Synthesis of Oxygen-Containing Spirobipyrrolidinium Salts for High Conductivity Room Temperature Ionic Liquids

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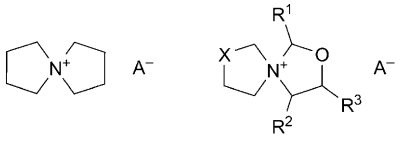
Synthesis of ionic liquids (IL) based on oxygen-containing spirobipyrrolidinium salts with BF_4, $BF_3C_2F_5$, and NTf_2 as counterions was undertaken. Their physical and electrochemical properties were evaluated for suitability for Room Temperature Ionic Liquids (RTIL) application. Reduction in melting point occurred upon exchange of C(2) by an O-atom of spirobipyrrolidinium, without sacrificing the electrochemical stability; while introduction of alkyl groups between the N- and O-atoms led to incorporation of asymmetry, and hence reduced the melting points, and viscosity.

Introduction. – Improvement of energy density of electric double layer capacitors (EDLCs) while maintaining the high power density, cycle life, and safety is one of the most awaited technological developments for sustainable society [1–4]. Electrolytes with wide operational (potential and temperature) window, high ion conductivity and concentration are important for further improvement. Several aspects of aliphatic room temperature ionic liquids (RTILs) meet these requirements; however, they have relatively low conductivity. Reduction in melting point and viscosity, upon introduction of O-atoms to aliphatic ammonium cations is well-known [5–9]. Meanwhile, 1,1′-spirobipyrrolidinium (SBP) salts of type **1** (*Table 1*) generally show high conductivity and solubility [10–18] and the application to EDLCs has been reported (for example [11–14][19–34]). Therefore, simultaneous implementation of these characters in cations depicted as type **2** in *Table 1* would lower the melting point and increase the conductivity of RTIL. In addition, introduction of alkyl groups in the molecules (R^1 to R^3, *Table 1*) would lower the crystallinity by introduction of asymmetry and the ion-ion interaction by shielding the localized positive charges. In this article, we report the synthesis and characterization of oxygen-containing, alkyl group decorated spirobipyrrolidinium salts.

Results and Discussion. – *Synthesis of Oxygen-Containing Spirobipyrrolidinium Salts of Type* **2**. There have been reports on the synthesis of oxygen-containing spirobipyrrolidinium salts [35][36]. *Cossar* and *Reynolds* used acetal exchange reaction of haloacetals with pyrrolidines. Our results show that a combination of aldehydes and haloalcohols instead of haloacetals also works well, and it provides flexibility in the synthesis (*Scheme 1*).

Table 1. *Type* **1**: *1,1′-Spirobipyrrolidinium; Type* **2**: *Various Functionalities Modifying the Parent Compound*[a])

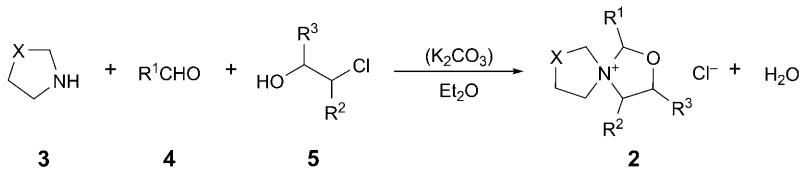


1 **2**

Salt	X	R^1	R^2	R^3	A^-	Salt formation
SBP BF_4[b])	–	–	–	–	BF_4	SBP Cl + HBF_4 → **SBP BF_4**
OP BF_4	CH_2	H	H	H	BF_4	OP Cl + HBF_4 → **OP BF_4**
OP $BF_3C_2F_5$	CH_2	H	H	H	$BF_3C_2F_5$	**OP BF_4** + $KBF_3C_2F_5$ → **OP $BF_3C_2F_5$**
OP NTf_2	CH_2	H	H	H	NTf_2	OP Cl + $LiNTf_2$ → **OP NTf_2**
2MOP BF_4	CH_2	Me	H	H	BF_4	2MOP Cl + HBF_4 → **2MOP BF_4**
2MOP $BF_3C_2F_5$	CH_2	Me	H	H	$BF_3C_2F_5$	**2MOP BF_4** + $KBF_3C_2F_5$ → **2MOP $BF_3C_2F_5$**
2MOP NTf_2	CH_2	Me	H	H	NTf_2	**2MOP BF_4** + $LiNTf_2$ → **2MOP NTf_2**
2EOP BF_4	CH_2	Et	H	H	BF_4	2EOP Cl + HBF_4 → **2EOP BF_4**
4MOP BF_4	CH_2	H	Me	H	BF_4	4MOP Cl + HBF_4 → **4MOP BF_4**
5MOP BF_4	CH_2	H	H	Me	BF_4	5MOP Cl + HBF_4 → **5MOP BF_4**
5MOP NTf_2	CH_2	H	H	Me	NTf_2	**5MOP BF_4** + $LiNTf_2$ → **5MOP NTf_2**
SBO BF_4	O	H	H	H	BF_4	SBO Cl + HBF_4 → **SBO BF_4**

[a]) The table provides a list of ammonium salts with corresponding anionic functionalities. For the way of their preparation, see also *Scheme 1*. [b]) Type **1**. Rest of the salts are of Type **2**.

Scheme 1



3 **4** **5** **2**

In the presence of K_2CO_3 except in the cases of paraformaldehyde ($R^1 = H$), pyrrolidine was added at low temperature to improve the purity of the crude products. The crude chloride salts were washed with CH_2Cl_2. 2MOP Cl, 2EOP Cl, and SBO Cl were further purified using a cation exchange column (H^+-form), which removes most of the color and basic by-products which cause the product to decompose at elevated temperatures. The chloride salts were subsequently treated with HBF_4 to generate BF_4 salts. Further purification of **2MOP BF_4** and **2EOP BF_4** was performed by acidic alumina column chromatography, which removed the protonated ammonium by-products. $BF_3C_2F_5$ and NTf_2 salts were prepared from Cl or BF_4 salts by the metathesis with $KBF_3C_2F_5$ [37–39] and $LiNTf_2$, respectively. The molecular weights and melting points are summarized in *Table 2*, along with the parent ammonium salt, 1,1′-spirobipyrrolidinium (SBP) tetrafluoroborate (**SBP BF_4**). The introduction of alkyl

Table 2. *Characterization of Spiroammonium Salts*

Salt	M_r	M.p. [°]	Conductivity [mScm^{-1}]	Viscosity [cP]
SBP BF_4	213.02	189	[a])	[a])
OP BF_4	215.00	104	[a])	[a])
OP $BF_3C_2F_5$	315.01	155	[a])	[a])
OP NTf_2	408.34	78	[a])	[a])
2MOP BF_4	229.02	28	2.15	412.0
2MOP $BF_3C_2F_5$	329.04	142	[a])	[a])
2MOP NTf_2	422.36	22	2.62	57.3
2EOP BF_4	243.05	15	1.60	195.3
4MOP BF_4	229.02	243	[a])	[a])
5MOP BF_4	229.02	56	[a])	[a])
5MOP NTf_2	422.36	20	2.72	78.3
SBO BF_4	216.97	168	[a])	[a])

[a]) Solid at r.t., hence the property was not determined.

groups next to the O-atom greatly reduced the melting points and they were below 30° in cases of **2MOP BF_4**, **2MOP NTf_2**, **2EOP BF_4**, and **5MOP NTf_2**. The conductivity and viscosity of these ionic liquids at 25° was 1.6 to 2.7 mS/cm as shown in *Table 2*. The ionic liquids except **2EOP BF_4** were purified by a low temperature recrystallization process down to −80° from MeOH, while **2EOP BF_4** showed liquid-liquid phase separation prior to the solidification with the contaminants. **2MOP BF_4** also showed partial phase separation by precipitating at the bottom of the flask along with crystallization from the rest of the solution. The crystalline part was repetitively collected from the precipitate.

Conductivity in MeCN. The measured conductivity of the electrolytes in MeCN at various concentrations at 25°, and the results are shown in *Fig. 1*.

Most of the new BF_4 salts exhibited highest conductivity around 2M, however, the conductivity was considerably lower than for **SBP BF_4**. The increased polarity of the fixed ring O-atom, and the ion-ion interaction in **OP BF_4** was responsible for lowering its conductivity. Conductivity measurement of **SBO BF_4** was not undertaken due to its low solubility in MeCN (<0.35M).

Potential Window in MeCN. The potential window of electrolytes at 0.65M in MeCN was measured using limiting current density of 1 mA/cm^2 [10]. The results are summarized in *Table 3*. A solution of 0.65M $TEABF_4$ (tetraethylammonium tetrafluoroborate) in MeCN is the industry standard for ultracapacitors, and the performance of electrolytes developed in house was compared with 0.65M $TEABF_4$/MeCN (potential window *ca.* 5.5 V).

The cathodic stability of the BF_4 salts of OP, 4MOP, and 5MOP was comparable with SBP in MeCN, but for the 2MOP and 2EOP salts, it was slightly lower. The alkyl group present between the N- and O-atoms was responsible for slight lowering of the stability. The instability seems to be a result of the β-elimination from the alkyl group between two electron-withdrawing atoms (*Scheme 2*).

Thermal Analysis. The thermal stability of the salts was estimated using thermogravimetric analysis. The results are shown in *Fig. 2*.

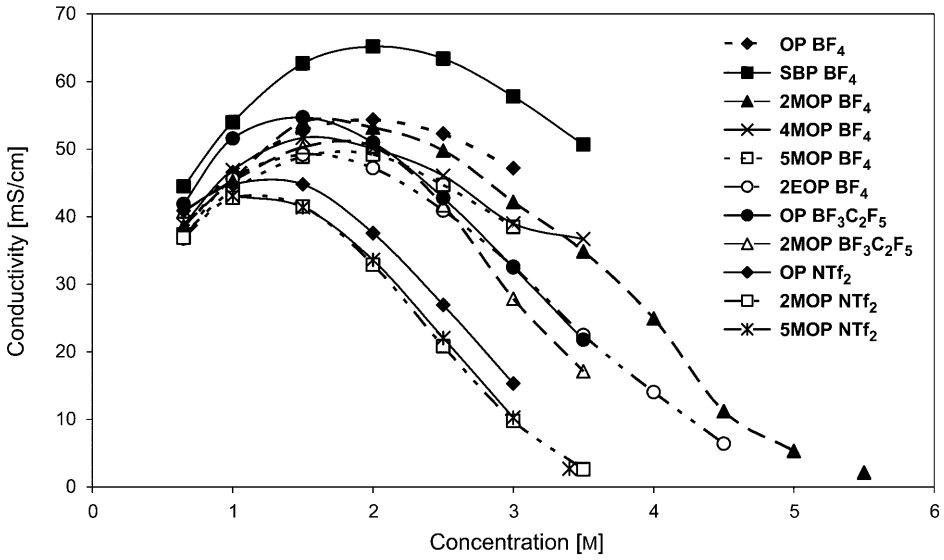


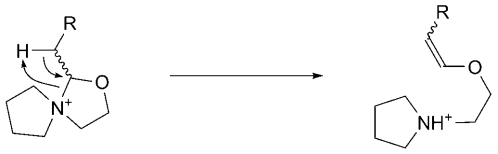
Fig. 1. *Conductivity of electrolytes at various concentrations in MeCN*

Table 3. *Potential Window of Oxygenated Spiroammonium Salts at 0.65*M *in MeCN*

Salt	Cathodic limit [V]	Anodic limit [V]	Potential window [V]
SBP BF_4	– 2.7	4.6	7.3
OP BF_4	– 2.8	4.5	7.3
OP $BF_3C_2F_5$	– 2.7	3.4	6.1
OP NTf_2	– 2.8	3.5	6.2
2MOP BF_4	– 2.6	4.6	7.2
2MOP $BF_3C_2F_5$	– 2.5	3.4	5.9
2MOP NTf_2	– 2.7	3.4	6.1
2EOP BF_4	– 2.6	4.6	7.2
4MOP BF_4	– 2.7	4.6	7.3
5MOP BF_4	– 2.7	4.5	7.2
5MOP NTf_2	– 2.7	3.5	6.2
SBO BF_4[a])	– 2.6	4.4	7.0

[a]) 0.3M (maximum solubility).

Scheme 2



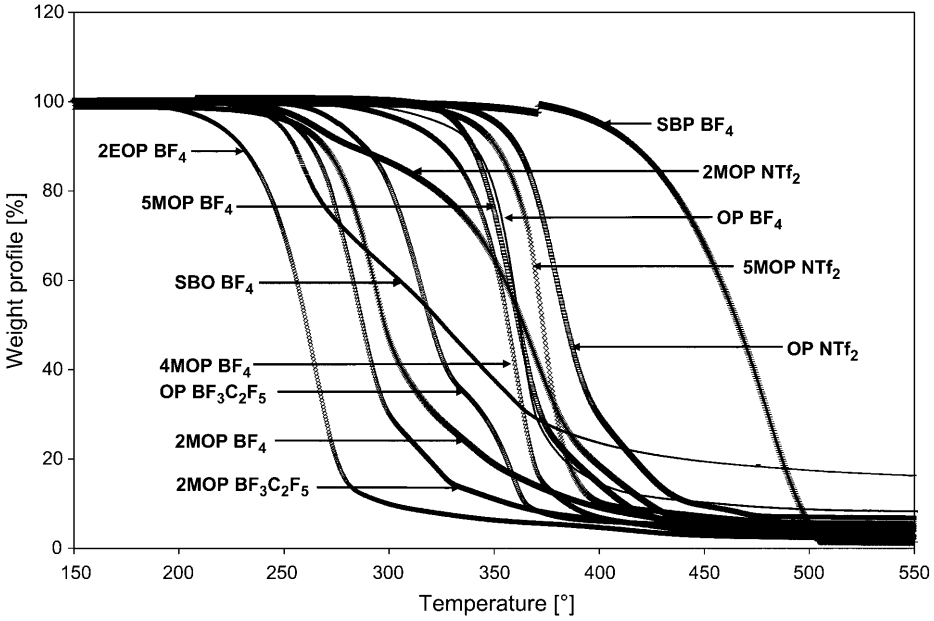


Fig. 2. *TGA Analysis of the synthesized salts*

The onset of the weight loss of each of the BF_4 salts occurred in the order of 2EOP < 2MOP ≈ SBO < OP ≈ 4MOP ≈ 5MOP < SBP. This trend is similar to that of the electrochemical stability. Reduction in thermal stability occurred upon introduction of the O-atom to the ring. The salts of OP, 2EOP, 2MOP, 4MOP, and 5MOP left a residue of carbonized material on the pan while the residue of SBP was colorless.

In summary, a variety of novel oxygen and alkyl group-containing spirobipyrrolidinium compounds were investigated for room temperature ionic liquid applications. Six novel cations, namely, OP, 2EOP, 2MOP, 4MOP, 5MOP, and SBO, were synthesized by employing aldehydes and haloalcohols. All together, eleven novel salts were produced. Three types of anions, BF_4^-, $BF_3C_2F_5^-$, and NTf_2^- were applied. The BF_4 and NTf_2 analogs were produced by conversion of chlorides, while the $BF_3C_2F_5$ analogs were generated by metathesis of BF_4.

The melting points and voltage windows were determined from TGA and linear sweep voltammetry. The melting point reduced from 189° (**SBP BF_4**) to below 100° in six salts, and was even below 30° (RTIL) in four salts.

Potential window measurement was performed at 0.65M solution dissolved in MeCN for each salt. The parent compound **SBP BF_4** had a voltage window of 7.3 V. Six out of eleven salts had a potential window ≥ 7.0 V. The potential window varied from 5.9 to 7.3 V. The potential window of commercial workhorse 0.65M $TEABF_4$ in MeCN was *ca.* 5.5 V.

Conductivity measurement was performed at various concentrations (0.65 to 5.0M in MeCN), and a conductivity maximum was observed around a 2M concentration for

all salts. The conductivity (at 2M) of all the salts was in the range *ca.* 48–55 mS/cm, as compared with 65 mS/cm for **SBP BF_4**.

The thermal stability of various salts was found to reduce from *ca.* 500 to 300–420° range, which is more than adequate for most of the high temperature EDLC applications.

Experimental Part

General. An overview of ions that were synthesized is shown in *Table 1*. Salt of $LiNTf_2$ and aq. 50% HBF_4 were purchased from *TCI* and *Acros Organics*, resp. The cation chlorides were reacted with $LiNTf_2$ and HBF_4 to convert them into NTf_2 and BF_4 salts, resp. Aluminum oxide (activated, acidic, *Brockmann* Grade I, 58 Å) was purchased from *Alfa Aesar*. Regeneration of H^+-form cation exchange resin (*BioRad AG MP-50* H^+-form) was undertaken as follows. Addition of 1M NaOH to the column until the eluent became basic, then H_2O was added to neutralize the eluent, subsequently 1M HCl in $MeOH/H_2O$ (1:1) was added until the eluent became acidic, 1M HCl (two bed volume), and then H_2O until the eluent became neutral.

Characterizations. Measurement of NMR spectra of salts in CD_3OD unless specified, and the solvent peaks of ^1H- and ^{13}C-NMR, and external $CFCl_3$ peak of ^{19}F-NMR were used as references for the chemical shifts, resp. Linear sweep voltammetry of 0.65M electrolyte was performed using *Princeton Applied Research PARSTAT 2273A* potentiostat with glassy carbon working electrode (*AFE1E050GC E1 Series* Glassy Carbon electrode, *Pine Research Instrumentation*), Pt wire counter electrode, and Ag wire *quasi*-reference electrode at a scan rate of 5 mV/s in a dry box and the potential window was determined with a limiting current at 1 mA/cm^2 [10]. Conductivity and viscosity were measured using *Radiometer Analytical CDM230 Conductivity Meter* and *Brookfield DV-II + Pro*, resp., at 25°. TGA Data was recorded on a *TA Instruments TGA 2050* thermogravimetric analyzer under dynamic N_2 flow (total flow rate 100 cm^3/min), using Pt pans and a ramp rate of 10°/min. DSC Data was recorded on a *TA Instruments DSC 2920* differential scanning calorimeter at 1 atm under dynamic N_2, using hermetically sealed Al pans, with a ramp rate of 10°/min.

Synthesis of $KBF_3C_2F_5$. $KBF_3C_2F_5$ was synthesized with slight modification of the previous method [37]. CF_3CF_2Br (43.8 g, 0.22 mmol) was condensed on a cold finger and introduced to anh. Et_2O (400 ml). PhMgBr (3M in Et_2O, 70 ml, 0.21 mol) was added dropwise to the mixture at a temp. below −65°, and stirred for 1 h. After dropwise addition of $(MeO)_3B$ (24.9 g, 0.24 mol), the temp. was raised to −40°, subsequently, the bath temp. was lowered to dry ice temp., and stirred for 2 h. The mixture was decanted into cold 50% HF (100) in a high density polyethylene container, and stirred overnight at r.t. Then, ice-cold aq. KOH (100 g in 100 ml H_2O) was added while maintaining the temp. below 15°. The org. layer was separated. The aq. layer was extracted three times with Et_2O. The combined org. layers were dried over K_2CO_3 and $MgSO_4$. Filtration removed the desiccant material, and the volatiles by evaporation, the residual solid was washed with hexane and then recrystallized from i-PrOH/toluene to give the salt (17.86 g, 33%).

Synthesis of 1,1′-Spirobipyrrolidinium Tetrafluoroborate (*=5-Azoniaspiro[4.4]nonane Tetrafluoroborate*; **SBP BF_4**). Synthesis of **SBP BF_4** was attempted according to the previous report using pyrrolidine, 1,4-dibromobutane, K_2CO_3, and KBF_4 in MeCN [40]. However, due to inefficient anion exchange metathesis between Br and BF_4, the anion was converted to Cl using cation exchange resin, and subsequently converted to BF_4 using HBF_4 [23][41][42]. The resulting product was recrystallized from i-PrOH several times.

Synthesis of 3-Oxazolidine-1′-spiropyrrolidinium Tetrafluoroborate (*=2-Oxa-5-azoniaspiro[4.4]nonane Tetrafluoroborate*; **OP BF_4**). Pyrrolidine (28.45 g, 0.40 mol), was added to a mixture of paraformaldehyde (12.01 g, 0.40 mol), Et_2O (150 ml), and 2-chloroethanol (32.20 g, 0.40 mol), and mildly refluxed. Stirring overnight at r.t. resulted in layer separation. The top Et_2O layer was discarded, and the bottom layer was dissolved in H_2O and subsequently filtered. CH_2Cl_2 was used to wash the filtrate three times, and the aq. layer was evaporated, and the residue dried *in vacuo* at 100° to yield a crude chloride salt (OP Cl, 57.15 g, 0.35 mmol). It was converted to BF_4 salt by adding 50% HBF_4

(61.35 g, 0.35 mol) and MeOH (150 ml), followed by evaporation. EtOH (100 ml) was added and subsequently evaporated to azeotropically remove moisture. The residue was recrystallized from MeOH, and subsequently dissolved in MeCN and filtered through a membrane filter (*Nylon*, 0.22 μ). The solvent was evaporated, and the crude product was repeatedly recrystallized from MeOH and dried *in vacuo* at 100° overnight to give **OP BF$_4$** (64.0 g, 74% overall yield). ^{1}H-NMR: 4.87 (*s*, 2 H); 4.34 (*t*, *J* = 7.3, 2 H); 3.81 (*t*, *J* = 7.3, 2 H); 3.76–3.60 (*m*, 4 H); 2.24 (*dd*, *J* = 7.8, 16.9, 4 H). ^{13}C-NMR: 92.6; 67.4; 62.7; 60.7; 23.2. ^{19}F-NMR: −154.4 (*m*).

3-Oxazolidine-1′-spiropyrrolidinium Trifluoro(pentafluoroethyl)borate(1−) (=*2-Oxa-5-azoniaspiro[4.4]nonane Trifluoro(pentafluoroethyl)borate(1−)*; **OP BF$_3$C$_2$F$_5$**). **OP BF$_3$C$_2$F$_5$** was synthesized by the metathesis of **OP BF$_4$** (24.34 g, 0.116 mol) and $KBF_3C_2F_5$ (26.17 g, 0.116 mol) by mixing the aq. solns. CH_2Cl_2 was added to extract **OP BF$_3$C$_2$F$_5$**. The org. layer was washed with two portions of H_2O. The solvent was removed by evaporation, and the residue was recrystallized from MeOH at −80° to give the product (17.2 g, 47%). ^{1}H-NMR: 4.87 (*s*, 2 H); 4.33 (*t*, *J* = 7.3, 2 H); 3.81 (*t*, *J* = 7.3, 2 H); 3.74–3.62 (*m*, 4 H); 2.24 (*dd*, *J* = 7.6, 17.2, 4 H). ^{13}C-NMR: 92.5; 67.2; 62.7; 60.5; 23.0. ^{19}F-NMR: −85.9 (*q*, *J* = 4.9); −139.1 (*q*, *J* = 20.0); −156.6 (*q*, *J* = 42.2).

3-Oxazolidine-1′-spiropyrrolidinium Bis[(trifluoromethyl)sulfonyl]azanide (=*2-Oxa-5-azoniaspiro[4.4]nonane Bis[(trifluoromethyl)sulfonyl]azanide*; **OP NTf$_2$**). **OP NTf$_2$** was prepared by the metathesis of crude OP Cl (29.6 g, 0.181 mol) and $LiNTf_2$ (51.9 g, 0.181 mol) in a similar way as described above and recrystallized from MeOH at −80° (63.0 g, 85%). ^{1}H-NMR: 4.87 (*s*, 2 H); 4.33 (*t*, *J* = 7.3, 2 H); 3.81 (*t*, *J* = 7.1, 2 H); 3.76–3.58 (*m*, 4 H); 2.24 (*dd*, *J* = 7.6, 17.2, 4 H). ^{13}C-NMR: 121.3 (*q*, *J* = 320.4); 92.7; 67.5; 62.9 (br.); 60.8 (br.); 23.3. ^{19}F-NMR: −81.1 (*s*).

Synthesis of 2-Methyl- (2MOP) *and 2-Ethyl-3-oxazolidine-1′-spiropyrrolidinium* (2EOP) *Salts. 2-Methyl-3-oxazolidine-1′-spiropyrrolidinium Tetrafluoroborate* (=*1-Methyl-2-oxa-5-azoniaspiro[4.4]nonane Tetrafluoroborate*; **2MOP BF$_4$**). Acetaldehyde (33.7 ml, 0.60 mol) was added to a chilled mixture of K_2CO_3 (20.7 g, 0.15 mol), Et_2O (150 ml), and 2-chloroethanol (48.3 g, 0.60 mol). To this mixture, pyrrolidine (42.7 g, 0.60 mol) was added dropwise while constantly stirring. Overnight, the temp. of the ice bath came to r.t. The volatile compounds were removed by evaporation, followed by addition of CH_2Cl_2 (200 ml) and subsequent filtration. H_2O (100 ml) was added, and the org. phase was removed. CH_2Cl_2 was used to wash the aq. phase twice, followed by subsequent evaporation. The residue was dissolved in H_2O to apply to H^+-form cation exchange column chromatography (CC; 300 ml). The product was eluted with 0.2M aq. HCl (1 l) and the solvent was evaporated. The residue was dissolved in EtOH, and the insoluble material was filtered off. The solvent was evaporated, and the residue was dried *in vacuo* at r.t. to give the crude chloride salt (2MOP Cl, 77.9 g, 0.44 mol). The crude product was dissolved in 50% HBF_4 (77.3 g, 0.44 mol) and MeOH (200 ml) and subsequently evaporated. The residue was dried *in vacuo* overnight at 50° and then dissolved in CH_2Cl_2 (200 ml) and applied to acidic alumina CC (200 ml) and eluted with CH_2Cl_2 (800 ml). The eluent was evaporated, and the residue was dissolved in H_2O, then washed with 20% Et_2O in CH_2Cl_2 three times. The aq. layer was evaporated and dried *in vacuo* at 70° overnight to give a crude orange oil, **2MOP BF$_4$** (71.6 g, 52%). Crude **2MOP BF$_4$** (18.8 g) was further purified by acidic alumina CC (150 ml) with CH_2Cl_2 eluent (600 ml). The eluent was evaporated and the residue dissolved in H_2O followed by washing with 20% Et_2O in CH_2Cl_2. The aq. phase was filtered, evaporated, and subsequently dried *in vacuo* at 70° overnight to give **2MOP BF$_4$** (16.9 g). The product was dissolved in MeOH (800 ml) and allowed to crystallize at −80°. The soln. separated into two phases. Most of the impurities settled down, while the product formed a turbid soln. The turbid soln. was filtered using a chilled *Büchner* funnel at 4°, and the product dried *in vacuo* at 70° overnight. The filtrate soln. was poured back into the impure product to dissolve more salt to yield additional crop. ^{1}H-NMR: 5.09 (*q*, *J* = 5.4, H−C(1)); 4.34–4,20 (*m*, 2 H); 3.96–3.71 (*m*, 2 H); 3.71–3.47 (*m*, 3 H); 3.47–3.33 (*m*, 1 H); 2.23 (br. *s*, 4 H); 1.58 (*d*, *J* = 5.6, Me−C(1)). ^{13}C-NMR: 99.0; 65.0; 61.5 (br.); 61.2 (br.); 57.5 (br.); 23.0; 22.6; 14.0. ^{19}F-NMR: −153.6 (*m*).

2-Methyl-3-oxazolidine-1′-spiropyrrolidinium Trifluoro(pentafluoroethyl)borate(1−) (=*1-Methyl-2-oxa-5-azoniaspiro[4.4]nonane Trifluoro(pentafluoroethyl)borate(1−)*; **2MOP BF$_3$C$_2$F$_5$**) *and 2-Methyl-3-oxazolidine-1′-spiropyrrolidinium Bis[(trifluoromethyl)sulfonyl]azanide* (=*1-Methyl-2-oxa-5-azoniaspiro[4.4]nonane Bis[(trifluoromethyl)sulfonyl]azanide*; **2MOP NTf$_2$**). Equimolar amounts of crude **2MOP BF$_4$** and $KBF_3C_2F_5$ or $LiNTf_2$, resp., were mixed in H_2O/CH_2Cl_2. The org. phase was separated,

and the aq. phase was subsequently extracted with CH_2Cl_2 several times. The combined org. phase was washed eight times with H_2O. The solvent was evaporated, and the residue was dried *in vacuo* at 50° to give each of the crude products (68 and 91%, resp.). **2MOP $BF_3C_2F_5$** and **2MOP NTf_2** were further recrystallized from MeOH at −20° and −80°, resp., and the crystals filtered at 4° and then dried *in vacuo* at 70°.

Data of **2MOP $BF_3C_2F_5$**. ^{1}H-NMR: 5.08 (*q*, H−C(1)); 4.37–4.14 (*m*, 2 H); 3.93–3.69 (*m*, 2 H); 3.59 (*td*-like, 3 H); 3.44–3.32 (*m*, 1 H); 2.22 (br. *s*, 4 H); 1.58 (*d*, *J* = 5.6, Me−C(1)). ^{13}C-NMR: 99.3; 65.1; 61.6 (br.); 61.5 (br.); 57.7 (br.); 23.2; 22.7; 14.0. ^{19}F-NMR: −85.8 (*q*, *J* = 4.9); −138.9 (*q*, *J* = 19.7); −156.6 (*q*, *J* = 41.8).

Data of **2MOP NTf_2**. ^{1}H-NMR: 5.07 (*q*, *J* = 5.6, H−C(1)); 4.36–4.18 (*m*, 2 H); 3.90–3.68 (*m*, 2 H); 3.69–3.48 (*m*, 3 H); 3.43–3.33 (*m*, 1 H); 2.22 (br. *s*, 4 H); 1.57 (*d*, *J* = 5.6, Me−C(1)). ^{13}C-NMR: 21.2 (*q*, *J* = 320.4); 65.2 (*m*); 61.2 (*m*); 57.3 (*m*); 23.0; 22.5; 14.0 (*m*). ^{19}F-NMR: −80.9 (*s*).

2-Ethyl-3-oxazolidine-1′-spiropyrrolidinium Tetrafluoroborate (= *1-Ethyl-2-oxa-5-azoniaspiro[4.4]-nonane Tetrafluoroborate*; **2EOP BF_4**). The same method using propionaldehyde instead of acetaldehyde produced a yield of 11% of **2EOP BF_4**. The recrystallization from MeOH or EtOH was not successful. ^{1}H-NMR: 4.87 (*d*, *J* = 9.6, H−C(1)); 4.34–4.22 (*m*, 2 H); 3.85–3.73 (*m*, 2 H); 3.69–3.51 (*m*, 3 H); 3.44–3.30 (*m*, 1 H); 2.22 (br. *s*, 4 H); 2.06–1.91 (*m*, 1 H); 1.78 (*ddd*, *J* = 7.1, 10.1, 13.6, 1 H); 1.10 (*t*, *J* = 7.6, Me). ^{13}C-NMR: 102.8; 64.8; 61.8; 61.1; 57.9; 22.9; 22.2; 22.2; 9.8. ^{19}F-NMR: −152.9; −153.0.

Synthesis of 4-Methyl-3-oxazolidine-1′-spiropyrrolidinium Tetrafluoroborate (= *3-Methyl-2-oxa-5-azoniaspiro[4.4]nonane Tetrafluoroborate*; **4MOP BF_4**). 2-Chloro-1-propanol was synthesized following the procedure described in [43]. To a mixture of $NaBH_4$ (14.19 g, 0.357 mol) and EtOH (150 ml), ethyl 2-chloropropionate (68.29 g, 0.50 mol) was added dropwise while maintaining the temp. below 45°. The mixture was stirred for 30 min and subsequently acidified using 2M HCl (200 ml) soln. Addition of CH_2Cl_2 (200 ml) separated the soln. into two layers. The org. phase was decanted and washed with H_2O (50 ml), followed by washing with aq. $NaHCO_3$, and subsequently dried over anh. $MgSO_4$. The solvent was gently evaporated after filtering off the drying reagent. The residue was subjected to fractional distillation (65–68°/70 mmHg, 31.20 g, 65%). Pyrrolidine (36.82 g, 0.511 mol) was added to a mixture of paraformaldehyde (15.35 g, 0.511 mol), Et_2O (120 ml), and 2-chloro-1-propanol (48.78 g, 0.511 mol), and refluxed overnight to form two layers. H_2O was added to dissolve the salt, and the aq. layer was separated, which was then washed with CH_2Cl_2 three times. The aq. phase was filtered and the solvent evaporated. The residue was dried *in vacuo* at r.t. to give the crude chloride salt, 4MOP Cl (24.08 g, 27%). 50% HBF_4 (23.8 g, 0.136 mol) and MeOH (70 ml) were added to the crude product, and the solvent was evaporated. EtOH (50 ml) was added and subsequently evaporated. This process was repeated twice. The resulting residue was recrystallized from EtOH (200 ml) at −20° to give **4MOP BF_4** (26.4 g, 85%) as a viscous solid. The product was further recrystallized from MeOH. ^{1}H-NMR: 4.87 (br. *s*, CH_2(1)); 4.53 (*t*, *J* = 8.3, 1 H); 4.13 (*qt*, *J* = 7.1, H−C(3)); 3.88–3.81 (*m*, 1 H); 3.73–3.64 (*m*, 1 H); 3.64–3.53 (*m*, 2 H); 3.51–3.43 (*m*, 1 H); 2.29–2.11 (*m*, 4 H); 1.47 (*d*, *J* = 6.6, Me). ^{13}C-NMR: 91.7; 73.4; 67.1; 61.7; 55.0; 22.9; 22.3; 12.8. ^{19}F-NMR: −154.4; −154.5.

Synthesis of 5-Methyl-3-oxazolidine-1′-spiropyrrolidinium (5MOP) *Salts. 5-Methyl-3-oxazolidine-1′-spiropyrrolidinium Tetrafluoroborate* (= *4-Methyl-2-oxa-5-azoniaspiro[4.4]nonane Tetrafluoroborate*; **5MOP BF_4**). Synthesis of crude 5MOP Cl was undertaken in a manner similar to OP Cl. The reaction between 1-chloro-2-propanol (technical grade, 75% purity, 18.91 g, 0.20 mol), paraformaldehyde (6.01 g, 0.20 mol), and pyrrolidine (14.22 g, 0.20 mol) in Et_2O (50 ml) gave crude 5MOP Cl as a waxy gel (29.53 g, 83%). 5MOP Cl was subsequently converted to **5MOP BF_4** with 50% HBF_4 (29.18 g, 0.166 mol) in MeOH (80 ml) followed by three sets of EtOH-evaporation procedure. Drying *in vacuo* overnight at r.t. gave the crude solid product (36.9 g, 81%), which was further recrystallized from MeOH at −80° in the same manner as **2MOP BF_4**. The product was dried *in vacuo* at 80° to yield **5MOP BF_4** (25.9 g, 55%). ^{1}H-NMR showed that the product contained about 6 mol-% of **4MOP BF_4** derived from the technical grade 1-chloro-2-propanol, and further recrystallization from MeOH did not remove **4MOP BF_4**. ^{1}H-NMR: 5.03 (*d*, *J* = 6.1, H−C(1)); 4.79 (*d*, *J* = 5.6, H−C(1)); 4.59 (*qdd*, *J* = 6.8, H−C(4)); 3.96 (*dd*, *J* = 7.3, 11.9, H−C(3)); 3.80–3.55 (*m*, 4 H); 3.35 (*dd*, *J* = 8.1, 11.6, H−C(3)); 2.38–2.07 (*m*, 4 H); 1.44 (*d*, *J* = 6.1, Me). ^{13}C-NMR: 92.2; 76.4; 66.5; 64.1; 62.4; 23.1; 23.0; 18.6. ^{19}F-NMR: −154.1; −154.2.

5-Methyl-3-oxazolidine-1′-spiropyrrolidinium Bis[(trifluoromethyl)sulfonyl]azanide (=*4-Methyl-2-oxa-5-azoniaspiro[4.4]nonane Bis[(trifluoromethyl)sulfonyl]azanide*; **5MOP NTf$_2$**). **5MOP NTf$_2$** was synthesized using metathesis of **5MOP BF$_4$** and $LiNTf_2$ in the same manner as the synthesis of **2MOP NTf$_2$** in 91% yield, and the product was further recrystallized from MeOH at $-80°$, in the same manner as **2MOP BF$_4$**. ^{1}H-NMR: 5.04 (*d*, *J* = 5.6, H–C(1)); 4.79 (*d*, *J* = 6.1, H–C(1)); 4.59 (*qdd*, *J* = 6.9, H–C(4)); 3.95 (*dd*, *J* = 7.1, 11.6, H–C(3)); 3.79–3.58 (*m*, 4 H); 3.35 (*dd*, *J* = 8.6, 11.6, H–C(3)); 2.30–2.14 (*m*, 4 H); 1.45 (*d*, *J* = 6.6, Me). ^{13}C-NMR: 121.2 (*q*, *J* = 320.5, 1 H); 92.3 (br.); 76.4; 66.6 (*m*); 64.3 (*m*); 62.6 (*m*); 23.0; 23.0; 18.6; 18.6. ^{19}F-NMR: −81.1 (*s*).

Synthesis of 3,3′-Spirobioxazolidinium Tetrafluoroborate (=*2,7-Dioxa-5-azoniaspiro[4.4]nonane Tetrafluoroborate*; **SBO BF$_4$**). 1,3-Oxazolidine was synthesized from paraformaldehyde (15.02 g, 0.50 mol) and 2-aminoethanol (30.54 g, 0.50 mol) [44]. The reaction between paraformaldehyde and aminoethanol yielded 1,3,5-tris(2-hydroxyethyl)hexahydro-1,3,5-triazine [45], which was thermally cracked to yield 1,3-oxazolidine. The crude distillate (34.4 g, 94%) was collected in a trap chilled at $-78°$ and was used without further purification. Crude 1,3-oxazolidine (34.4 g, 0.47 mol) was added to paraformaldehyde (14.11 g, 0.47 mol) and 2-chloroethanol (37.8 g, 0.47 mol) in Et_2O (120 ml) at $-78°$. The temp. was raised to $0°$ and then slowly to r.t. overnight while stirring continuously. The volatile materials were removed by evaporation, and the residue was dissolved in H_2O. The insoluble material was filtered, and the filtrate was washed three times with CH_2Cl_2, and then applied to a column of H^+-form cation exchange resin (250 ml). The column was washed with H_2O to neutralize the eluent, and subsequently eluted with 1 to 2M HCl. Solvent evaporation yielded a crude SBO Cl (51.04 g, 66%, 0.31 mol), which was converted to **SBO BF$_4$** with 50% HBF_4 (54.17 g, 0.31 mol) in MeOH (100 ml) to immediately generate a white precipitate. The product was filtered and subsequently recrystallized from H_2O, and dried *in vacuo* at $100°$ to yield **SBO BF$_4$** (23.55 g, 35%). ^{1}H-NMR ((D$_6$)DMSO): 5.27 (*d*, *J* = 5.6, 2 H); 5.13 (*d*, *J* = 5.6, 2 H); 4.50 (*t*, *J* = 7.1, 4 H); 4.19–4.07 (*m*, 4 H). ^{13}C-NMR ((D$_6$)DMSO): 90.0 (*m*); 66.1 (*m*); 56.6 (*m*). ^{19}F-NMR: −148.7; −148.7.

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