Supporting Information

for

New triazinephosphonate dopants for Nafion proton exchange membranes (PEM)

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Experimental data
1. Experimental

1.1. Materials and Methods

Cyanuric chloride (1) and diethyl (4-aminophenyl)methylphosphonate (17) are commercially available (Sigma-Aldrich, Alfa Aesar). Other acquired reagents and deuterated solvents were used as received, without further purification. Solvents and air-sensitive reagents were distilled under a dry nitrogen atmosphere. Dry THF was distilled from sodium benzophenone ketyl.

A Nafion N115 film was acquired from FuelCell Store and a 20 wt % mixture in lower aliphatic alcohols and water (34%) of Nafion perfluorinated resin solution was purchased from Sigma Aldrich.

Purification of reaction products was done by column chromatography on silica gel (230–400 mesh) with the appropriate eluent mixture and using a positive pressure of nitrogen.

1.2. Spectroscopic characterization

The characterization of the dopants was carried out by Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopy and mass spectra spectrometry (MS). $^1$H, $^{13}$C and $^{31}$P NMR characterization was done using different one- and two-dimensional techniques, and were
obtained on a Bruker Avance III HD 400 (\(^1\)H 400 MHz, \(^{13}\)C NMR 100 MHz, \(^{31}\)P 162 MHz) spectrometers, with the chemical shifts (\(\delta\)) indicated in ppm, and coupling constants (\(J\)) in Hz.

The FTIR characterization of the dopants was done on a PerkinElmer FT-IR Spectrum BX Fourier Transform spectrometer, using KBr discs, and the characterization of the membranes was carried out on a Perkin Elmer Spectrum Two, with an attenuated total reflectance (ATR) module, with a wavenumber range from 450 to 4000 cm\(^{-1}\), and their band wavelengths are quoted in cm\(^{-1}\).

Low-resolution and high-resolution (HRMS) mass spectra (MS) were performed on an APEX-Q (Bruker Daltonics) instrument at ‘C.A.C.T.I. - Unidad de Espectrometria de Masas’, at University of Vigo, Spain. Melting points were determined on a Reichert Thermovar melting point apparatus and are uncorrected.

1.3. Proton conductivity

In-plane proton conductivity (\(\sigma\)) evaluation of the new membranes was performed by electrochemical impedance spectroscopy (EIS), on a commercial BT-112 BekkTech conductivity cell (Scribner Associates Inc.), with a frequency response analyzer Solartron 1250, coupled to a Solartron 1286 electrochemical interface. The measurements were performed with a test signal amplitude of 10 mV, over a frequency range of 65 kHz to 5 Hz. The bulk resistance (\(R_b\)) of the membranes were calculated using the ZView software (Version2.6b, Scribner Associates). A Binder KBF 115 climatic chamber was used to perform the measurements at a temperature of 60 \(^\circ\)C and different relative humidity (RH) conditions (40, 60 and 80%). The measurements were performed directly from the temperature-controlled humidity chamber, after a 2 h equilibration period.

The proton conductivity (\(\sigma\)) was calculated using the equation (1)

\[
\sigma = \frac{L}{AR_b}
\]

where \(L\) - distance between the two electrodes (cm), \(R_b\) – bulk resistance (\(\Omega\)), and \(A\) - cross-sectional area (cm\(^2\)).
1.4. Preparation of the dopants

Synthesis of diethyl 4-hydroxyphenylphosphonate (2)

![Ph3P](image)

To a solution of 4-bromophenol (3, 400 mg, 2.31 mmol) in EtOH (25 mL) was added diethyl phosphonate (0.45 mL, 3.48 mmol), triethylamine (0.65 mL, 4.62 mmol) and Pd(PPh₃)₄ (134 mg, 0.116 mmol, 5%). The reaction mixture was heated to reflux and stirred under N₂ for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure, the residue was dissolved in EtOAc and extracted with 10% aqueous NaOH solution. The aqueous phase was washed with EtOAc, acidified with 10% aqueous HCl solution and extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (1:1 EtOAc:acetone) to give compound 2 [1] (383 mg, 72%) as an oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.31 (t, J = 7.2, 6H, 2x OCH₂C₃H₃), 4.04-4.13 (m, 4H, 2x OC₃H₂CH₃), 6.98 (dd, J = 8.4 and J = 3.6, 2H, ArH), 7.64 (dd, J = 13.2 and J = 8.4, 2H, ArH). ³¹P NMR (162 MHz, H₃PO₄/ CDCl₃): δ (ppm) = 20.6.

Synthesis of diethyl 4-nitrophenylphosphonate (6)

![Ph3P](image)

To a solution of 1-bromo-4-nitrobenzene (5, 500 mg, 2.48 mmol) in EtOH (25 mL) was added diethyl phosphonate (0.48 mL, 3.72 mmol), triethylamine (0.69 mL, 4.96 mmol) and Pd(PPh₃)₄ (150 mg, 0.124 mmol, 5%). The reaction mixture was heated to reflux and stirred under N₂ for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (EtOAc) to give compound 6 [1] (511 mg, 79%) as a solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.33 (t, J = 7.2, 6H, 2x OCH₂C₃H₃), 4.09-4.20 (m, 4H, 2x OC₃H₂CH₃), 7.99 (dd, J = 12.6 and J = 8.4, 2H, ArH), 8.29 (dd, J = 8.4 and J = 3.2, 2H, ArH). ³¹P NMR (162 MHz, H₃PO₄/ CDCl₃): δ (ppm) = 15.0.
Synthesis of diethyl (4-aminophenyl)phosphonate (4)

To a solution of compound 6 (350 mg, 1.35 mmol) in EtOH (10 mL) was added 10% palladium on activated carbon (70 mg, 20 w/w %) and the solution was stirred at room temperature under H_2 atmosphere during 2 h. The reaction mixture was filtered through a plug of Celite®, washed through with EtOH and concentrated in vacuo to yield compound 4 [2] as a yellow solid (293 mg, 95%). ^1H NMR (400 MHz, CDCl₃): δ (ppm) = 1.30 (t, J = 7.2, 6H, 2x OCH_3CH₂), 4.02-4.13 (m, 4H, 2x OCH_3CH₃), 6.92 (d, J = 5.2, 2H, ArH), 7.63 (dd, J = 12.6 and J = 8.4, 2H, ArH). ^31P NMR (162 MHz, H_3PO₄/ CDCl₃): δ (ppm) = 20.0.

Synthesis of 1-(benzyloxy)-4-(bromomethyl)benzene (9)

A solution of [4-(benzyloxy)phenyl]methanol (8, 2.40 g, 11.20 mmol) in acetic acid (7.5 mL) was cooled to 0 ºC, and a solution of hydrobromic acid (7.2 mL, 33% in acetic acid) was added to the solution. The mixture was warmed to room temperature during 30 min. The reaction mixture was added to ice-water, and the white solid was filtered and washed with water. The white solid was redissolved in EtOAc, washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure to afford compound 9 [3] (2.53 g, 81%) as a white solid. ^1H NMR (400 MHz, CDCl₃): δ (ppm) = 4.50 (s, 2H, CH₂), 5.07 (s, 2H, OCH₃), 6.93-6.95 (m, 2H, ArH), 7.32-7.44 (m, 7H, ArH).

Synthesis of diethyl [4-(benzyloxy)phenyl]methylphosphonate (10)
1-(Benzylxy)-4-(bromomethyl)benzene (9, 1.02 g, 3.68 mmol) and triethyl phosphite (1 mL, 5.83 mmol) in a DMF solution (3 mL), under a nitrogen atmosphere, were heated at 155 °C for 3 h. Upon cooling, water was added to the mixture. The resulting aqueous layer was extracted with EtOAc and the combined organic extract was dried over anhydrous MgSO₄ and filtered. The solution was dried in a vacuum rotary evaporator to afford an oil that, after being purified by column chromatography (2:3 acetone/petroleum ether), gave compound 10 [4] as colorless oil, in quantitatively yield. 

1H NMR (400 MHz, CDCl₃): δ (ppm) = 1.28 (t, J = 7.2, 6H, 2x OCH₂CH₃), 3.09 (d, J = 21.2, 2H, CH₂P), 3.95-4.05 (m, 4H, 2x OCH₂CH₃), 5.04 (s, 2H, OCH₂Ar), 6.92 (d, J = 8.4, 2H, ArH), 7.21 (dd, J = 8.8 and J = 2.4, 2H, ArH), 7.30-7.44 (m, 5H, ArH). 31P NMR (162 MHz, H₃PO₄/CDCl₃): δ (ppm) = 26.9.

Synthesis of diethyl 4-hydroxybenzylphosphonate (7)

To a solution of compound 10 (1.28 g, 3.83 mmol) in EtOH (25 mL) was added 10% palladium on activated carbon (256 mg, 20 w/w %) and the solution was stirred at room temperature under H₂ atmosphere for 24 h. The reaction mixture was filtered through a plug of Celite®, rinsed with EtOH and concentrated in vacuo to yield compound 7 [4] as a white solid (930 mg, 99%). 1H NMR (400 MHz, CDCl₃): δ (ppm) = 1.26 (t, J = 7.2, 6H, 2x OCH₂CH₃), 3.06 (d, J = 20.8, 2H, CH₂P), 3.97-4.07 (m, 4H, 2x OCH₂CH₃), 6.14 (br s, 1H, OH), 6.64 (d, J = 8.0, 2H, ArH), 7.03 (dd, J = 8.4 and J = 2.8, 2H, ArH). 31P NMR (162 MHz, H₃PO₄/CDCl₃): δ (ppm) = 27.6.

Synthesis of diethyl [hydroxy(4-hydroxyphenyl)methyl]phosphonate (11) and tetraethyl [(4-hydroxyphenyl)methylene]bisphosphonate (13)

To a solution of 4-hydroxybenzaldehyde 12 (337 mg, 2.759 mmol) and triethyl phosphite (1.4 mL, 8.278 mmol), was added ZnBr₂ (62 mg, 0.276 mmol) and the mixture was stirred overnight, under N₂, at room
temperature. The reaction mixture was poured into an ice aqueous HCl (1 M) solution and the obtained aqueous layer was extracted with EtOAc. The combined organic extracts were dried over anhydrous MgSO₄, filtered and the solvent removed under vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound 11 [5] (328 mg, 46%) and compound 13 [6] (434 mg, 42%), as white solids.

Compound 11: ¹H NMR (400 MHz, DMSO): δ (ppm) = 1.12 (t, J = 7.2, 3H, OCH₂CH₃), 1.18 (t, J = 7.2, 3H, OCH₂CH₃), 3.79 - 4.00 (m, 4H, 2x CH₂CH₂), 4.78 (dd, J = 12.0 and J = 5.6, 1H, CHP(OH)), 5.97 (dd, J = 16.0 and J = 5.6, 1H, CHP(OH)), 6.72 (d, J = 8.0, 2H, ArH), 7.22 (dd, J = 8.4 and J = 2.0, 2H, ArH), 9.38 (s, 1H, ArOH). ³¹P NMR (162 MHz, H₃PO₄/ DMSO): δ (ppm) = 22.3.

Compound 13: ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.13 (t, J = 7.0, 6H, 2x OCH₂CH₂), 1.28 (t, J = 7.0, 6H, 2x OCH₂CH₂), 3.63 (t, J = 25.4, 1H, P₂CH₂), 3.87 (m, 2H, OCH₂CH₂), 4.01 (m, 2H, OCH₂CH₂), 4.11 (m, 4H, 2x CH₂CH₂), 6.68 (d, J = 8.4, 2H, ArH), 7.20 (d, J = 8.8, 2H, ArH). ³¹P NMR (162 MHz, H₃PO₄/ DMSO): δ (ppm) = 19.0.

**Synthesis of tetraethyl [(4-hydroxyphenyl)methylene]bisphosphonate (13)**

Small portions of sodium metal (0.3 g, 13 mmol) were cautiously added to diethyl phosphonate (5 mL) at room temperature. Compound 12 (122 mg, 1.0 mmol) was carefully added to this solution and the reaction mixture was stirred at room temperature for 48 h, after which it was quenched with water (100 mL). The aqueous layer was extracted with CHCl₃ (3x 50 mL). The CHCl₃ solution was concentrated under reduced pressure and the obtained residue was washed with hexane and dried in vacuo. The resulting oil was purified by column chromatography (1:1 EtOAc:Acetone) to give compound 13 [6] (326 mg, 86%) as colourless crystals.
Synthesis of diethyl (4-nitrophenyl)(hydroxy)methylphosphonate (16)

\[
\begin{align*}
\text{HO} & \quad \text{PO}_3\text{Et}_2 \\
\text{NO}_2 & \\
\end{align*}
\]

In a manner similar to [7], diethyl phosphonate (2.1 mL) was added to a suspension of NaOMe (1.530 g, 82.65 mmol) in DCM (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C, under N\textsubscript{2}, during 1 h, and 4-nitrobenzaldehyde (15, 2.00 g, 13.23 mmol) was added. The mixture was stirred overnight at room temperature. The reaction mixture was then quenched by addition of aqueous HCl solution (0.1 M) and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and dried over anhydrous MgSO\textsubscript{4}. After filtration, the solvent was removed under reduced pressure, followed by recrystallization from Et\textsubscript{2}O to give compound 16 [8] as a white solid (3.10 g, 81%).

\[\text{^{1}H NMR (400 MHz, CDCl}_3): \delta (ppm) = 1.27 (t, J = 7.2, 3H, OCH}_2\text{CH}_3), 1.30 (t, J = 7.2, 3H, OCH}_2\text{CH}_3), \]
\[4.07-4.15 (m, 4H, 2x OC\text{H}_2\text{CH}_3), 5.18 (d, J = 12.0, 1H, CHP(OH)), 7.68 (d, J = 7.2, 2H, ArH), 8.23 (d, J = 8.8, 2H, ArH). \]
\[\text{^{31}P NMR (162 MHz, H}_3\text{PO}_4/\text{CDCl}_3): \delta (ppm) = 19.7. \]
\[\text{^{1}H NMR (400 MHz, DMSO): \delta (ppm) = 1.67 (t, J = 7.2, 3H, OCH}_2\text{CH}_3), 1.78 (t, J = 7.2, 3H, OCH}_2\text{CH}_3), 3.91 -4.06 (m, 4H, 2x OC\text{H}_2\text{CH}_3), \]
\[5.20 (dd, J = 15.6 and J = 5.6, 1H, CHP(OH)), 6.53 (dd, J = 14.6 and J = 5.6, 1H, CHP(OH)), 7.69 (dd, J = 8.8 and J = 2.0, 2H, ArH), 8.22 (d, J = 8.4, 2H, ArH). \]
\[\text{^{31}P NMR (162 MHz, H}_3\text{PO}_4/\text{DMSO}): \delta (ppm) = 20.3. \]

Synthesis of diethyl (4-aminophenyl)(hydroxy)methylphosphonate (14)

\[
\begin{align*}
\text{HO} & \quad \text{PO}_3\text{Et}_2 \\
\text{NH}_2 & \\
\end{align*}
\]

To a solution of compound 16 (384 mg, 1.328 mmol) in EtOH (10 mL) was added 10% palladium on activated carbon (77 mg, 20 w/w %) and the solution was stirred at room temperature under H\textsubscript{2} during 3 h. The reaction mixture was filtered through a plug of Celite\textsuperscript{®}, washed through with EtOH and concentrated in vacuo to yield compound 14 [8] as a pale yellow solid (341 mg, 99%).

\[\text{^{1}H NMR (400 MHz, DMSO): \delta (ppm) = 1.10 (t, J = 7.2, 3H, OCH}_2\text{CH}_3), 1.18 (t, J = 7.2, 3H, OCH}_2\text{CH}_3), 3.74 -3.98 (m, 4H, 2x OC\text{H}_2\text{CH}_3), 4.66 (dd, J = 11.6 and J = 5.2, 1H, CHP(OH)), 5.06 (br s, 2H, ArNH}_2), 5.82 (dd, J =
\]

16.4 and J = 5.6, 1H, CHP(OH), 6.50 (d, J = 8.0, 2H, ArH), 7.06 (d, J = 8.0, 2H, ArH). \(^{31}\)P NMR (162 MHz, H\(_2\)PO\(_4\)/ DMSO): \(\delta\) (ppm) = 22.7.

**Synthesis of tetraethyl \(((6\text{-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl)bis(4,1-phenylene)bis(phosphonate)}} (TP1)**

![Chemical structure of TP1](image)

To a solution of diethyl (4-aminophenyl)phosphonate (4, 272 mg, 1.186 mmol, 3.3 equiv) in THF (10 mL), under \(N_2\), was added cyanuric chloride (1, 65 mg, 0.351 mmol) and DIPEA (0.6 mL, 3.580 mmol). The mixture was heated to reflux and stirred under \(N_2\) overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound TP1 (58 mg, 22%) as a white solid.  

\(\nu_{\text{max}}\) (KBr) (cm\(^{-1}\)): 3266, 3132, 3049, 2982, 2931, 2908, 1616, 1603, 1568, 1548, 1489, 1451, 1407, 1371, 1318, 1296, 1277, 1224, 1190, 1164, 1135, 1097, 1053, 1026, 986, 962, 838, 801, 761, 686, 667, 561, 538, 464. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 1.33 (t, \(J = 7.2\), 12H, 4x OCH\(_2\)CH\(_3\)), 4.06-4.19 (m, 8H, 4x OCH\(_2\)CH\(_3\)), 7.74-7.83 (m, 8H, ArH), 8.18 (brs, 3H, NH). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 16.5 (d, \(J_{CP} = 6.5\), CH\(_3\)), 62.4 (d, \(J_{CP} = 5.3\), OCH\(_2\)), 120.4 (d, \(J_{CP} = 12.6\), Ar:C), 123.5 (d, \(J_{CP} = 190.4\), Ar:C), 133.0 (d, \(J_{CP} = 10.8\), Ar:C), 141.4 (Ar:C), 163.9 (C Triazine), 169.5 (C-Cl Triazine). \(^1\)P NMR (162 MHz, H\(_2\)PO\(_4\)/ CDCl\(_3\)): \(\delta\) (ppm) = 18.4. MS (ESI): \(m/z = 572\) (MH\(^{+}\)+2, 30%), 570 (MH\(^{+}\), 100%). HRMS (ESI) \(m/z\) calcd for C\(_{23}\)H\(_{31}\)ClN\(_5\)O\(_6\)P\(_2\) 570.1426 (\(^{35}\)Cl isotope) [MH]\(^{+}\), found 570.14199.

**Synthesis of tetraethyl (((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl)bis(4,1-phenylene)bis(methylene))bis(phosphonate}) (TP2)**

![Chemical structure of TP2](image)

S8
To a solution of diethyl (4-aminophenyl)methylphosphonate (17, 200 mg, 0.822 mmol, 3.4 equiv) in THF (10 mL), under N₂, was added cyanuric chloride (1, 45 mg, 0.243 mmol) and DIPEA (0.43 mL, 2.479 mmol). The mixture was heated to reflux and stirred under N₂ overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound TP2 as a white solid (159 mg, 82%). mp 211-212 °C. νmax (KBr) (cm⁻¹): 3254, 3191, 3165, 3084, 2981, 2930, 2908, 1624, 1574, 1506, 1436, 1420, 1396, 1321, 1268, 1227, 1190, 1164, 1099, 1056, 1023, 983, 970, 845, 804, 766, 713, 690, 591, 546, 537, 509. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.25 (t, J = 7.2, 12H, 4x OCH₂CH₃), 3.14 (d, J = 21.6, 4H, 2x CH₂P), 4.00-4.08 (m, 8H, 4x OCH₂CH₃), 7.25 (d, J = 8.4, 4H, Ar H), 7.51 (d, J = 8.0, 4H, Ar H), 8.31 (brs, NH). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 16.5 (d, J = 5.9, CH₃), 33.2 (d, JCP = 137.7, CH₂P), 62.4 (d, JCP = 6.7, OCH₂), 121.3 (Ar: C), 127.7 (d, JCP = 9.1, Ar: C), 130.3 (d, JCP = 5.5, Ar: C), 136.3 (d, JCP = 3.5, Ar: C), 163.6 (C Triazine), 167.8 (C-Cl Triazine). ³¹P NMR (162 MHz, H₃PO₄/ CDCl₃): δ (ppm) = 26.4. m/z = 600 (MH⁺+2, 30%), 598 (MH⁺, 100%). HRMS (ESI) m/z calcd for C₆₂H₃₅ClN₅O₆P₂ 598.17456 ([³⁵Cl isotope] [MH⁺], found 598.17323.

Synthesis of tetraethyl (((6-chloro-1,3,5-triazine-2,4-diyl)bis(azanediyl))bis(4,1-phenylene))bis(hydroxymethylene))bis(phosphonate) (TP3)

To a solution of diethyl (4-hydroxyphenyl)hydroxymethylphosphonate (14, 1.00 g, 3.857 mmol, 0.34 equiv) in THF (20 mL), under N₂, was added cyanuric chloride (1, 211 mg, 1.141 mmol) and DIPEA (2.04 mL, 11.641 mmol). The mixture was heated to reflux and stirred under N₂ overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound TP3 as a white solid (604 mg, 84%). mp 152-153 °C. νmax (KBr) (cm⁻¹): 3376, 3269, 3200, 3110, 2988, 2931, 2908, 1618, 1572, 1524, 1508, 1434, 1419, 1396, 1314, 1302, 1233, 1213, 1181, 1124, 1096, 1044, 1022, 984, 863, 842, 801, 768, 731, 697, 637, 617, 561, 472. ¹H NMR (400 MHz, DMSO): δ (ppm) = 1.15 (t, J = 7.2, 6H,
2x OCH\textsubscript{2}CH\textsubscript{3}), 1.19 (t, J = 7.2, 6H, 2x OCH\textsubscript{2}CH\textsubscript{3}), 3.86-4.01 (m, 8H, 4x OCH\textsubscript{2}CH\textsubscript{3}), 4.90 (dd, J = 12.8 and J = 5.2, 2H, 2 x CHP(OH)), 6.18 (dd, J = 15.2 and J = 4.4, 2H, 2 x CHP(OH)), 7.38 (d, J = 7.2, 4H, Ar\textsubscript{H}), 7.62 (br s, 4H, Ar\textsubscript{H}). \textsuperscript{13}C NMR (100 MHz, DMSO): δ (ppm) = 16.4 (dd, J\textsubscript{CP} = 7.4 and J\textsubscript{CP} = 5.2, C\textsubscript{H}\textsubscript{3}), 61.5 (dd, J\textsubscript{CP} = 34.6 and J\textsubscript{CP} = 7.0, OCH\textsubscript{2}), 69.0 (d, J\textsubscript{CP} = 162.5, CHP(OH)), 120.2 (Ar:C), 127.6 (Ar:C), 133.6 (Ar:C), 137.6 (Ar:C), 137.6 (Ar:C), 163.8 (C Triazine), 168.2 (C-Cl Triazine). \textsuperscript{31}P NMR (162 MHz, H\textsubscript{3}PO\textsubscript{4}/DMSO): δ (ppm) = 21.8.

m/z = 632 (MH\textsuperscript{+}+2, 30%), 630 (MH\textsuperscript{+}, 100%). HRMS (ESI) m/z calcd for C\textsubscript{25}H\textsubscript{35}ClN\textsubscript{5}O\textsubscript{8}P\textsubscript{2} 630.16439 (Cl-35 isotope) [MH\textsuperscript{+}], found 630.16318.

Synthesis of hexaethyl \{[(1,3,5-triazine-2,4,6-triyl)tris(oxy)]tris(benzene-4,1-diyl)}tris(phosphonate) (TP\textsubscript{4})

\begin{equation}
\text{ET}_2\text{O}_3\text{P} - \text{N} - \text{N} - \text{N} \quad \text{P} \quad \text{ET}_2\text{O}_3\text{P} - \text{O} - \text{O} - \text{O} - \text{N} - \text{N} - \text{N} \quad \text{P} \quad \text{ET}_2\text{O}_3\text{P}
\end{equation}

a) To a solution of diethyl (4-hydroxyphenyl)phosphonate (2, 309 mg, 1.342 mmol, 3.4 equiv) in THF (10 mL), under N\textsubscript{2}, was added cyanuric chloride (1, 73 mg, 0.397 mmol) and DIPEA (0.7 mL, 4.050 mmol). The mixture was heated to reflux and stirred under N\textsubscript{2} overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound TP\textsubscript{4} (53 mg, 17%) as white solid.

b) A mixture of diethyl 4-hydroxyphenylphosphonate (2, 256 mg, 1.112 mmol, 5.0 equiv), cyanuric chloride (1, 41 mg, 0.222 mmol) and Na\textsubscript{2}CO\textsubscript{3} (685 mg) in toluene (30 mL) was heated to reflux and stirred under N\textsubscript{2} during 48 h. The reaction mixture was cooled to room temperature and the white solid was filtered and washed with hot EtOAc. After filtration, the solvent was removed under reduced pressure to afford an oil. The resulting oil was purified by column chromatography (1:1 EtOAc/acetone) to give compound TP\textsubscript{4} (129 mg, 76%) as white solid. mp 93-95 °C. ν\textsubscript{max} (KBr) (cm\textsuperscript{-1}): 3096, 3066, 2988, 2942, 2911, 1602, 1570, 1496, 1445, 1370, 1232, 1207. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ (ppm) = 1.34 (t, J = 7.2, 18H, 6x OCH\textsubscript{2}CH\textsubscript{3}), 4.05-4.14 (m, 12H, 6x OCH\textsubscript{2}CH\textsubscript{3}), 7.28 (dd, J = 8.6 and J = 3.4, 6H, Ar\textsubscript{H}), 7.85 (dd, J = 12.8 and J = 8.4, 6H, Ar\textsubscript{H}). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ (ppm) = 16.4 (d, J\textsubscript{CP} = 6.4, CH\textsubscript{3}), 62.4 (d, J\textsubscript{CP} = 5.5, OCH\textsubscript{2}), 121.7 (d, J\textsubscript{CP} = 15.9, Ar:C), 126.8 (d, J\textsubscript{CP} = 190.4, Ar:C), 133.7 (d, J\textsubscript{CP} = 11.9, Ar:C).
Ar:C), 154.4 (d, JCP = 3.9, Ar:C), 173.3 (C Triazine). 31P NMR (162 MHz, H3PO4/CDCl3): δ (ppm) = 17.4. MS (ESI): m/z = 766 (MH+, 100%). HRMS (ESI) m/z calcd for C33H43N3O12P3 766.20541 [MH]+, found 766.20331.

**Synthesis of hexaethyl ([([1,3,5-triazine-2,4,6-triyl]tris(oxy)]tris(benzene-4,1-diyl)]tris(methylene))tris(phosphonate) (TP5)**

![Chemical Structure](image)

a) To a solution of compound 7 (500 mg, 2.047 mmol, 4 equiv) in THF (20 mL), under N2, was added cyanuric chloride (1, 94 mg, 0.508 mmol) and DIPEA (0.5 mL, 2.56 mmol). The mixture was heated to reflux and stirred under N2 overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. The resulting oil was purified by column chromatography (1:1 ethyl acetate/acetone) to give compound TP5 (104 mg, 25%) as white solid.

b) A mixture of compound 7 (345 mg, 1.413 mmol, 5.0 equiv), cyanuric chloride (1, 52 mg, 0.283 mmol) and Na2CO3 (870 mg) in toluene (40 mL), was heated to reflux and stirred under N2 overnight. The reaction mixture was cooled to room temperature and the solid was filtered and washed with hot EtOAc. After filtration, the solvent was removed under reduced pressure to afford an oil. The resulting oil was purified by column chromatography (1:1 ETOAc:Acetone) to give compound TP5 (164 mg, 72%) as white solid. mp 130-131 °C. vmax (KBr) (cm⁻¹): 3077, 3051, 2985, 2932, 2912, 1608, 1581, 1508, 1479, 1383, 1367, 1243, 1217, 1178, 1090, 1055, 1024, 964, 861, 852, 805, 725, 631, 588, 499, 430. 1H NMR (400 MHz, CDCl3): δ (ppm) = 1.23 (t, J = 7.2, 18H, 6x OCH2CH3), 3.14 (d, J = 21.6, 6H, 3x CH2P), 3.94-4.07 (m, 12H, ArCH3), 7.09 (d, J = 8.0, 6H, ArH), 7.30 (dd, J = 8.6 and J = 2.8, 6H, ArH). 13C NMR (100 MHz, CDCl3): δ (ppm) = 16.5 (d, JCP = 5.8, CH3), 33.3 (d, JCP = 138.3, CH2P), 62.4 (d, JCP = 7.1, OCH3), 121.6 (d, JCP = 2.6, Ar:C), 129.7 (d, JCP = 9.5, Ar:C), 131.0 (d, JCP = 6.1, Ar:C), 150.6 (d, JCP = 4.2, Ar:C), 173.7 (C Triazine). 31P NMR (162 MHz, H3PO4/CDCl3): δ (ppm) = 26.0. MS (ESI): m/z = 808 (MH+, 100%). HRMS (ESI) m/z calcd for C36H49N3O12P3 808.25236 [MH]+, found 808.24953.
Synthesis of dodecaethyl \([[[(1,3,5-\text{triazine}-2,4,6-\text{triyl})\text{tris(oxy)}]\text{tris(benzene-4,1-diyl}))\text{tris(methanetriyl))hexakis(phosphonate)}} \text{(TP6)}

A mixture of compound 13 (330 mg, 0.868 mmol, 5.0 equiv), cyanuric chloride (1, 32 mg, 0.174 mmol) and Na₂CO₃ (670 mg) in toluene (75 mL), was heated to reflux and stirred under N₂ overnight. The reaction mixture was cooled to room temperature and the solid was filtered and washed with hot EtOAc. After filtration, the solvent was removed under reduced pressure to afford an oil. The resulting oil was purified by recrystallisation from DCM/n-hexane to give compound TP6 (154 mg, 73%) as a white solid. mp 174-176°C. \( \text{v}_{\text{max}} \) (KBr) (cm⁻¹): 3066, 2988, 2937, 2910, 2874, 1609, 1577, 1507, 1477, 1458, 1444, 1420, 1380, 1246, 1216, 1182, 1165, 1064, 1022, 972, 892, 867, 810, 749, 639, 629, 608, 571, 546, 493. ¹'H NMR (400 MHz, CDCl₃): \( \delta \) (ppm) = 1.16 (t, \( J = 7.1 \), 18H, 6x OCH₂CH₃), 1.28 (t, \( J = 7.1 \), 18H, 6x OCH₂CH₃), 3.76 (t, \( J = 25.0 \), 3H, 3x P₂C₂H₄), 3.93-4.17 (m, 24H, 12x OCH₂CH₃), 7.14 (d, \( J = 8.4 \), 6H, ArH), 7.52 (d, \( J = 8.4 \), 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): \( \delta \) (ppm) = 16.3 (m, CH₃), 16.4 (m, CH₃), 45.2 (t, \( J_{CP} = 132.4 \), 3x P₂CH), 63.1 (m, OCH₂), 63.7 (m, OCH₂), 121.7 (Ar:C), 128.4 (t, \( J_{CP} = 7.2 \), Ar:C), 131.8 (t, \( J_{CP} = 6.3 \), Ar:C), 151.2 (t, \( J_{CP} = 3.1 \), Ar:C), 173.6 (C Triazine). ³¹P NMR (162 MHz, H₃PO₄/CDCl₃): \( \delta \) (ppm) = 18.3. MS (ESI): \( m/z \) = 1216 (MH⁺, 100%). HRMS (ESI) \( m/z \) calcd for C₄₈H₇₆N₃O₂₁P₆ 1216.33915 [MH]⁺, found 1216.33949.
Attempt of synthesis of hexaethyl \(((1,3,5\text{-}tri\text{azine}\text{-}2,4,6\text{-}triyl)}\text{tris(oxy)}\text{tris(benzene-4,1-diyl)})\text{tris(hydroxymethylene)}\text{tris(phosphonate)}\) (TP7) from 11

To a solution of diethyl [hydroxy(4-hydroxyphenyl)methyl]phosphonate (11, 206 mg, 0.792 mmol, 3.4 equiv) in THF (10 mL), under N₂, was added cyanuric chloride (1, 43 mg, 0.234 mmol) and DIPEA (0.21 mL, 1.17 mmol). The mixture was heated to reflux and stirred under N₂ overnight. The reaction mixture was cooled to room temperature and the solvent was removed in vacuum. The analysis of the ¹H NMR spectrum of the crude reaction mixture showed a 1:1.119 mixture of TP7 and compound 11, respectively, had been produced. Attempts of separation of these compounds by column chromatography did not afford a pure sample of the desired compound TP7.

NMR spectra of compound TP7 (in the crude reaction mixture): ¹H NMR (400 MHz, DMSO): δ (ppm) = 1.15 (t, J = 7.2, 6H, 2x OCH₂CH₃), 1.19 (t, J = 6.8, 6H, 2x OCH₂CH₃), 3.95 -4.03 (m, 8H, 4x OCH₂CH₃), 5.01 (d, J = 13.6, 2H, 2 x CHP(OH)), 7.26 (d, J = 8.4, 4H, ArH), 7.52 (dd, J = 8.8 and J = 2.0, 4H, ArH). ¹³C NMR (100 MHz, DMSO): δ (ppm) = 16.3 (m, CH₃), 61.9 (OCH₂), 62.3 (OCH₂), 68.8 (d, J = 162.1, CHP(OH)), 120.7 (Ar:C), 128.7 (Ar:C), 136.7 (Ar:C), 150.5 (Ar:C), 172.0 (C Triazine). ³¹P NMR (162 MHz, H₂PO₄/ DMSO): δ (ppm) = 21.5. MS (ESI): m/z = 856 (MH⁺, 100%). HRMS (ESI) m/z calcd for C₃₆H₄₉N₃O₁₅P₃ 856.23710 [MH⁺], found 856.23569.

Synthesis of 4,4',4''-[(1,3,5-triazine-2,4,6-triy)tris(oxy)]tribenzaldehyde (19)
A mixture of 4-hydroxybenzaldehyde (12, 2.40 g, 19.65 mmol) and cyanuric chloride (1, 900 mg, 4.88 mmol) and Na₂CO₃ (15.0 g) in toluene (75 mL), was heated to reflux and stirred overnight under N₂. The reaction mixture was cooled to room temperature and the white solid was filtered and washed with hot EtOAc. The filtrated solution was washed with 10% aqueous Na₂CO₃ solution twice. The combined organic extracts were washed with H₂O and dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure to afford compound 19 [9] (1.87 g, 87%) as a white solid. 

\[ 1^H \text{NMR (400 MHz, CDCl}_3) : \delta (ppm) = 7.33 (d, J = 8.2, 6H, ArH), 7.93 (d, J = 8.4, 6H, ArH), 10.00 (s, 3H, 3x ArCO). \]

**Attempt of synthesis of hexaethyl ((([(1,3,5-triazine-2,4,6-triyl)tris(oxy)]tris(benzene-4,1-diyl))tris(hydroxymethylene))tris(phosphonate) (TP7) from 19**

A mixture of compound 19 (200 mg, 0.453 mmol), diethyl phosphonate (0.2 mL, 1.495 mmol) and triethylamine (0.21 mL, 1.495 mmol) in toluene (10 mL) was stirred at room temperature overnight. The reaction mixture was acidified with 10% aqueous HCl solution and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (1:1 EtOAc/acetone) to give compound 20 (35 mg, 13%) as white solid. mp 88-90 °C. 

\[ \nu_{\text{max}} \text{(KBr) (cm}^{-1}) : 3386, 3072, 2985, 2930, 2909, 2850, 2834, 2742, 1702, 1604, 1593, 1572, 1503, 1475, 1466, 1459, 1420, 1375, 1300, 1216, 1163, 1019, 970, 843, 808, 620, 561, 503. \]

\[ 1^H \text{NMR (400 MHz, CDCl}_3) : \delta (ppm) = 1.21-128 (m, 6H, 2x OCH}_2CH}_3), 4.00 (m, 4H, 2x OCH}_2CH}_3), 5.02 (d, J = 11.2, 1H, CHP(OH)), 7.12 (d, J = 8.0, 2H, ArH), 7.32 (d, J = 8.0, 4H, ArH), 7.50 (d, J = 8.0, 2H, ArH), 7.91 (d, J = 8.0, 4H, ArH), 9.94 (s, 2H, 2x ArCHO). \]

\[ 1^C \text{NMR (100 MHz, CDCl}_3) : \delta (ppm) = 16.5 (m, CH}_3), 63.5 (m, OCH}_2), 70.3 (d, J = 158.7, CHP(OH)), 121.3 (d, J_{CP} = 2.1, Ar:C), 122.4 (Ar:C), 128.5 (d, J_{CP} = 5.6, Ar:C), 131.4 (Ar:C), 134.4 (Ar:C), 135.0 (d, J_{CP} = 2.0, Ar:C), 151.2 (m, Ar:C), 155.9 (Ar:C), 173.3 (C Triazine), 173.9 (C Triazine), 191.0 (Ar:CHO). \]

\[ 3^1P \text{NMR (162 MHz, H}_3PO}_4/ CDCl}_3 : \delta (ppm) = 20.8. \]

MS (ESI): \text{m/z} = 580 (MH⁺, 100%). HRMS (ESI) \text{m/z} calcd for C$_2$H$_{27}$N$_3$O$_9$P 580.14794 [MH]$^+$, found 580.14692.
1.5. Membrane Preparation

Membranes were prepared by a casting method using Naftion®/DMAc solutions, based on our previous works, using 1 wt% loading of TP dopants. The 20 wt% Naftion solution was dried under reduced pressure, at 40 °C, until a dry residue was obtained. A new 10 wt % solution of Naftion was obtained by dissolution of the dried Naftion in the required amount of N,N-dimethylacetamide (DMAc). The TP dopant quantity was added to DMAC solution and the mixture was stirred during 1–5 h, in an ultrasonic bath, to guarantee the complete dissolution of dopants. The resulting solutions were casted on a Petri dish and slowly evaporated, until obtaining homogeneous membranes. The resulting membranes were dried in a vacuum oven at 60 °C, and were followed by their anellation for 2 h, at 140 °C. The membranes were activated by a sequential treatment, with 1 h for each step, by boiling them in H₂O₂ solution (3%), washing with hot deionized water, boiling in a 0.5 M sulfonic acid solution, and washing again with hot deionized water. After activation, the membranes were kept in deionized water until their use. The new membranes were labelled as Naftion/TP-i-1.0, respectively, where i indicates the specific triazine used, and 1.0 specifies the wt% of dopant. Recast Naftion films were also prepared, for comparison, without the incorporation of TPs.

Doped and recast Naftion membranes had an average thickness of 94 ± 6 µm.
1.6. FTIR-ATR spectra of the new membranes

Figure S1: FTIR-ATR spectra of the new membranes.

2. References
