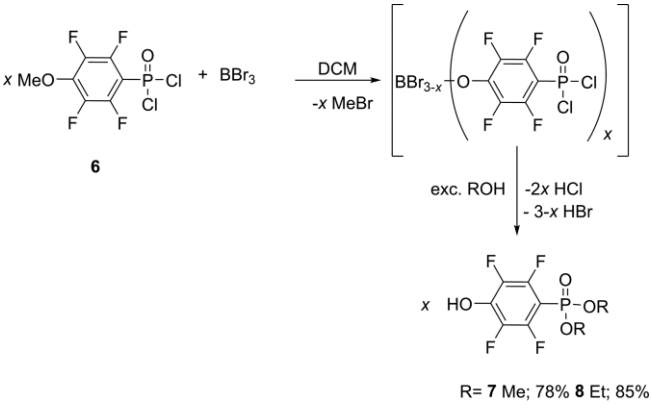
Scheme 2. Synthesis of phosphonic acid **5**.

are observed at –131.0 ppm (2 and 6 position) and –155.6 ppm (3 and 5 position) in the ^{19}F NMR spectrum. The band for the ν[P=O] stretching in the IR spectrum is observed at 1196 cm^{-1}.



Scheme 3. Synthesis of phosphonic acid chloride **6**.

Dealkylation of the methoxy functionality of **6** is achieved by BBr_3 in dichloromethane (Scheme 4).[17] After the dealkylation reached completion, the addition of alcohols (MeOH, EtOH) to the reaction mixture leads to the cleavage of the boron–oxygen bond and to the esterification of the phosphonic acid. Removal of all volatile compounds and recrystallization from tetrahydrofuran yields the pure methyl ester **7** (78 %). The ethyl ester **8** is isolated in an 85 % yield after column chromatographic workup. ^{31}P NMR spectroscopic analysis of the ethyl ester **8** in DMSO-[D_6] reveals a resonance at 5.8 ppm. The resonance of the phenolic proton is observed at 12.50 ppm as a broad singlet in the ^{1}H NMR spectrum. IR spectroscopic analysis confirms the formation of the ethyl ester **8**. The band at 3372 cm^{-1} is assigned to the ν[O–H] stretching vibration. Characteristic bands for alkyl phosphonic esters are observed at1013 cm^{-1} (ν[P–O–C]) and 966 cm^{-1} (ν[O–P–O]).



Scheme 4. Formation of phosphonic acid esters **7** and **8** from precursor **6**.

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Colorless single crystals of **8**, suitable for an X-ray diffraction analysis, are grown from tetrahydrofuran. The compound crystallizes in the triclinic space group $P\bar{1}$. Hydrogen bridging of O4–H1 to O1# in the crystal leads to the formation of infinite chains (Figure 1). The O4–O1# distance amounts to 255.5(1) pm.

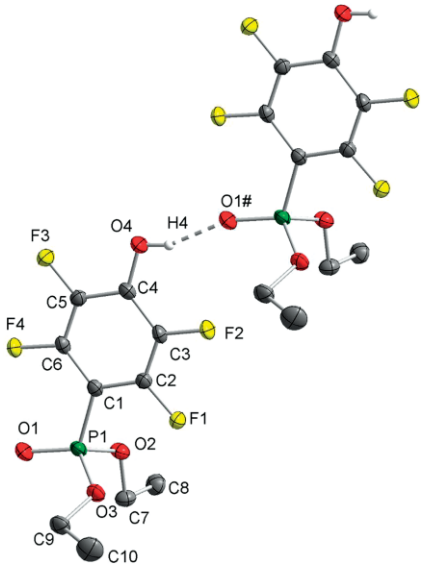


Figure 1. Molecular structure of phosphonic acid ester **8** (thermal ellipsoids are set to 50 % probability; aliphatic H atoms omitted). Symmetry code used: $x - 1, y - 1, z$.

Synthesis and Characterization of Cyclic Triphosphazenes and Polyphosphazenes

Functionalization of hexachlorotriphosphazene with phosphonic esters **7** and **8** was performed in tetrahydrofuran in the presence of K_2CO_3 (Scheme 5).[18] Substituted aryloxy phosphazenes **9** and **10** were isolated in good yields (**9**: 90 %; **10**: 66 %). Complete substitution of the chlorine atoms was proved by ^{31}P NMR spectroscopy. Resonances for the symmetric phosphazene **9** are observed at 8.8 ppm [P=N] and 6.1 ppm [P(O)(OMe)$_2$]. ESI mass spectrometric analysis of phosphazene **9** reveals the basis peak at 1795.8 *m/z* which is assigned to the [M + Na]$^+$ fragment. The ESI mass spectrum of phosphazene **10** exhibits the [M + Na]$^+$ fragment at 1964.1 *m/z* (30 %).

In addition to the spectroscopic data, suitable crystals of phosphazene **9** were grown by layering a tetrahydrofuran solution with *n*-pentane. The crystals were subjected to an X-ray diffraction analysis. The analysis confirms the full substitution of the chlorine atoms of the cyclic phosphazene. The distances of the phosphorus–nitrogen atoms in the phosphazene ring are ranging from 157.3(2) pm to 157.8(2) pm and agree with multiple bonding (Figure 2).[19]

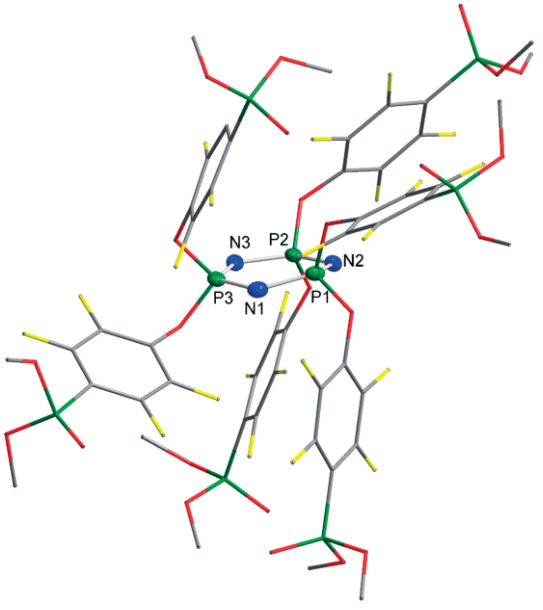
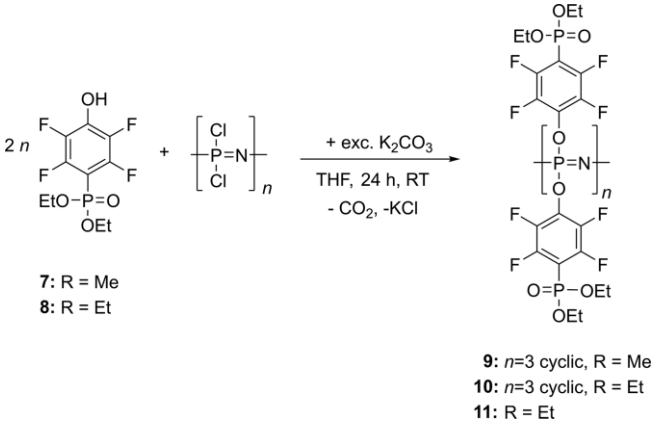


Figure 2. Molecular structure of phosphazene **9**. (Thermal ellipsoids are set to 50 %, organic substituents are featured in wire and stick for clarity, hydrogen atoms, solvent THF and minor occupied disordered atoms are omitted for clarity.)



7: R = Me
8: R = Et

9: *n*=3 cyclic, R = Me
10: *n*=3 cyclic, R = Et
11: R = Et

Scheme 5. Synthesis of cyclic aryloxy triphosphazenes **9** and **10** and polyphosphazene **11**.

In addition to the functionalization of the cyclotriphosphazene we studied the functionalization of polydichlorophosphazene with phosphonic ester **8** (Scheme 5). The here employed polydichlorophosphazene was synthesized from $Cl_3P{=}NSiMe_3$ as reported by *Allcock* et al.[20] The substitution by the hydroxyl fluorophenyl phosphonic ester **8** was performed analogously to the trimeric derivatives. The resulting off-white solid **11** is well soluble in DMF and DCM. GPC analysis of the obtained material was performed in DMF (+0.05 M LiBr). The elugram is depicted in Figure 3. Evaluation of the molar mass distribution relative to PMMA standards results in M_n = 1860 g/mol and M_w = 1910 g/mol. The obtained dispersity D: 1.03 is as narrow as expected for polyphosphazenes derived from a controlled polymerization of $Cl_3P{=}NSiMe_3$ with PCl_5.[20]

NMR spectroscopic analysis reveals resonances assigned to the phosphorus atom of the phosphonic ester at 3.45–5.73 ppm. Signals assigned to the phosphorus atoms of the phosphazene backbone are observed at –15.7 to –22.0 ppm. The intensities of the signals match the expected ratio of 2:1 (Figure 4).

Dealkylation of the phosphonic ester functionality of phosphazenes **10** and **11** is achieved with Me_3SiBr in dichloromethane at room temperature. When the silylation of the ester

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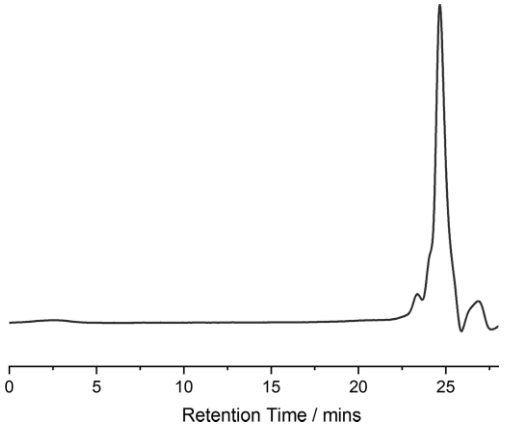


Figure 3. Elugram of polyphosphazene **11**, eluent: DMF (+0.05 M LiBr).

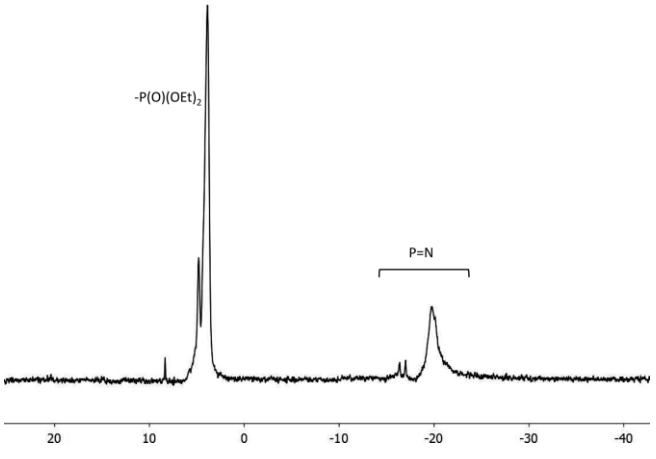


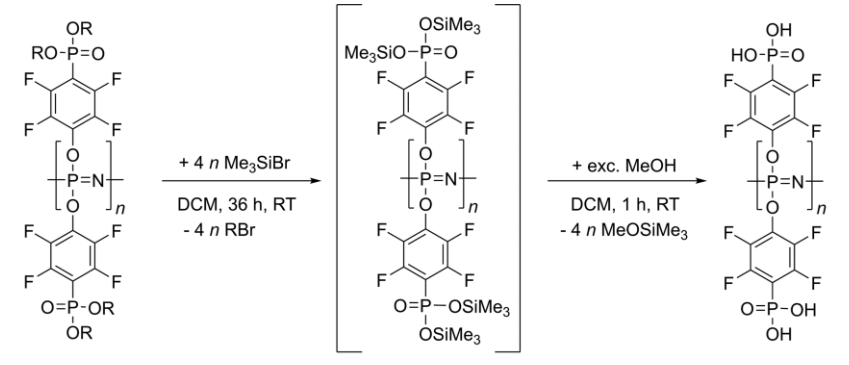
Figure 4. ^{31}P NMR spectrum of polyphosphazene **11**.

had reached completion, the addition of an excess of methanol afforded the corresponding aryloxy phosphazenes decorated by tetrafluorophenylene phosphonic acid units (**12, 13**) (Scheme 6).

Quantitative dealkylation of the tricyclophosphazene species was confirmed by ESI mass spectrometry where the $[M - H]^-$ fragment is observed at 1603.7 *m/z* as the base peak. The ^{31}P NMR spectrum of the product displays two resonances due to the phosphorus atoms of the phosphazene ring at 8.8 ppm and to the phosphonic acid at -2.6 ppm. Volumetric titration of the acid **12** in water with 0.1 M NaOH reveals the expected titration curve with two equivalence points. The pK_{S1} and pK_{S2} values amount to 2.1 and 6.7. The pK_{S1} value is only tentative due to the inapplicability of the Nernst equation at pK_S values near 2.[21] Dealkylation of the polymeric ester **11** results in a brittle material after cleavage of the silyl ester moieties by methanol. The ion exchange capacity (IEC) of the polymer **13** was determined by volumetric titration with 0.1 M NaOH containing 0.1 mol/L NaCl and amounts to 6.8 mmol g^{-1}. An IR spectroscopic analysis reveals broad signals in the range of 2460–1990 cm^{-1} which are indicating hydrogen-bridging of P=O and P–OH functionalities. Besides the signal for O–H stretching vibrations of water (3700–3120 cm^{-1}) a broad band in the range of 3120–2480 cm^{-1} results from P–OH stretching vibrations. At 1293 cm^{-1} and 1273 cm^{-1} the characteristic P=N stretching vibrations of polyphosphazenes are observed. The ^{31}P NMR spectrum of the polymeric acid **13** reveals two characteristic groups of signals. Signals assigned to the phosphorus atom of the acid functionality are observed from –1.5 to –3.5 ppm, those of the phosphorus atom in the polymeric backbones resonate from –12.0 to –23.0 ppm.

Proton Conductivity Measurements

The conductivity of the phosphonic acid functionalized triphosphazene **12** and polyphosphazene **13** is ascertained by electrochemical impedance spectroscopy under anhydrous conditions. All samples were dried in vacuo for 24 hours to remove traces of water from the solid materials, as water has a drastic influence on the conductivity of the presented materials. In addition to Nafion® powder, $C_6H_5P(O)(OH)_2$ and $C_6F_5P(O)(OH)_2$ were analysed as references (Figure 5). As expected, all fluorinated derivatives exhibit a higher conductivity than $C_6H_5P(O)(OH)_2$. At 120 °C the conductivity of all fluorinated derivatives is two orders of magnitude higher than the one of phenylphosphonic acid (1.98×10^{-7} S cm^{-1}). Phosphazene **12** exhibits a conductivity of 1.60×10^{-5} S cm^{-1} at 120 °C. For the polyphosphazene **13** a conductivity of 6.58×10^{-5} S cm^{-1} is determined. Noticeable



10: *n*=3 cyclic, R = Et
11: R = Et

12: *n*=3 cyclic; **13**

Scheme 6. Dealkylation of **10** and **11**.

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is the rampant increase in conductivity of polyphosphazene **13** in comparison to the other samples, starting at 3.67×10^{-9} at 20 °C up to 6.58×10^{-5} S cm^{-1} (120 °C) covering four orders of magnitude. Whilst **13** exhibits the lowest conductivity of the fluorinated samples from 20 °C up to 70 °C (1.64×10^{-6} S cm^{-1}) the strong temperature dependent increase in conductivity leads to a significantly higher value at 120 °C than that of triphosphazene **12**. The values at 120 °C for **13** and **12** are well comparable with the measured data for Nafion® (7.66×10^{-5} S cm^{-1} at 120 °C) and $C_6F_5P(O)(OH)_2$ (7.38×10^{-5} S cm^{-1} at 120 °C). As the conductivity of Nafion® ranges in the same order of magnitude as that of phosphazenes **12** and **13**, it is obvious that they are also a powerful candidate for the use in proton conduction and other ionomer applications. As the proton conduction studies were performed under strictly water free conditions, additional studies on the influence of water on the conductivity should be considered for further investigations on these materials.

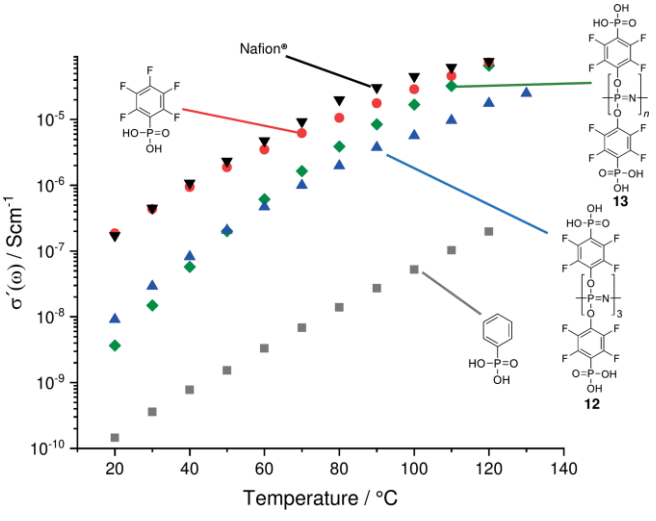

Figure 5. Conductivity of cyclic phosphazene **12** and polyphosphazene **13** as a function of temperature at water free conditions. Conductivities of Nafion®, $C_6F_5P(O)(OH)_2$ and $C_6H_5P(O)(OH)_2$ are given as references.

Conclusion

A convergent approach for the incorporation of the tetrafluoroaryl phosphonate building block into cyclic and polymeric phosphazenes is described. The synthesis is based on the reaction of the precursors *p*-HO(C_6F_4)P(O)(OR)$_2$ (R = Me: **7**, Et: **8**) with polymeric or trimeric chlorinated phosphazenes in the presence of K_2CO_3. The reaction produces the corresponding organophosphazenes in good yields. The cyclotriphosphazenes **9**–**10** are fully characterized by spectroscopy (NMR, IR) and mass spectrometry. The crystal structure of the cyclotriphosphazene **9** proves the complete substitution of the chlorine atoms of hexachlorotriphosphazene. Addition of Me_3SiBr to phosphazene **10** and subsequent addition of methanol led to the corresponding cyclophosphazene decorated by phosphonic acid functions (**12**). The pK_S values were measured by volumetric titration (pK_{S1} = 2.1; pK_{S2} = 6.7). The corresponding polyphosphazenes are synthesized in accordance to the cyclic trimers and are characterized by spectroscopy (NMR, IR) and GPC. The ion exchange capacity of polymeric phosphonic acid **13** was measured by volumetric titration and amounts to 6.8 mmol g^{-1}. The proton conductivities of the phosphonic acid analogues of the cyclic trimer **12** and the homologous polyphosphazene **13** were investigated by electrochemical impedance spectroscopy under water free conditions. Both phosphazenes (**12**: 1.60×10^{-5} S cm^{-1}: **13**: 6.58×10^{-5} S cm^{-1}) exhibit a high proton conductivity which is comparable to Nafion® (7.66×10^{-5} S cm^{-1}) at 120 °C which renders these materials promising candidates for the design of novel ionomers for high temperature applications.

Experimental Section

The starting material $(Et_2N)_2PCl$[22] was synthesized as described in the literature. For the synthesis of $Cl_3P{=}NSiMe_3$,[23] polydichlorophosphazene[20] and compounds **2**, **4** and **5** please refer to the supporting information. All other chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all experiments. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques. IR spectra were recorded with a Bruker Alpha FT-IR spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with an ATR unit with a diamond crystal for liquids and solids. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (^{31}P 121.5 MHz; ^{19}F 282.4 MHz; ^{13}C 75.5 MHz; ^{1}H 300.1 MHz) with positive shifts being downfield from the external standards [TMS (^{13}C; ^{1}H), CCl_3F (^{19}F); 85 % H_3PO_4 (^{31}P)]. ESI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. EI mass spectra were recorded using an Autospec Xmagnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI or CI source. Melting points were measured on a Mettler Toledo Mp70 Melting Point System. The pH value measurements were performed with a Portavo 907 Multi (Knick Elektronische Messgeräte GmbH & Co. KG). Measurements of the molecular weight of the derived polymers were performed with a GPC Analysis System of Shimadzu (Kyoto, Japan) equipped with a degasser (DGU-20A$_{3R}$), two pumps (LC-20AD), autosampler (SIL-20A$_{HT}$), a column oven (CTO-20A, 30 °C), RI-Detector (RID-20A, 50 °C), control unit (CBM-20A) and GRAM columns (PSS Polymer Standard Services GmbH, Mainz – pre column: GRAM 50 × 8 mm, 10 µm, one separation columns: GRAM 300 × 8 mm, 10 µm, 1000 Å, one separation column: GRAM 300 × 8 mm, 10 µm, 3000 Å). Column temperature: 50 °C; Eluent: DMF (+0.05 M LiBr); Flowrate: 1 mL/min; Inject: 50 µL; Sample concentration: 2.5mg/mL. Calibration was performed with PMMA standards.

Pellets of the samples with a diameter of 12 mm for the electrochemical impedance spectroscopy were prepared by applying a pressure of around 265 MPa for 30 min. Self-standing pellets were obtained which were then sputter-coated with a thin Au layer. For the measurements, a TSC battery measuring cell (rhd instruments GmbH & Co. KG), in combination with a modified Microcell HC setup (rhd instruments GmbH & Co. KG) has been used. As current collectors, two planar stainless steel electrodes with an effective contact area of 8 mm in diameter were used. The contact pressure was adjusted to 40.7 kPa using a gold-plated spring with a spring constant of 2.3 N/mm. The temperature of the modified Microcell HC setup was controlled via a Peltier element which enabled adjusting

sample temperatures ranging from –40 °C up to +120 °C. A Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used for the impedance measurements. Using the Au-plated contact area of the pellet and the thickness of the pellet (measured by means of a micrometer screw, COOLANT PROOF Micrometer IP65, Mitutoyo Corp.), the cell constant C was calculated (C = d/A). The resulting values are listed in the following: Nafion: 0.072 cm^{-1}; $C_6H_5P(O)(OH)_2$: 0.089 cm^{-1}; $C_6F_5P(O)(OH)_2$: 0.032 cm^{-1}; cyclotriphosphazene **12**: 0.032 cm^{-1}; polyphosphazene **13**: 0.041 cm^{-1}.

Suitable single crystals of **8** and **9** were measured on a Rigaku Supernova diffractometer. The crystals were kept at 100.0(1) K during data collection.

Deposition Numbers 1908916 and 1908917 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis of *p*-MeO(C_6F_4)P(O)(Cl_2) (6): The phosphonic acid **5** (4.08 g; 15.7 mmol) was dissolved in chlorotrimethylsilane (20 mL) at 0 °C and stirred for 10 minutes. A sample of DMF (30 mg; 3 mol-%) was added to the solution and oxalyl chloride (5.92 g; 47.0 mmol) was added very carefully under vigorous gas formation. The solution was stirred for 24 hours at room temperature. Removal of all volatile compounds yielded 4.63 g of the product (15.6 mmol; 100 %) as a yellow solid. ^{1}H NMR ($CDCl_3$, RT): δ = 4.29 (t, ^5J(F,H) = 2 Hz, 3H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): δ = 62.1 (t, ^5J(F,C) = 5 Hz, OCH_3) ppm; $^{13}C\{^{19}F\}$ NMR ($CDCl_3$, RT): δ = 105.1 (d, ^1J(P,C) = 164 Hz, CP), 140.1 (d, ^2J(P,C) = 18 Hz, CF), 144.5 (m, C-O), 147.0 (s, CF) ppm; ^{19}F NMR ($CDCl_3$, RT): δ = –131.0 (m, 2F, CF-*ortho*), –155.6 (m, 2F, CF-*meta*) ppm; ^{31}P NMR ($CDCl_3$, RT): δ = 11.2 (m, 1P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2969 (w), 2902 (w), 2853 (w), 1674 (w), 1635 (w), 1584 (w), 1507 (w), 1474 (m), 1433 (w), 1392 (w), 1296 (w), 1274 (m), 1196 (w), 1124 (m), 1027 (w), 990 (m), 849 (w), 805 (w), 772 (w), 728 (w), 655 (w), 641 (w), 568 (m, shoulder), 543 (s), 486 (m), 442 (w), 421 (m), 404 (m) cm^{-1}.

Synthesis of *p*-HO(C_6F_4)P(O)($OMe)_2$ (7): A solution of acid chloride **6** (3.54 g, 13.8 mmol) in DCM (30 mL) was cooled to 0 °C and borontribromide (6.90 g, 27.6 mmol) was added. The reaction mixture was stirred at room temperature for 72 hours. A sample of methanol (20 mL) was added at 0 °C to the solution. Evaporation of the solvent and recrystallization from THF yielded 2.96 g of the pure product (10.8 mmol, 78 %) as colorless crystals. ^{1}H NMR ([D_6]DMSO, RT): δ = 3.74 (d, ^3J(P,H) = 12 Hz, 6H, OCH_3), 12.58 (s broad, 1H, OH) ppm; $^{13}C\{^{19}F\}$ NMR ([D_6]DMSO, RT): δ = 53.1 (m, OCH_3), 94.7 (d, ^1J(P,C) = 187 Hz, P-C), 138.0 (d, ^2J(P,C) = 15 Hz, CF), 141.1 (s, C-OH), 147.1 (s, C-F) ppm; ^{19}F NMR ([D_6]DMSO, RT): δ = –134.7 (m, 2F, CF-*ortho*), –159.5 (m, 2F, CF-*meta*) ppm; ^{31}P NMR ([D_6]DMSO, RT): δ = 9.0 (m, 1P, P) ppm. IR (ATR): $\tilde{\nu}$ = 2961 (w), 2906 (w), 2856 (w), 2808 (w), 2655 (w), 2592 (w), 2542 (w), 1643 (w), 1601 (w), 1528 (w), 1485 (m), 1401 (w), 1379 (w), 1343 (w), 1296 (w), 1270 (w), 1242 (m), 1212 (m), 1183 (m), 1133 (m), 1120 (m), 1111 (m), 1031 (s), 1015 (s), 969 (s), 880 (m), 845 (s), 782 (m), 756 (m), 728 (w), 650 (w), 610 (w), 600 (m), 577 (s), 483 (m), 449 (w), 420 (w), 400 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 570.9 (14) $[2M + Na]^+$, 381.4 (28), 353.3 (31), 297.0 (100) $[M + Na]^+$. (ESI, neg.): *m/z* (%) = 272.8 (100) $[M – H]^–$. HRMS: calcd. for $C_8H_7O_4F_4PH^+$ 275.00909, found 275.0094.

Synthesis of *p*-HO(C_6F_4)P(O)($OEt)_2$ (8): A solution of acid chloride **6** (4.46 g, 17.1 mmol) in DCM (30 mL) was cooled to 0 °C and borontribromide (7.44 g, 29.7 mmol) was added. The reaction mixture was stirred at room temperature for 48 hours. A sample of ethanol (20 mL) was added at 0 °C to the solution. The solvent was evaporated. Purification with column chromatographie (THF/ethyl acetate = 1:1) yielded 3.78 g of the product (12.5 mmol, 85 %) as a colorless solid. ^{1}H NMR ([D_6]DMSO, RT): δ = 1.26 (t, ^3J(P,H) = 7 Hz, 6H, CH_3), 4.11 (m, 4H, OCH_2), 12.50 (s broad, OH) ppm; $^{13}C\{^1H\}$ NMR ([D_6]DMSO, RT): δ = 16.0 (d, ^3J(P,C) = 6 Hz, CH_3), 62.6 (d, ^2J(P,C) = 6 Hz, OCH_2) ppm; $^{13}C\{^{19}F\}$ NMR ([D_6]DMSO, RT): δ = 95.8 (d, ^1J(P,C) = 188 Hz, P-C), 138.0 (d, ^2J(P,C) = 15 Hz, CF), 141.3 (d, ^3J(P,C) = 3 Hz, C-OH), 147.0 (d, ^4J(P,C) = 2 Hz, C-F) ppm; ^{19}F NMR ([D_6]DMSO, RT): δ = –135.2 (m, 2F, CF-*ortho*), –160.2 (m, 2F, CF-*meta*) ppm; $^{31}P\{^1H\}$ NMR ([D_6]DMSO, RT): δ = 5.8 (m, 1P, P) ppm. IR (ATR): $\tilde{\nu}$ = 3372 (w), 2958 (w), 2882 (w), 2652 (w), 2596 (w), 2544 (w), 1774 (w), 1724 (w), 1645 (w), 1599 (w), 1524 (m), 1483 (w), 1441 (w), 1394 (w), 1369 (w), 1339 (w), 1297 (w), 1271 (w), 1233 (m), 1190 (w), 1164 (w), 1136 (m), 1128 (m), 1108 (m), 1020 (s), 966 (s), 873 (w), 852 (w), 804 (m), 779 (w), 748 (w), 727 (w), 652 (w), 600 (m), 572 (m), 508 (w), 481 (w), 456 (w), 438 (w), 412 (w) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 627.0 (65) $[2M + Na]^+$, 366.1 (12), 325.1 (100) $[M + Na]^+$, 303.1 (19) $[M + H]^+$. (ESI, neg.): *m/z* (%) = 300.9 (100) $[M – H]^–$. HRMS: calcd. for $C_{10}H_{11}O_4F_4PNa^+$ 325.02233, found 325.02240.

Synthesis of Cyclotriphosphazene 9: A sample of dry K_2CO_3 (2.61 g, 18.9 mmol) was suspended in dry THF and hexachlorotriphosphazene (470 mg, 1.35 mmol) was added. After stirring for 10 minutes *p*-HO(C_6F_4)P(O)($OMe)_2$ (**7**) (2.41 g, 8.80 mmol) in dry THF (10 mL) was added in one portion. After stirring for 18 hours the solvent was evaporated. The crude product was dissolved in ethyl acetate (70 mL) and washed twice with NaOH solution (1 M, 50 mL) and water (50 mL). The organic phase was dried with $MgSO_4$. Evaporation of the solvent yielded 2.14 g of the pure product (1.21 mmol, 90 %) as a colorless solid. Single crystals suitable for X-ray analysis were obtained by diffusion of *n*-pentane into a THF solution of the product. ^{1}H NMR ([D_6]DMSO, RT): δ = 3.80 (d, ^3J(P,H) = 12 Hz, 36H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR ([D_6]DMSO, RT): δ = 53.7 (t, ^1J(P,C) = 6 Hz, OCH_3) ppm; $^{13}C\{^{19}F\}$ NMR ([D_6]DMSO, RT): δ = 105.5 (d, ^1J(P,C) = 180 Hz, CP), 130.7 (m, C-O), 140.2 (dm, ^2J(P,C) = 15 Hz, CF), 146.8 (d, ^3J(P,C) = 2 Hz, CF) ppm; ^{19}F NMR ([D_6]DMSO, RT): δ = –131.7 (m, 2F, CF-*ortho*), –152.6 (m, 2F, CF-*meta*) ppm; ^{31}P NMR ([D_6]DMSO, RT): δ = 8.8 (s, 3P, N-P=N), 6.1 (m, 6P, P(O)$(OMe)_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3472 (m), 3013 (m), 2966 (w), 2917 (w), 2859 (w), 1645 (m), 1504 (s), 1486 (s), 1399 (w), 1305 (m), 1293 (m), 1269 (s), 1241 (s), 1184 (m), 1109 (s), 1051 (s), 1029 (s), 982 (s), 915 (s), 884 (w), 843 (m), 833 (m), 795 (m), 775 (w), 754 (w), 656 (w), 598 (m), 578 (m), 550 (m), 516 (w), 490 (w), 455 (w), 419 (w), 411 (w), 398 (w) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 1795.8 (100) $[M + Na]^+$, 909.3 (13) $[M + 2Na]^{2+}$. MS (ESI, neg.): *m/z* (%) = 1757.7 (100), $[M – CH_3]^–$, 1515.7 (94) $[M – \{C_6F_4P(O)(OCH_3)_2\}]^–$. HRMS: calcd. for $C_{48}H_{36}O_{24}F_{24}N_3P_9H_2^{2+}$ 887.4545, found 887.4564.

Synthesis of Cyclotriphosphazene 10: Dried K_2CO_3 (2.96 g; 21.4 mmol) was suspended in THF (60 mL) and hexachlorotriphosphazene (530 mg; 1.5 mmol) was added. A sample of HO(C_6F_4)P(O)$(OEt)_2$ (**8**) (3.00 g; 9.9 mmol) was dissolved in THF (30 mL) and added to the reaction mixture. After stirring for 3 days at room temperature the solvent was evaporated and the crude product dissolved in ethyl acetate (100 mL). The organic phase was washed with aqueous NaOH (2 × 50 mL; 1 M) and water (100 mL). The organic layer was separated and dried with Mg_2SO_4. Evaporation of the solvent and column chromatographic workup (EtOAc/THF = 2:1) yielded 1.96 g of cyclic phosphazene **10** (1.01 mmol; 66 %; R_f = 0.5) as a colorless oil. ^{1}H NMR ([D_6]DMSO, RT): δ = 1.27 (td, ^3J(H,H) = 7 Hz, ^4J(P,H) = 1 Hz, 36H, CH_3), 4.17 (m, 24H, OCH_2) ppm; $^{13}C\{^1H\}$ NMR ([D_6]DMSO, RT): δ = 15.8 (d, ^3J(P,C) = 6 Hz, CH_3), 63.4 (d, ^2J(P,C) = 6 Hz, O-CH_2) ppm; $^{13}C\{^{19}F\}$ NMR ([D_6]DMSO, RT): δ = 106.6 (d, ^1J(P,C) = 178 Hz, C-P), 130.7 (m, C-O), 140.2 (dm, ^2J(P,C) = 14 Hz, C-F), 146.8 (d, ^3J(P,C) = 2 Hz, C-F) ppm; ^{19}F NMR

([D_6]DMSO, RT): δ = –131.8 (m, 2F, CF-*ortho*), –152.8 (m, 2F, CF-*meta*) ppm; ^{31}P NMR ([D_6]DMSO, RT): δ = 8.9 (s, 3P, P=N), 3.0 (s, 6P, P(O)$(OEt)_2$) ppm. IR (ATR): $\tilde{\nu}$ = 2958 (w), 2921 (w), 2852 (w), 1736 (w), 1641 (w), 1501 (w), 1473 (m), 1395 (w), 1375 (w), 1292 (w), 1257 (m), 1236 (m), 1161 (w), 1092 (s), 1011 (s), 981 (s), 907 (m), 878 (m), 792 (s), 702 (w), 660 (w), 629 (w), 572 (m), 490 (w), 458 (w), 395 (m), 386 (m) cm^{-1}. MS (ESI, pos.): *m/z* (%) = 1964.1 (30) [M + Na]$^+$, 993.5 (100) [M + 2Na]$^{2+}$. HRMS: calcd. for $C_{60}H_{60}N_3O_{24}F_{24}P_9H_2^{2+}$ 971.54839, found 971.5480.

Synthesis of Polyphosphazene 11: Dried K_2CO_3 (3.60 g; 26.0 mmol) was suspended in THF (40 mL) and HO(C_6F_4)P(O)$(OEt)_2$ (**8**) (3.32 g; 11.0 mmol) was added to the suspension. After stirring for 30 minutes polydichlorophosphazene (640 mg; 5.52 mmol)in THF (20 mL) was added in one portion. After stirring for 2 days at room temperature the solvent was evaporated and the crude product dissolved in ethyl acetate (70 mL). The organic phase was washed with aqueous NaOH (1 × 10 mL; 1 M) and water (10 mL). The phases were separated and the aqueous phases extracted with DCM (2 × 20 mL). The combined organic phases were dried with Mg_2SO_4. Separation from the solvent in vacuo yielded 1.70 g of polyphosphazene **11** (2.63 mmol; 48 %). GPC: M_n:1860 g/mol; M_w: 1910 g/mol; *D*: 1.03. ^{1}H NMR ($CDCl_3$, RT): δ = 1.23–1.42 (m, 3H, CH_3), 4.05–4.32 (m, 2H, OCH_2) ppm; ^{19}F NMR ($CDCl_3$, RT): δ = –136.7 (broad, m, 2F, CF-*ortho*), –156.7 (broad, m, 2F, CF-*meta*) ppm; ^{31}P NMR ($CDCl_3$, RT): δ = 3.45–5.73 (m, 2P, P(O)$(OEt)_2$), –15.7 to –22.0 (m, 1P, P=N) ppm. IR (KBr): $\tilde{\nu}$ = 3443 (m), 2989 (m), 2964 (m), 2935 (m), 2916 (m), 2873 (w), 1644 (m), 1502 (s), 1485 (s), 1445 (w), 1396 (m), 1370 (m), 1296 (s), 1262 (s), 1164 (m), 1102 (s), 1051 (s), 1021 (s), 983 (s), 901 (m), 887 (w), 799 (m), 746 (w), 655 (w), 576 (m), 506 (w), 478 (w), 392 (w) cm^{-1}.

Synthesis of Cyclotriphosphazene 12: A sample of phosphazene **10** (1.94 g, 99.9 µmol) was dissolved in DCM (15 mL) and Me_3SiBr (3.7 g; 24 mmol) was added at 0 °C in one portion. After stirring the reaction mixture for 24 hours methanol (20 mL) was added slowly at 0 °C. Separation from the solvent and drying in vacuo at 120 °C yielded 1.55 g of phosphazene **12** (96.5 µmol; 97 %). ^{1}H NMR ([D_6]DMSO, RT): δ = 10.07 (s, 12H, P-OH) ppm; ^{13}C{^{19}F} NMR ([D_6]DMSO, RT): δ = 112.0 (d, ^1J(P,C) = 164 Hz, P-C), 129.0 (m, CO), 139.7 (d, ^2J(P,C) = 13 Hz, CF), 154.9 (s, CF) ppm; ^{19}F NMR ([D_6]DMSO, RT): δ = –132.2 (m, 2F, CF-*ortho*), –153.5 (m, 2F, CF-*meta*) ppm; ^{31}P NMR ([D_6]DMSO, RT): δ = 8.8 (s, 3P, P=N), –2.6 (s, 6P, P(O)$(OH)_2$) ppm. IR (ATR): $\tilde{\nu}$ = 2962 (w), 2686 (w), 2196 (w), 1686 (w), 1639 (w), 1503 (w), 1472 (s), 1401 (w), 1306 (w), 1294 (w), 1249 (m), 1234 (m), 1187 (w), 1164 (w), 1110 (s), 1094 (s), 1008 (m), 976 (s), 900 (s), 868 (s), 822 (s), 790 (s), 761 (s), 731 (s), 662 (m), 572 (s), 516 (m), 470 (s), 451 (s), 417 (s) cm^{-1}. MS (ESI, neg.): *m/z* (%) = 1603.7 (100) [M – H]$^-$, 1523.7 (50) [M – H_2PO_3]$^-$, 1505.7 (41) [M – H_2O – H_2PO_3]$^-$, 1487.7 (19), 1443.7 (44), 1425.7 (29) [M – $H_5O_7P_2$]$^-$, 1407.7 (29), 1363.7 (39), 1345.7 (84), 1283.7 (19), 1265.8 (78), 1245.7 (18), 1068.7 (12), 801.2 (36) [M – 2H]$^{2-}$, 791.8 (11), 533.7 (10) [M – 3H]$^{3-}$. HRMS: calcd. for $C_{36}H_{12}N_3O_{24}F_{24}P_9H^+$ 1605.7144, found 1605.7153.

Syntheses of Polyphosphazene 13: A sample of polyphosphazene **11** (1.23 g; 1.9 mmol)) was dissolved in dichloromethane (40 mL). At 0 °C Me_3SiBr (1.23 g; 1.9 mmol) was added dropwise. The reaction mixture was stirred for 36 hours. The solvent was evaporated and methanol (10 mL) and water (10 mL) were added to the crude product. After stirring the mixture for one hour the solvents were evaporated to yield 910 mg of the polymeric phosphazene **13** (1.7 mmol; 90 %) s.o.as a brittle brown solid. ^{1}H NMR ([D_6]DMSO, RT): δ = 9.95 (broad, s, P-OH) ppm; ^{19}F NMR ([D_6]DMSO, RT): δ = –133.2 (broad, m, 2F, CF-*ortho*), –153.1 (broad, m, 2F, CF-*meta*) ppm; ^{31}P NMR ([D_6]DMSO, RT): δ = –12.0 to –23.0 (m, 1P, P=N), –1.5 to –3.5 (m, 2P, P(O)$(OH)_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3397 (m, broad), 2300 (m, broad), 1731 (m, broad), 1644 (s), 1504 (s), 1484 (s), 1397 (m), 1293 (s), 1273 (s), 1107 (s), 1024 (s), 983 (s), 888 (s), 816 (m), 795 (m), 762 (m), 737 (m), 660 (w), 560 (s), 505 (m), 490 (m), 467 (m), 458 (m), 417 (m) cm^{-1}. IEC [mmol g^{-1}]: calcd. 3.7 (-PO_3H^-), 7.5 (-PO_3^{2-}), found: 3.5 (-PO_3H^-), 6.8 (-PO_3^{2-}).

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