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 polyand cyclotriphosphazenes with p-HO(C6F4)P(O)(OR)3 (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 fulfill 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. H2 or MeOH) and oxidant (e.g. O2), 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 side-groups 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,6] They feature sulfonic acid groups as well as sulfonamide 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
Results and Discussion

Synthesis and Characterization of the Precursor \( p\text{-HO(C}_6\text{F}_4\text{)}\text{P(O)(OR)}_2 \); \( R = \text{Me, Et} \)

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 tetrafluoroanisolinate 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.

\[ \text{MeOH, 24 h, reflux} \]

\[ \text{OH} \]

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 catalytic 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 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 \( \nu(\text{P=O}) \) stretching vibration. Characteristic bands for alkyl phosphonic esters are observed at 1196 cm\(^{-1}\).

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 \( \nu(\text{P=O}) \) stretching vibration. Characteristic bands for alkyl phosphonic esters are observed at 1196 cm\(^{-1}\) (\( \nu(\text{P=O}) \)) and 966 cm\(^{-1}\) (\( \nu(\text{P=O}) \))
Colorless single crystals of 8, suitable for an X-ray diffraction analysis, are grown from tetrahydrofuran. The compound crystallizes in the triclinic space group $P \overline{1}$. 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).

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).

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

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$_3$P=NSiMe$_3$ as reported by Allcock et al.

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$_3$P=NSiMe$_3$ with PCl$_5$.

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$_3$SiBr in dichloromethane at room temperature. When the silylation of the ester...
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 31P 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 pKs1 and pKs2 values amount to 2.1 and 6.7. The pKs1 value is only tentative due to the inapplicability of the Nernst equation at pKs 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 31P 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, C₆H₅P(O)(OH)₂ and C₆F₅P(O)(OH)₂ were analysed as references (Figure 5). As expected, all fluorinated derivatives exhibit a higher conductivity than C₆H₅P(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
is the rampant increase in conductivity of polyphosphazene 13 in comparison to the other samples, starting at 3.67 × 10⁻⁸ 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 C₆F₅P(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.

**Conclusion**

A convergent approach for the incorporation of the tetrafluorophosphonate building block into cyclic and polymeric phosphazenes is described. The synthesis is based on the reaction of the precursors p-HO(C₆F₅)P(O)(OR)₂ (R = Me: 7, Et: 8) with polymeric or trimeric chlorinated phosphazenes in the presence of K₂CO₃. The reaction produces the corresponding organophosphazenes. The cyclotriphosphazenes 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 (Et₂N)₂PCl [22] was synthesized as described in the literature. For the synthesis of Cl₃P=NSiMe₃ [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 N₂ 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. IR spectra were recorded with a Bruker Model Avance III 300 spectrometer (31P 121.5 MHz; 19F 282.4 MHz; 13C 75.5 MHz; 1H 300.1 MHz) with positive shifts being downfield from the external standards [TMS (31P); HCl, CCl₂F₂ (19F); 85% H₃PO₄ (31P)]. 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. ESI mass spectra were recorded using an Autospec X magnetic 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 Elektro nische 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-20A5), two pumps (LC-20AD), autosampler (SIL-20AHT), 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 column: 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 % LiBr); Flowrate: 1 mL/min; Inject: 50 μL; Sample concentration: 2.5 mg/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 (rh instruments GmbH & Co. KG), in combination with a modified Microcell HC setup (rh 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 Met-.
rohm 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; C6H5P(O)(OH)2:
0.089 cm−1; C6F5-P(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 Su-
pernova diffractometer. The crystals were kept at 100.0(1) K during
data collection.

Deposition Numbers 1908916 and 1908917 contain the supplemen-
tary crystallographic data for this paper. These data are provided
for X-ray analysis were obtained by diffusion of n-pentane into a THF
solution of the product. 1H NMR (CDCl3, R T ) : δ = 3.86 (d, 3P, N-P=N), 6.1 (s,
δ = 5.8 (m, 1P, P) ppm. IR (ATR):
ν = 95.8 (d,1
ν = 600 (m), 572 (m), 508 (w),
1528 (w), 2858 (w), 2808 (w), 2655 (w), 2592 (w), 2544 (w), 2544 (w), 1774 (w),
1465 (w), 1599 (m), 1524 (m), 1483 (w), 1441 (w), 1394 (w),
1369 (w), 1339 (w), 1297 (w), 1271 (w), 1233 (m), 1190 (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. M5 (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: calc.
for C48H36O24F24N3P9H2PNa+ : 523.02233, found 523.02240.

Synthesis of Cyclotriphosphazene 9: A sample of dry K2CO3
(2.61 g, 18.9 mmol) was suspended in dry THF and hexachlorotri-
phosphazene (470 mg, 1.35 mmol) was added. After stirring for 10
minutes p-HO(CF3)2P(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. 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

Synthesis of Cyclotriphosphazene 10: Dried K2CO3
(2.96 g, 21.4 mmol) was suspended in THF (60 mL) and hexachlorotri-
phosphazene (530 mg, 1.5 mmol) was added. A sample of
HClO4 (50 mL, 6 mol/L) was added to the solution. 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 NaOH solution (2 x 50 mL) and water (100 mL).

The organic layer was separated and dried with MgSO4. Evapora-
tion of the solvent and column chromatographic workup (EtOAc/THF = 2:1) yielded 1.96 g of cyclophosphazene 10 (1.01 mmol; 66 %; Rf = 0.5) as a colorless oil. 1H NMR (CDCl3, R T ) : δ = 1.27 (td, 1J(H) = 7 Hz, 1J(P) = 1 Hz, 36H, CH3), 4.17 (m, 24H, OCH3) ppm;
13C{1H} NMR (CDCl3, R T ) : δ = 15.8 (d, 2J(C) = 6 Hz, CH3), 63.4 (d, 2J(C) = 6 Hz, O-C6H5) ppm; 19F NMR (CDCl3, R T ) : δ = 106.6 (d, 1J(F) = 178 Hz, C-F) ppm; 13C{19F} NMR (CDCl3, R T ) : δ = 157.6 (m, CF, OCH3).
Synthesis of Polyphosphazene 11: Dried K₂CO₃ (3.60 g; 26.0 mmol) was dissolved in THF (40 mL) and HO(C₆F₄)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; 1M) and water (10 mL). THF (20 mL) was added in one portion. After stirring for 2 days at 0 °C. Separation from the solvent and drying in vacuo at 40 °C yielded 1.70 g of the product. 

The phases were separated and the aqueous phases extracted with dichloromethane (2 × 20 mL). The combined organic phases were dried with MgSO₄. Separation from the solvent in vacuo yielded 1.70 g of the product. 1H NMR (CDCl₃, δ): δ = 1.03.1H NMR (CDCl₃, δ): δ = 2962 (w), 2686 (w), 2196 (w), 1686 (w), 1639 (w), 1549 (s), 1487 (s), 1433 (s), 1370 (s), 1367 (s), 1345 (s), 1283 (s), 1266 (s), 1245 (s), 1226 (s), 1216 (s), 1102 (s), 1012 (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 Me₃SiBr (3.7 g; 24 mmol) was added at 0 °C in one portion. After stirring at room temperature for 24 hours methanol (20 mL) was added to the reaction mixture for 24 hours. Methanol (20 mL) was added to the reaction mixture for 24 hours. The solvent was evaporated and the crude product dissolved in dichloromethane (40 mL). The solvent was evaporated and methanol (10 mL) and water (10 mL) were added to the crude product. After stirring the mixture for 1 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. 1H NMR (CD₂Cl₂, δ): δ = 9.95 (broad, s, P=O) ppm; 13F NMR (CD₂Cl₂, δ): δ = −133.2 (broad, m, CF, ortho), −153.1 (broad, m, CF, meta) ppm; 31P NMR (CD₂Cl₂, δ): δ = −12.0 to −23.0 (m, 1P, P=O), −1.5 to −3.5 (m, 2P, P(O)H₂) ppm. IR (KBr): 9 = 3397 (m, broad), 2300 (m, broad), 1731 (m, broad), 1644 (s), 1504 (s), 1484 (s), 1397 (m, 1293), 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): calcld.: 3.7 (PO₃H⁻), 7.5 (PO₃⁻), found: 3.5 (PO₃H⁻), 6.8 (PO₃⁻).

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