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Synthesis, Thermochemical, and Thermomechanical Characterization of High Conductivity 4-Azoniaspiro[3,4]octane Salts

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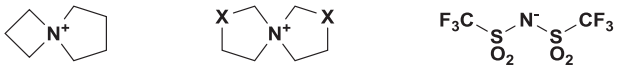
Electrolytes based on the spiro-type quaternary ammonium salt, 1,1′-spirobipyrrolidinium tetrafluoroborate (SBP BF_4, 4-azoniaspiro[4.4]nonane tetrafluoroborate, *Figure 1*) are widely being investigated for electric double layer capacitor (EDLC) applications owing to their high conductivity.[1-6] The SBP cation comprises two symmetric 5-membered rings joined together by a N^+ functionality. Replacing one of the 5-membered rings with a 4-membered ring results in the 1-azetidyl-1′-spiropyrrolidinium cation (AP, 4-azoniaspiro [3.4]octane, Scheme 1). The highest conductivity among all the quaternary ammonium salts has been reported for AP salts in several patents.[7-10] However, there are no reports on a facile synthesis of AP salts nor on the thermochemical properties of high purity AP salts. In this paper, we report a novel method for the synthesis of AP salts (BF_4, PF_6 and NTf_2), and compare and contrast properties of AP BF_4, AP PF_6, AP NTf_2 with these of SBP BF_4.



AP **X=CH_2: SBP, X=O: SBO** **NTf_2**

Figure 1. Structures and abbreviations of salt components.

AP Cl was synthesized from pyrrolidine and 1-bromo-3-chloropropane *via* a two-step method as shown in *Scheme 1*.

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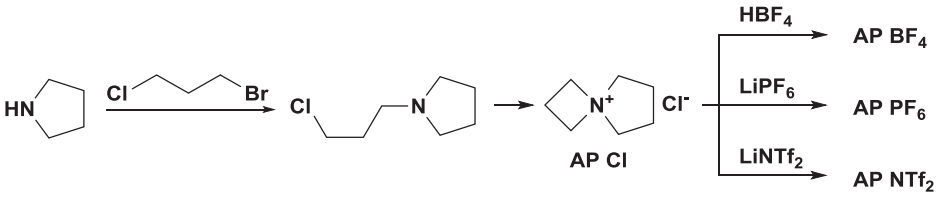

Scheme 1.

We evaluated and modified two methods for intramolecular cyclization of 1-(3-chloropropyl)pyrrolidine under diluted homogeneous and non-homogeneous conditions; both had been previously described in a patent for the preparation of AP Cl and AP PF_6, respectively.[11] Under homogeneous conditions, the reactant concentration was deliberately maintained at a low level to minimize formation of byproducts, particularly the "intractable" byproduct.[12] Despite addition of 1-(3-chloropropyl)pyrrolidine dissolved in EtOH in a dropwise manner to boiling EtOH for maintaining low concentration, a significant amount of byproducts was formed that reduced the conversion rates and required additional purification. Non-homogeneous conditions using hot H_2O as a solvent exclusively produced AP Cl; however, this required optimization of the amount of boiling water. Using the amount of H_2O stated in the original patent[11] frequently lead to formation of homogeneous mixtures upon addition of 1-(3-chloropropyl)pyrrolidine that resulted in low yields with large amounts of byproducts. Using five times more H_2O than the original procedure ensured formation of two-phases, and the existence of non-homogeneous condition upon addition of 1-(3-chloropropyl)pyrrolidine.

Since 1-(3-chloropropyl)pyrrolidine can be isolated by vacuum distillation without significant decomposition, the intra-/inter-molecular reactions proceed preferably in polar media. Low solubility of 1-(3-chloropropyl)pyrrolidine in H_2O appears to facilitate the intramolecular cyclization, resulting in high yield and high purity. The utilization of low solubility reactants in polar solvents for selective intramolecular reactions is applicable to other intramolecular reactions which require highly diluted conditions.

Earlier attempts of AP Cl synthesis from 1-(3-chloropropyl)pyrrolidine failed, resulting in formation of large amounts of intractable byproduct.[12] Cyclization of 1-(3-chloropropyl)pyrrolidine (13.8 g) in acetonitrile (850 ml) at 60–65°C for 16 h has been reported by Jin *et al.*[13] However, our protocol (1-(3-chloropropyl)pyrrolidine (116.24 g) in boiling H_2O (400 mL) for 30 min) is green, faster, inexpensive, and scalable. Nishino *et al.* disclosed a two-step preparation of AP BF_4 starting from azetidine, 1-bromo-4-fluorobutane, and trifluoroborane ethylamine complex,[7] however, the yield of 1-(4-fluorobutyl)azetidine is low and the reagents are significantly more expensive compared to pyrrolidine, 1-bromo-3-chloropropane, and aqueous tetrafluoroboric acid and thus unsuitable for the large scale synthesis.

For the AP salts, we measured the glass transition temperatures (ΔT_g), melting points (ΔT_m), and related enthalpy (ΔH_g and ΔH_m, respectively) and entropy changes (ΔS_g and ΔS_m, respectively) using differential scanning calorimetry (DSC). The data are summarized in *Table 1*.

Both AP BF_4 and AP NTf_2 exhibit significantly higher total phase enthalpy change ($\Delta H_{total} = \Delta H_g + \Delta H_m$) as compared to the reported value for the loosely-packed SBP BF_4 crystal (8.9 kJ/mol). Moreover, their ΔH_{total} values are closer to that of 3,3′-spirobioxazolidinium tetrafluoroborate (SBO BF_4, 24.6 kJ/mol) which is polar and forms a tightly packed crystal (*Figure 1*).[14,15] This closeness of ΔH_{total} values of AP salts to SBO

Table 1.
Thermodynamic Parameters of AP Salts.

	AP BF_4	AP NTf_2	AP PF_6
MW ($gmol^{-1}$)	199.00	392.34	257.16
T_g (°C)	42.0	24.3	128.4
ΔH_g ($kJmol^{-1}$)	8.1	14.4	2.6
ΔS_g ($JK^{-1}mol^{-1}$)	23.7	44.5	6.0
T_m (°C)	206.3	111.4	
ΔH_m ($kJmol^{-1}$)	15.3	10.5	
ΔS_m ($JK^{-1}mol^{-1}$)	30.3	25.5	
ΔH_{total} ($kJmol^{-1}$)	23.4	24.9	

BF_4 is attributed to smaller ion size and close packing of AP salts. Interestingly, AP PF_6 started decomposing before melting and exhibited stable crystal behavior despite the thermal instability of PF_6 anion.

The crystallographic parameters and calculated thermodynamic parameters (U_{POT} (potential energy) and $\Delta_{latt}H°$ (lattice enthalpy)) consistent with volume-based thermodynamics (VBT) theory[15] are summarized in *Table 2*.

Both crystals of AP BF_4 and SBP BF_4 belong to *R3c* space group. The smaller molecular unit volume (V_m) of AP BF_4 (0.238 nm^3 vs. 0.261 nm^3 for SBP BF_4) leads to stronger charge-charge interactions in the closer-packed AP BF_4 crystal that results in a difference of 11.6 $kJmol^{-1}$ in lattice formation energy ($\Delta_{latt}H°$) per VBT theory. This also explains the difference in the total phase change enthalpy of 14.5 $kJmol^{-1}$ between AP BF_4 and SBP BF_4.

Figure 2 shows the thermogravimetric analysis (TGA) spectra of SBP BF_4, AP BF_4, AP NTf_2, and AP PF_6.

Among the AP salts, the onset temperatures for weight loss is lowest in case of AP BF_4, followed by AP NTf_2 and AP PF_6. While the highest onset temperature in the case

Table 2.
Crystallographic and VBT Parameters of AP, SBP and SBO Salts at 100 K.

Salt	AP BF_4	AP NTf_2	SBP BF_4[13]	SBO BF_4[13]
Crystal system	Rhombohedral	Orthorhombic	Rhombohedral	Orthorhombic
Space group	*R3c*	$P2_12_12_1$	*R3c*	$Pna2_1$
a (Å)	19.9273(7)	8.7228(10)	20.791(3)	12.0719(11)
b (Å)	19.9273(7)	13.5149(16)	20.791(3)	6.4498(6)
c (Å)	12.4592(5)	38.143(4)	12.561(4)	11.6510(11)
α	90	90	90	90
β	90	90	90	90
γ	120	90	120	90
V_{cell} ($Å^3$)	4284.67	4496.56	4702.25	907.16(15)
Z	18	12	18	4
V_m ($Å^3$)	238	375	261	227
V_m (nm^3)	0.238	0.375	0.261	0.227
U_{POT} ($kJmol^{-1}$)	482.3	429.2	470.8	488.5
$\Delta_{latt}H°$ ($kJmol^{-1}$)	487.3	434.2	475.7	482.8

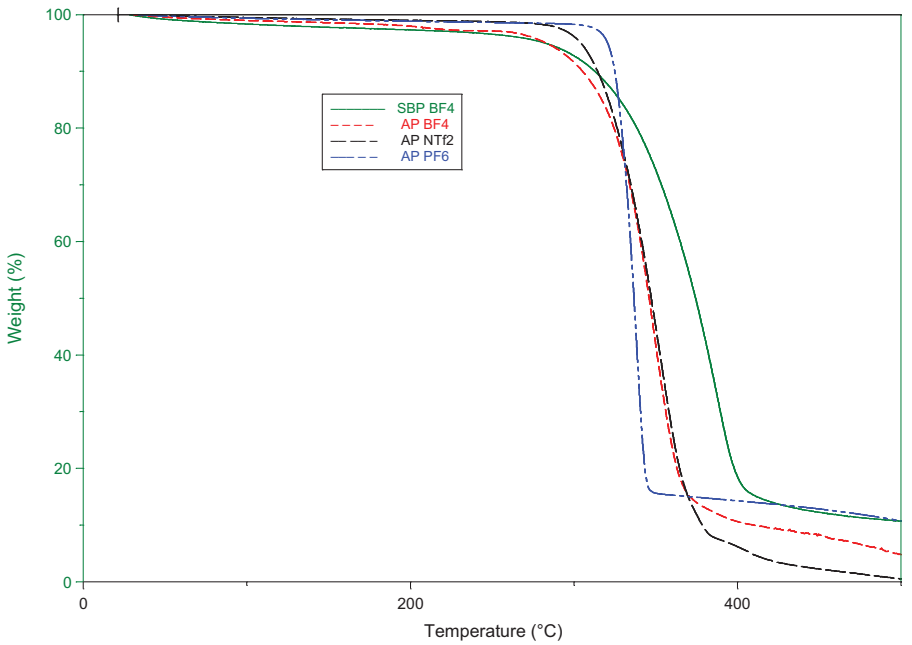

Figure 2. TGA analysis of AP and SBP salts.

of AP PF_6 is presumably due to its stable crystal structure, there is no correlation between the melting points (or glass transition temperatures) and onset temperatures for weight loss in AP BF_4 and AP NTf_2 salts. Comparison of temperatures at which maximum weight loss is observed (T_{mwl}, the temperature at the maximum of the first derivative of the weight loss) for SBP BF_4 and AP BF_4 shows that the weight loss occurs at significantly higher temperature in SBP BF_4 (at 388°C) as compared to AP BF_4 (at 348°C). The lower weight loss temperature in AP BF_4 is attributed to greater instability of the four-membered ring of the AP cation.

We performed quantum chemical calculations to evaluate the strain in the 4- and 5-membered rings. The energies of spiro-structures (AP and SBP) were compared with ring-opened structures by β-elimination (allyl-P and homoallyl-P, respectively, *Figure 3*), and the energy differences between the closed and open structures are summarized in *Table 3*.

The $\Delta E_{open\text{-}close}$ of AP cation is negative due to the release of strained 4-membered ring while the $\Delta E_{open\text{-}close}$ of the SBP cation is positive due to replacement of one sigma bond with one double bond. The difference in ring strain between 4- and 5-membered rings is calculated to be 14.1 $kcalmol^{-1}$. It has been reported the ring strain energies for cyclobutane and cyclopentane are 26.5 and 6.2 $kcal.mol^{-1}$, respectively.[16] Our estimate is slightly smaller than this difference (20.3 $kcal.mol^{-1}$), probably due to presence of N^+ in the SBP and AP cation.

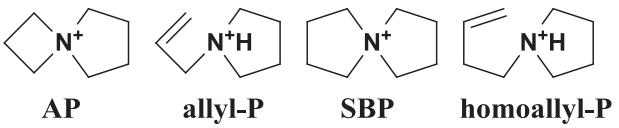

Figure 3. Spiro- and ring-opened and refluxed structures of AP and SBP cation.

Table 3.
Calculated Energy Differences of Spiro- and One-ring-opened and Relaxed AP and SBP Ions.

	$\Delta E_{\text{open-close}}$	
	(kJmol^{-1})	(kcalmol^{-1})
AP	-16.2	-3.9
SBP	42.8	10.2
$\Delta E_{\text{SBP-AP}}$	59.0	14.1

The room temperature electrical conductivity of various salts (AP BF_4, AP PF_6, and SBP BF_4) dissolved in multiple solvents in molarities ranging from 0.5 to 4.0 M in steps of 0.5 is summarized in *Figure 4*.

Comparison of the conductivity of AP BF_4 and AP PF_6 in acetonitrile (AN) shows significantly higher conductivity for AP BF_4 /AN (44 to 70 mS/cm) than for AP PF_6 /AN (37 to 60 mS/cm). Moreover, AP BF_4 has greater solubility in AN (up to 4 M) than AP PF_6 (up to 2.5 M) which is an important consideration from the electrolyte perspective. The conductivity of SBP BF_4 /AN ranged from 44 mS/cm to 65 mS/cm (at various molarities) and was lower than that of AP BF_4 /AN; nevertheless both showed conductivity maxima in the same concentration range (between 2 and 2.5 M) and high solubility up to 4 M. The conductivity maxima for AP PF_6 /AN was observed between 1.5 M and 2.0 M. The conductivity of AP BF_4 in propylene carbonate (PC, a common solvent used in electrochemical capacitors) was significantly poor as compared to all other solvent systems investigated.

The dissolution of AP BF_4 in two low polarity and viscous solvents, namely, dimethyl carbonate (DMC) and dichloromethane (DCM) at salt concentrations $\geq$2.5 M in DMC and $\geq$2.0 M in DCM, resulted in the formation of homogeneous solutions; however, the conductivity was poor. This low conductivity was attributed to the clustering behavior of ions in less polar solvents and was confirmed by the broad peaks observed in

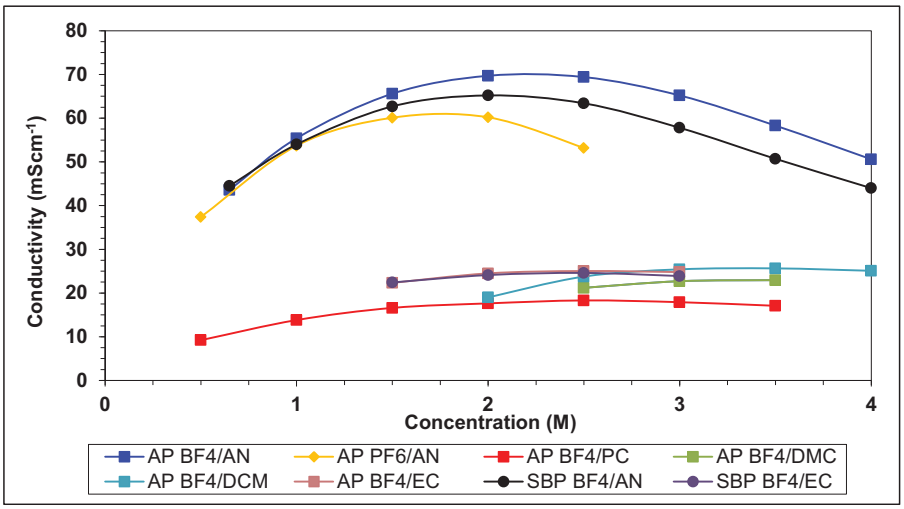

Figure 4. Conductivity of solutions of AP and SBP salts at 25 °C.

the NMR spectrum of AP BF_4 (chloroform-*d*). In ethylene carbonate (EC), both AP BF_4 and SBP BF_4 at $\geq$1.5 M concentration exhibited nearly identical conductivity and they both formed eutectic mixtures.

In conclusion, we successfully synthesized high purity AP salts (> 99.9%) for electrochemical energy storage applications in good yields using inexpensive and scalable synthesis protocols. Intramolecular cyclization of 1-(3-chloropropyl)pyrrolidine under non-homogeneous conditions exclusively produced AP Cl that eliminated prolonged and expensive purification protocols for high purity AP salts. The cyclization under homogeneous conditions produced large amounts of byproducts, which were difficult to remove by recrystallization due to the low solubility. This non-homogeneous intramolecular reaction is applicable for other intramolecular reactions, which need high dilution of reactants for preventing competitive intermolecular reactions.

The AP salts were less stable than their SBP counterparts, but showed higher conductivity, especially in acetonitrile. The stability was closely dependent on the anion type. We investigated thermomechanical properties using volume based thermodynamic modeling, TGA and DSC; and we studied the thermochemical properties of AP salts and compared their properties with SBP BF_4 and SBO BF_4.

Experimental Section

1-(3-Chloropropyl)pyrrolidine was prepared by the reaction of pyrrolidine and 1-bromo-3-chloropropane according to the literature procedure.[17] 1-Bromo-3-chloropropane and pyrrolidine were obtained from Acros Organics (NJ, USA). 50% HBF_4 was purchased from GFS Chemicals (Powell, OH, USA). Aluminum oxide (activated, acidic, Blockmann Grade I, 58 angstroms) was purchased from Alfa Aesar (Ward Hill, MA, USA). Lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) was purchased from TCI America (Portland, OR, USA). Lithium hexafluorophosphate ($LiPF_6$) was purchased from BASF Battery Materials (Iselin, NJ, USA). Nylon membrane, Whatman 7402-004, 0.2 μm, was purchased from GE Healthcare Life Sciences (Pittsburgh, PA, USA). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), ^{19}F (376.5 MHz) and ^{31}P (162.0 MHz) NMR were measured on Bruker Avance 400 spectrometer. NMR spectra of salts were measured in CD_3OD (Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) unless otherwise specified, and the solvent peaks of ^{1}H (3.31 ppm) and ^{13}C NMR (49.0 ppm) and external $CFCl_3$ and H_3PO_4 peaks of ^{19}F NMR and ^{31}P NMR were used as references for the chemical shifts. Conductivity was measured using a Radiometer Analytical CDM230 Conductivity Meter at 25°C. TGA data were recorded on a TA Instruments TGA 2050 thermogravimetric analyzer under dynamic nitrogen flow (total flow rate 100 cm^3/min), using platinum pans and a ramp rate of 10°C/min. DSC data were recorded on a TA Instruments DSC 2920 differential scanning calorimeter at 1 atm under dynamic nitrogen, using hermetically sealed aluminum pans, with a ramp rate of 10°C/min. Unit cell parameters indexing of AP BF_4 and AP NTf_2 were performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS detector equipped with a Mo-target X-ray tube (λ = 0.71073Å) at T = 100(±2) K. Quantum chemical calculations were carried out using the Firefly QC package (version 8.1.1, build number 9295)[18] at restricted B3LYP density function, using 6–311 basis set with s diffuse and p polarization functions for hydrogen and sp diffuse and d polarization functions for the other elements (similar to RB3LYP/6-311++G(d,p) level).

Synthesis of 1-azetidyl-1′-spiropyrrolidinium (4-azoniaspiro[3.4]octane) tetrafluoroborate (AP BF_4)

Two methods were examined, namely non-homogeneous and homogeneous, for the synthesis of AP Cl as described in a patent.[11]

A (non-homogenous method): 1-(3-Chloropropyl)pyrrolidine (116.24 g, 0.80 mol) was added dropwise to boiling H_2O (400 mL) for 15 min and further refluxed for additional 15 min. The resulting homogenous and pale yellow solution was washed with three portions of CH_2Cl_2 (50, 30, 30 mL) and then the volatiles were removed by evaporation yielding a yellow oil of crude AP Cl. Assuming 100% conversion by NMR analysis, 50% aqueous HBF_4 (138.39 g, 0.80 mol) and EtOH (150 mL) were added and the volatile materials were removed by evaporation. Addition of EtOH (150 mL) and evaporation were repeated two more times and the residue was recrystallized from EtOH (1.0L) to give the crude product. The crude product was dissolved in CH_2Cl_2 (1.5 L) and applied to acidic aluminum oxide (150 mL) column and fractions containing the product were collected. The column was further eluted with CH_2Cl_2 (500 mL) and the combined eluent was filtered using a Nylon membrane (Whatman 7402-0004, 0.2 μm). The volatiles were removed by evaporation and the residue was recrystallized from EtOH (1.0 L) to give the product (143.3 g, 92% yield). The recrystallization was repeated and the purified product was dried *in vacuo* at 70 °C for 12 h.^{1}H NMR (methanol-d_4) δ = 4.33 (t, 4 H, J = 8.2 Hz), 3.62 (m, 4 H), 2.60 (quintet-t, 2 H, J = 8.2, 2.2 Hz), 2.09 (tt, 4 H, J = 7.1, 1.5 Hz); ^{19}F NMR δ = -154.52, -154.57 (2 s, 19:81 (^{10}B:^{11}B)); ^{13}C NMR δ = 64.1 (br), 22.1, 15.3.

Anal. Calcd for $C_7H_{14}BF_4N$: C, 42.25; H, 7.09; N, 7.04; Found: C, 41.99; H, 7.00; N, 6.75.

B (homogenous method): 1-(3-Chloropropyl)pyrrolidine (182.1 g, 1.23 mol) was dissolved in 3.75 L of EtOH and added to boiling EtOH (250 mL) over 2 h and further refluxed for 1 h. The solvent was removed by evaporation and the residue was dissolved in H_2O (400 mL). The aqueous phase was washed with three portions of CH_2Cl_2 (150, 100, 100 mL). The volatiles were removed by evaporation and then dried under vacuum at ambient temperature overnight while stirring continuously, resulting in a yellow oil of crude AP Cl. The CH_2Cl_2 layer was dried over anhydrous $MgSO_4$. The drying reagent was removed by filtration and solvent was removed by evaporation to recover unreacted 1-(3-chloropropyl)pyrrolidine (8.4 g, 5%, therefore the maximum yield of AP Cl was 95%, 1.17 mol). The crude AP Cl thus obtained was mixed with MeOH (250 mL) which partially dissolved the salt. The Cl salt was converted to the BF_4 salt by addition of 50% aqueous HBF_4 (206.3 g, 1.17 mol) and the volatile materials in the resulting cloudy solution were removed by evaporation. EtOH (200 mL) was added and evaporated for azeotropic removal of aqueous HCl. This azeotropic removal of water and HCl was repeated two more times and the residue was recrystallized from EtOH (1 L) (insoluble materials were removed by filtration while the solution was hot). The resulting crystalline solid (216.3 g) was dissolved in CH_2Cl_2 at a concentration less than 50 g/L and applied to an acidic alumina (~200 mL) column. The product was eluted with CH_2Cl_2, fractions containing AP BF_4 collected, and the solvent was removed by evaporation. It may be necessary to repeat the column chromatography to obtain sufficiently pure fractions. There needs to be less than 1% of byproduct peak at 2.2 ppm, compared to product peak at 2.1 ppm, in ^{1}H NMR for the subsequent efficient removal by recrystallization. The product (148.5 g) was repeatedly recrystallized from EtOH (1.6 L) until the byproduct was undetectable in the concentrated filtrate to give pure product after the fourth recrystallization. The peak integration ratio of 2.2 ppm to 2.1 ppm was less than 0.05% as per ^{1}H NMR which resulted in 140.5 g, 57% yield of 99.95% pure salt.

Synthesis of 1-azetidyl-1′-spiropyrrolidinium (4-azoniaspiro[3.4]octane) bis(triflluoromethanesulfonyl)imide (AP NTf_2)

AP BF_4 (47.53 g, 0.238 mol) and $LiNTf_2$ (68.57 g, 0.238 mol) were mixed with H_2O (100 mL) and CH_2Cl_2 (50 mL) for 10 min. This resulted in the separation of the organic phase, which was washed with 5 portions of H_2O and subsequently filtered using a Nylon membrane (Whatman 7402-0004, 0.2 μm). The volatiles were removed by evaporation and the residue was repeatedly recrystallized from EtOH or isopropyl alcohol to give the product (84.8 g, 91% yield). The product turned gummy after drying *in vacuo* at 70°C for 12 h due to the low glass transition temperature. ^{1}H NMR (methanol-d_4) $\delta = 4.33$ (t, 4 H, $J = 8.2$ Hz), 3.62 (m, 4 H), 2.61 (quintet-t, 2 H, $J = 8.2$, 2.2 Hz), 2.09 (m, 4 H); ^{19}F NMR δ = -81.10; ^{13}C NMR $\delta = 121.10$ (q, $J = 320.5$ Hz), 64.1 (br), 22.0, 15.2.

Anal. Calcd for $C_7H_{14}F_6N_2O_4S_2$: C, 27.55; H, 3.60; N, 7.14; Found: C, 27.62; H, 3.54; N, 6.97.

Synthesis of 1-azetidyl-1′-spiropyrrolidinium (4-azoniaspiro[3.4]octane) hexafluorophosphate (AP PF_6)

Crude AP Cl (prepared on 0.121 mol scale) was dissolved in H_2O (50 mL, the total weight with AP Cl was about 60 g), and $LiPF_6$ (20.22 g, 0.133 mol) dissolved in H_2O (50 mL) was added dropwise to the AP Cl solution at ambient temperature. This resulted in immediate formation of a white precipitate, which was collected by filtration. After brief drying under vacuum at ambient temperature, the wet product was dissolved in hot H_2O and filtered by Nylon membrane (Whatman 7402-004, 0.2 μm) and subsequently recrystallized. The product was further recrystallized from H_2O and dried *in vacuo* at 70°C for 12 h to give the product (24.8 g, 80% yield). ^{1}H NMR (methanol-d_4) $\delta = 4.33$ (t, 4 H, $J = 8.2$ Hz), 3.62 (m, 4 H), 2.60 (quintet-t, 2 H, $J = 8.2$, 2.2 Hz), 2.09 (m, 4 H); ^{19}F NMR δ = -74.93 (d, $J = 708.3$ Hz); ^{13}C NMR $\delta = 64.1$ (br), 22.1, 15.3; ^{31}P NMR δ = 144.57 (septet, $J = 707.6$ Hz).

Anal. Calcd for $C_7H_{14}F_6NP$: C, 32.69; H, 5.49; N, 5.45; Found: C, 32.40; H, 5.22; N, 5.27.

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