

Pentafluorosulfanyl (SF<sub>5</sub>) Containing Energetic SaltsHaixiang Gao,<sup>[a]</sup> Chengfeng Ye,<sup>[a]</sup> Rolf W. Winter,<sup>[b]</sup> Gary L. Gard,<sup>[b]</sup>  
Michael E. Sitzmann,<sup>[c]</sup> and Jean'ne M. Shreeve\*<sup>[a]</sup>**Keywords:** Ionic liquids / Pentafluorosulfanyl nitramide / Quaternization / Salts / Heats of formation / Energetic materials

New quaternary salts of pentafluorosulfanyl-substituted (SF<sub>5</sub>) *N*-methylimidazole (**1**), 4-amino-1,2,4-triazole (**3**) or pyridine (**5**) were prepared and characterized. Most of the salts exhibit good thermal stabilities and low melting points placing them in the ionic liquid class. Their densities range between 1.4 and 1.8 g/cm<sup>3</sup>. The standard enthalpies of for-

mation for the new salts were calculated by the use of computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on densities of salts.

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## Introduction

Energetic materials are vital to the improvement and advancement in our lives; essential in peace and in armed conflict. These materials are controllable energy sources which deliver power as a function of the rate at which the energy is liberated. Propellants that release energy over a period of a few milliseconds to seconds by evolving gases are useful for driving turbines or propelling rockets. However, explosives, which evolve energy at rapid rates are employed to produce intense shock waves and find great value in mining, cutting, and initiation of detonation phenomena. Nearly all of the industrially used energetics are based on ammonium nitrate, while for military purposes nitroglycerin, nitrocellulose, HMX, TNT, or RDX are most frequently used. Currently, the research in the field of energetic materials has tended to be directed towards the synthesis of simple molecules with high energy, high density, high heat resistance and low sensitivity by often focusing on the design of nitrogen-containing heterocyclic-based, energetic, low-melting salts.<sup>[1,2]</sup> Energetic materials that are salts often possess advantages over molecular analogues since they tend to exhibit lower vapor pressures and higher densities.

High on the list of important characteristics for energetic materials are density and energy released. Earlier we reported new thermally stable, pentafluorosulfanyl polyfluoroalkyl-substituted quaternary salts whose melting points were less than 0 °C and where the presence of the pentafluorosulfanyl group markedly increased the densities of

these room-temperature ionic liquids vis-à-vis most of their perfluoroalkyl or alkyl analogues.<sup>[3]</sup> Based on those results and the following observations: (1) indications that the SF<sub>5</sub> group can provide energetic salts with improved properties, i.e., increased density, decreased sensitivity and good thermal stability; and (2) the larger energy release found due to formation of HF in the detonation of SF<sub>5</sub> explosives [compare the average S–F bond energy (79 kcal/mol) to that of H–F (136 kcal/mol)],<sup>[4]</sup> we examined the impact of the pentafluorosulfanyl group on the properties of energetic salts. In the present work, we report the preparation and characterization of pentafluorosulfanylalkyl-substituted imidazolium, triazolium and pyridinium salts that contain highly oxidizing anions.

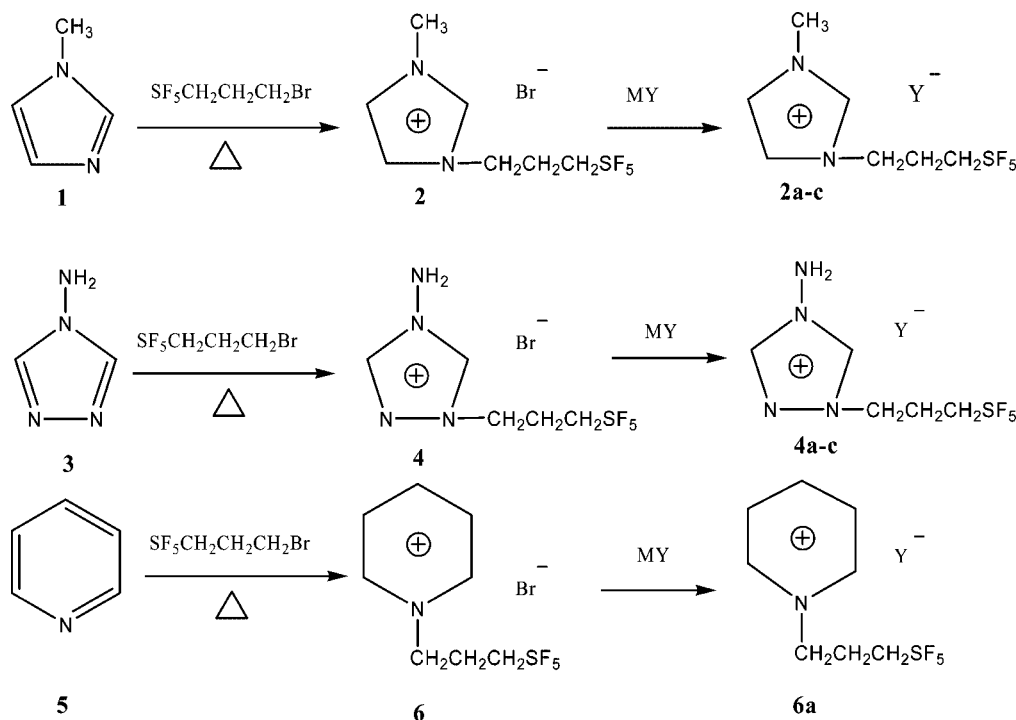
## Results and Discussion

Initially, we attempted to quaternize *N*-methylimidazole (**1**), 4-amino-1,2,4-triazole (**3**) or pyridine (**5**) with SF<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>Br or SF<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>OTs, but failed because major decomposition of the pentafluorosulfanyl-containing precursor occurred due to the loss of HBr or HOTs. In sharp contrast, by simply elongating the alkyl chain in the SF<sub>5</sub> electrophile from ethyl to propyl, excellent yields resulted. For example, reaction of SF<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br with *N*-methylimidazole (**1**) in a 1:1 molar ratio without solvent at 65 °C for 12 h led to the formation of the quaternary salt **2** in 90% isolated yield (Scheme 1). Analogously, reactions of SF<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br with 4-amino-1,2,4-triazole (**3**) and pyridine (**5**) gave the monoquaternary bromides **4** and **6** in >85% isolated yields. Nitrate, perchlorate, dinitramide, and pentafluorosulfanyl nitramide salts were synthesized by metathesis of the monoquaternary salts with silver nitrate, silver perchlorate, ammonium dinitramide, and potassium pentafluorosulfanyl nitramide,<sup>[5]</sup> respectively, in aqueous

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Scheme 1.

solution (Scheme 1). Because some of the nitrate salts were hygroscopic, they were dried under vacuum for 24 h and stored in a desiccator for further analysis.

Phase-transition temperatures [midpoints of melting points ( $T_m$ ) or glass phase transition temperatures ( $T_g$ )] were determined by differential scanning calorimetry (DSC), and decomposition points ( $T_d$ ) were recorded using thermogravimetric analysis (TGA) (Table 1). It is seen that the decomposition temperatures and heats of formation for the perchlorate salts are higher than those of the nitrate and dinitramide salts. The melting points of the imidazolium (2)

and pyridinium (6) salts are considerably lower than that of triazolium salts (4).

Density is one of the important physical properties of energetic salts. Some of the experimental densities obtained by using a helium pycnometer for the new salts are also listed in Table 1. For all of the compounds, densities exceeded  $1.40 \text{ g cm}^{-3}$ , likely arising from the presence of the  $\text{SF}_5$  moiety. This is particularly noticeable in the case of 4d, which exhibits a density of  $1.82 \text{ g cm}^{-3}$  due to the  $\text{SF}_5$  functional groups found in both anion and cation, which markedly enhance this property.

Table 1. Structure and properties of  $\text{SF}_5$ -containing salts.

Cation	Anion	No.	$T_m/T_g$ [°C]	$T_d$ [°C]	$d$ [g/cm <sup>3</sup> ]	$H_L^{[a]}$	$\Delta_f H_m^{o[b]}$ (cation)	$\Delta_f H_m^{o[b]}$ (anion)	$\Delta_f H_m^{o[b]}$ (salts)	$D^{[c]}$	$P^{[d]}$
	Br	2	90.5	—	—	—	−66.3	—	—	—	—
	NO <sub>3</sub>	2a	−33.7	172.3	1.54	106.5	−66.3	−73.6	−246.4	5819	11.4
	ClO <sub>4</sub>	2b	−68.0	247.1	1.46	102.2	−66.3	−66.4	−234.8	5538	10.4
	[N(NO <sub>2</sub> ) <sub>2</sub> ]	2c	−50.7	201.7	1.52	102.7	−66.3	−26.9	−195.9	6118	13.0
	Br	4	101.3	—	—	—	−33.3	—	—	—	—
	NO <sub>3</sub>	4a	58.6	145.8	1.43	104.4	−33.3	−73.6	−211.2	5726	10.8
	ClO <sub>4</sub>	4b	50.7	242.7	1.41	101.1	−33.3	−66.4	−200.8	5712	11.3
	[N(NO <sub>2</sub> ) <sub>2</sub> ]	4c	84.8	160.9	1.44	101.2	−33.3	−26.9	−161.4	6145	13.2
	[SF <sub>5</sub> NNO <sub>2</sub> ]	4d	−20.6	188.2	1.82	102.0	−33.3	−284.3	−419.5	6680	16.7
	Br	6	95.4	—	—	—	−77.9	—	—	—	—
	[N(NO <sub>2</sub> ) <sub>2</sub> ]	6a	11.0	182.3	1.47	102.1	−77.9	−26.9	−206.8	5636	10.7

[a] Lattice energy [kcal/mol]. [b] [kcal/mol]. [c] Detonation velocity [m/s]. [d] Detonation pressure [GPa].

### Thermochemistry

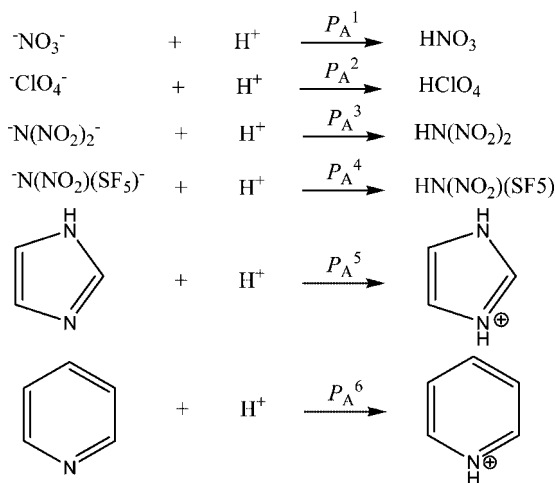
According to Born–Haber energy cycles, heats of formation of ionic salts can be simplified by the formula:

$$\Delta H_f^\circ (\text{ionic salts, 298 K}) = \Delta H_f^\circ (\text{cation, 298 K}) + \Delta H_f^\circ (\text{anion, 298 K}) - \Delta H_L$$

where  $\Delta H_L$  is the lattice energy of the ionic salts. For 1:1 salts and considering the nonlinear nature of the cation and anion we currently used,  $\Delta H_L$  [kJ/mol] can be predicted by the formula suggested by Jenkins et al.<sup>[6]</sup> as:

$$\Delta H_L = 1981.2 \cdot (\rho_m/M_m)^{1/3} + 108.8$$

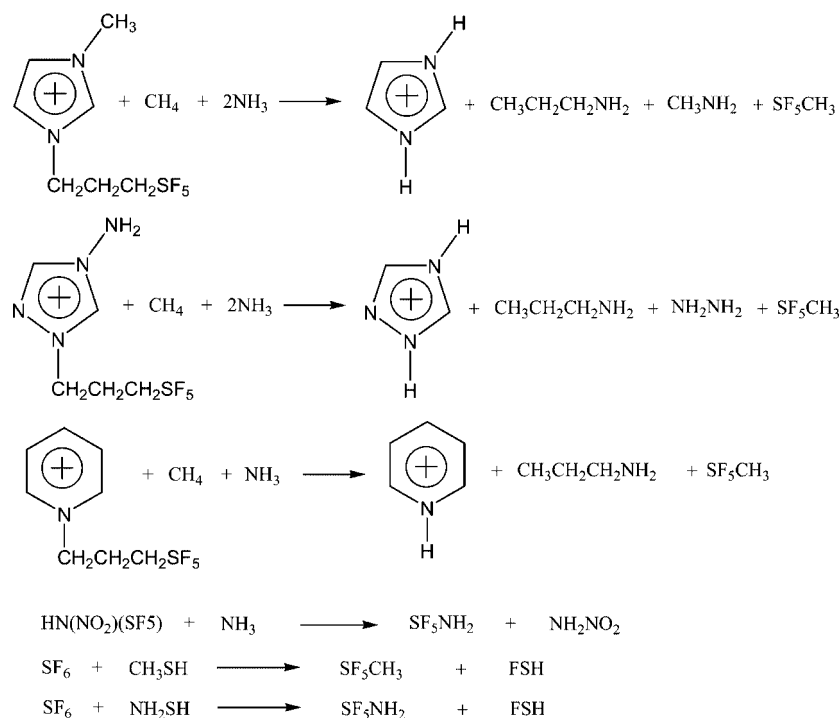
Heats of formation of the NO<sub>3</sub><sup>−</sup>, ClO<sub>4</sub><sup>−</sup> and N(NO<sub>2</sub>)<sub>2</sub><sup>−</sup> anions can be easily obtained by the reactions in Scheme 2.



Scheme 2.

The proton affinities ( $P_A$ ) were calculated using the G2 method or taken from the literature.<sup>[7]</sup> A value of 1528.085 kJ mol<sup>−1</sup> with correction of 6.197 kJ mol<sup>−1</sup> was adopted for  $\Delta H_f^\circ$  (H<sup>+</sup>, 298 K).<sup>[8,9]</sup> Heats of formation of HNO<sub>3</sub> and HN(NO<sub>2</sub>)<sub>2</sub> in the gas phase are available (−32.1 and 29.9 kcal/mol, respectively),<sup>[7]</sup> while the heat of formation of HClO<sub>4</sub> (g) is a little uncertain. In this work, 0.6 kcal mol<sup>−1</sup> was used. This was derived by computation using W1 and W2 methods.<sup>[10]</sup> This molecule exhibits particularly severe degrees of inner polarization, and as such obtaining a basis-set limit SCF component to the total atomization energy becomes a challenge. However, the G2 calculation gives 10.8 kcal/mol. Heats of formation of NO<sub>3</sub><sup>−</sup>, ClO<sub>4</sub><sup>−</sup> and N(NO<sub>2</sub>)<sub>2</sub><sup>−</sup> were calculated to be −73.6, −66.4, and −26.9 kcal/mol, respectively.

Then the remaining task was to determine the heats of formation of the cations, and of N(NO<sub>2</sub>)(SF<sub>5</sub>)<sup>+</sup>, which were computed using the method of isodesmic reactions (Scheme 3). The 1,2,4-triazolium species was purposely conserved, because its heat of formation has been experimentally determined to be 835 kJ mol<sup>−1</sup>.<sup>[8]</sup> With the experimental heat of formation of imidazole and pyridine, the imidazolium and pyridinium cations were calculated by the proton-affinity reactions shown in Scheme 2 using the G2 method. The enthalpies of reactions ( $\Delta H_r^\circ$ , 298) are obtained by combining the MP2(full)/6-311++G\*\* energy difference for the reactions, the scaled zero-point energies, and other thermal factors. Thus, the heats of formation of the cations and of N(NO<sub>2</sub>)(SF<sub>5</sub>)<sup>+</sup> can be readily extracted. The results are listed in Table 1. The calculated enthalpies of formation ( $\Delta_f H_m$ ) range from −419.5 kcal mol<sup>−1</sup> to −161.5 kcal mol<sup>−1</sup>.



Scheme 3.

All of the values are negative mainly as a result of the large negative heat of formation of  $\text{SF}_5$  ( $-216.3 \text{ kcal/mol}$ ).<sup>[11]</sup>

The expected detonation pressures ( $P$ ) and detonation velocities ( $D$ ) based on the traditional Chapman–Jouget thermodynamic detonation theory were calculated (Table 1).<sup>[12]</sup> For all the salts, the calculated detonation pressures lie in the range between  $P = 10.4 \text{ GPa}$  (**2b**) and  $P = 16.7 \text{ GPa}$  (**4d**). These values are similar to that of tetranitromethane ( $14.4 \text{ GPa}$ ).<sup>[13]</sup> Detonation velocities range between  $D = 5538 \text{ m s}^{-1}$  and  $D = 6630 \text{ m s}^{-1}$  (**4d**), higher than those of ammonium dinitramide ( $D \geq 5300 \text{ m s}^{-1}$ ) and lead azide ( $D = 5300 \text{ m s}^{-1}$ ).

Of all of the new energetic compounds, **4b** is thermally considerably more stable than **4d**, but its density is lower by  $0.4 \text{ g/cm}^3$ . Also, the pentafluorosulfanylnitramide derivative **4d** has a melting point which is  $71^\circ\text{C}$  lower than **4b**. The densities of the new (pentafluorosulfanyl)alkyl quaternary salts are surprisingly low compared to their (pentafluorosulfanyl)polyfluoroalkyl quaternary analogs that exhibit densities around  $2 \text{ g/cm}^3$  making them among the most dense of any of the non-chloroaluminate salts reported to date.<sup>[14]</sup> Comparisons must be made carefully because the (pentafluorosulfanyl)polyfluoroalkyl derivatives were only studied with bis(trifluoromethanesulfonyl)amide as the anion.<sup>[3]</sup> However, it may be concluded that density may be enhanced by the presence of fluorine in fluoroalkyl and/or pentafluorosulfanyl moieties.

## Conclusions

Syntheses of  $\text{SF}_5$ -propyl derivatives of imidazole, 4-amino-1,2,4-triazole, and pyridine and their subsequent quaternization led to new energetic salts. Most of the new salts exhibit good physical properties, including moderately high density ( $>1.40 \text{ g/cm}^3$ ), good thermal and hydrolytic stabilities and low melting points ( $<100^\circ\text{C}$ ). The molar enthalpies of formation were calculated by theoretical methods. Perchlorate salts have slightly higher molar enthalpies of formation than the analogous nitrates. The calculated heats of formation for dinitramide-containing salts are the highest. Utilization of pentafluorosulfanylnitramide as the anion contributes to a decrease in the melting point because of its asymmetry and of the tendency for the negative charge to be dispersed over the entire anionic structure, as is the case for dinitramide.

## Experimental Section

**Caution:** While we have experienced no difficulties with shock and friction sensitivity of these compounds with high nitrogen content and rather high heats of formation, they should be synthesized in mmol amounts and handled with extreme care.

**General Methods:** All the reagents used were analytical reagents purchased from commercial sources and used as received.  $^1\text{H}$ ,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a 300-MHz NMR spectrometer operating at 300.13, 282 and 75.48 MHz, respectively.

Chemical shifts are reported relative to  $\text{Me}_4\text{Si}$  or  $\text{CCl}_3\text{F}$ . The solvent was  $\text{D}_2\text{O}$  unless otherwise specified. The melting and decomposition points were recorded with a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of  $10^\circ\text{C/min}$ , respectively. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Densities of ionic liquids were measured at room temperature using a pycnometer. Densities of solid salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were performed with an EXETER CE-440 Elemental Analyzer.

**Theoretical Study:** Computations were performed with the Gaussian03 (Revision D.01) suite of programs.<sup>[15]</sup> The geometric optimization and the frequency analyses are carried out using B3-LYP functional analyses with 6-31+G\*\* basis set.<sup>[16]</sup> Single energy points were calculated at the  $\text{MP}_2(\text{full})/6-311++\text{G}^{**}$  level.<sup>[17,18]</sup> All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

**General Procedure:** *N*-Methylimidazole (**1**), 4-amino-1,2,4-triazole (**3**), or pyridine (**5**) (2 mmol) and  $\text{SF}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  were sealed in a Pyrex glass tube in vacuo by cooling to liquid nitrogen temperature and then heated at  $65^\circ\text{C}$  for 12 h. After cooling to room temperature, the tube was opened and the volatile materials were removed at reduced pressure. Washing of the crude products with an acetone/pentane mixture (1:3) gave **2**, **4**, and **6** in good yields. The nitrate, perchlorate, dinitramide and pentafluorosulfanylnitramide salts were synthesized by metathesis of the monoquaternary bromides with silver nitrate, silver perchlorate, ammonium dinitramide, and potassium pentafluorosulfanylnitramide<sup>[5]</sup> in water. Reactions of these bromides with silver salts in water in a 1:1 molar ratio were carried out at  $25^\circ\text{C}$ . After 2 h, silver bromide was removed by filtration. The filtrate was concentrated and dried in vacuo to give **2a–b**, **3a–b** in high yields. Reactions of analogous substrates with ammonium dinitramide or potassium pentafluorosulfanylnitramide in water were stirred at room temperature for 2 h to give a heterogeneous mixture. The water was removed under reduced pressure at  $50^\circ\text{C}$  until constant weight was reached. To the remaining suspension were added chloroform and anhydrous magnesium sulfate. After 1 h, the suspension was filtered and the volatile material was removed under reduced pressure at  $30^\circ\text{C}$  for 2 h to afford the dinitramide or pentafluorosulfanylnitramide salts.

**1-Methyl-3-[3-(pentafluorosulfanyl)propyl]imidazolium Bromide (**2**):** Yield 90% (0.596 g). IR (KBr pellet):  $\tilde{\nu} = 3433, 3146, 3069, 2982, 2858, 2750, 2069, 1749, 1639, 1574, 1462, 1379, 1286, 1244, 1169, 1073, 831, 624, 595, 563 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 8.78$  (s, 1 H), 7.53 (s, 1 H), 7.48 (s, 1 H), 4.34 (t,  $J = 0.79 \text{ Hz}$ , 2 H), 3.91 (m, 5 H), 2.58 (m, 2 H) ppm.  $^{13}\text{C}$  NMR:  $\delta = 124.84, 123.05, 68.90$  (m), 48.15, 36.69, 27.36 (m) ppm.  $^{19}\text{F}$  NMR:  $\delta = 85.65$  (m, 1 F), 64.84, (d, m, 4 F) ppm.  $\text{C}_7\text{H}_{12}\text{BrF}_5\text{N}_2\text{S}$  (331.14): calcd. C 25.39, H 3.65, N 8.46; found C 25.46, H 3.59, N 8.41.

**1-Methyl-3-[3-(pentafluorosulfanyl)propyl]imidazolium Nitrate (**2a**):** Yield 90% (0.282 g). IR (KBr pellet):  $\tilde{\nu} = 3433, 3149, 3092, 2395, 2289, 2067, 1631, 1571, 1377, 1169, 1082, 1037, 829, 758, 655, 627, 595, 563, 482 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta = 8.80$  (s, 1 H), 7.56 (s, 1 H), 7.50 (s, 1 H), 4.36 (t,  $J = 4.82 \text{ Hz}$ , 2 H), 3.94 (m, 5 H), 2.60 (m, 2 H) ppm.  $^{13}\text{C}$  NMR:  $\delta = 137.16, 124.96, 123.14, 69.01$  (m), 48.22, 36.78, 27.36 (m) ppm.  $^{19}\text{F}$  NMR:  $\delta = 85.43$  (m, 1 F), 64.78, (d, m, 4 F) ppm.  $\text{C}_7\text{H}_{12}\text{F}_5\text{N}_3\text{O}_3\text{S}$  (313.25): calcd. C 26.84, H 3.86, N 13.41; found C 26.54, H 4.02, N 12.97.

**1-Methyl-3-[3-(pentafluorosulfanyl)propyl]imidazolium Perchlorate (**2b**):** Yield 89% (0.312 g). IR (KBr pellet):  $\tilde{\nu} = 3429, 3088, 2379, 1716, 1566, 1388, 1087, 826, 754, 625, 598, 544 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$



= 9.02 (s, 1 H), 7.80 (s, 1 H), 7.71 (s, 1 H), 4.52 (t,  $J$  = 4.87 Hz, 2 H), 4.06 (m, 5 H), 2.66 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  = 137.11, 124.86, 123.07, 69.04 (m), 48.16, 36.67, 27.40 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 84.93 (m, 1 F), 64.34, (d, m, 4 F). C<sub>7</sub>H<sub>12</sub>ClF<sub>5</sub>N<sub>2</sub>O<sub>4</sub>S (350.69): calcd. C 23.97, H 3.45, N 7.99; found C 23.82, H 3.44, N 7.97 ppm.

**1-Methyl-3-[3-(pentafluorosulfanyl)propyl]imidazolium Dinitramide (2c):** Yield 84% (0.300 g). IR (KBr pellet):  $\tilde{\nu}$  = 3154, 3115, 2974, 1566, 1517, 1432, 1336, 1187, 1105, 1009, 756, 624, 595, 563 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 9.20 (s, 1 H), 7.85 (s, 1 H), 7.74 (s, 1 H), 4.56 (t,  $J$  = 4.81 Hz, 2 H), 4.06 (m, 5 H), 2.67 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  =  $\delta$ 138.11, 125.02, 123.34, 69.44 (m), 48.15, 36.66, 27.85 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 84.91 (m, 1 F), 64.20, (d, m, 4 F). C<sub>7</sub>H<sub>12</sub>F<sub>5</sub>N<sub>5</sub>O<sub>4</sub>S (357.26): calcd. C 23.53, H 3.39, N 19.60; found C 23.68, H 3.48, N 19.32.

**4-Amino-1-[3-(pentafluorosulfanyl)propyl]triazolium Bromide (4):** Yield 84% (0.280 g). IR (KBr pellet):  $\tilde{\nu}$  = 3297, 2958, 2704, 1807, 1623, 1564, 1524, 1417, 1333, 1193, 1074, 1020, 993, 914, 871, 822, 694, 615, 565, 486, 415 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 8.87 (s, 1 H), 8.51 (s, 1 H), 4.55 (t,  $J$  = 4.52 Hz), 3.98 (m, 2 H), 2.64 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  =  $\delta$ 146.45, 68.89 (m), 51.35, 26.05 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 85.75 (m, 1 F), 64.67, 2 H (d, m, 4 F). C<sub>5</sub>H<sub>10</sub>BrF<sub>5</sub>N<sub>4</sub>S·1.5 H<sub>2</sub>O (360.14): calcd. C 16.67, H 3.64, N 15.56; found C 16.58, H 3.58, N 15.43.

**4-Amino-1-[3-(pentafluorosulfanyl)propyl]triazolium Nitrate (4a):** Yield 88% (0.277 g). IR (KBr pellet):  $\tilde{\nu}$  = 3451, 3305, 3196, 3121, 2395, 1762, 1627, 1525, 1385, 1194, 1073, 1012, 864, 835, 679, 618 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 8.90 (s, 1 H), 8.79 (s, 1 H), 4.56 (t,  $J$  = 4.66 Hz, 2 H), 3.99 (m, 2 H), 2.65 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  = 146.46, 69.11 (m), 51.37, 26.03 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 85.32 (m, 1 F), 64.55, (d, m, 4 F) ppm. C<sub>5</sub>H<sub>10</sub>F<sub>5</sub>N<sub>5</sub>O<sub>3</sub>S (315.22): calcd. C 19.05, H 3.20, N 22.22; found C 19.30, H 3.25, N 22.43.

**4-Amino-1-[3-(pentafluorosulfanyl)propyl]triazolium Perchlorate (4b):** Yield 87% (0.307 g). IR (KBr pellet):  $\tilde{\nu}$  = 3456, 3101, 2448, 2289, 2021, 1619, 1556, 1446, 1377, 1282, 1086, 829, 626, 561 cm<sup>-1</sup>. <sup>1</sup>H NMR ([D<sub>6</sub>]acetone):  $\delta$  = 9.96 (s, 1 H), 9.11 (s, 1 H), 4.74 (t,  $J$  = 4.54 Hz), 4.16 (m, 2 H), 2.76 (m, 2 H) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]acetone):  $\delta$  =  $\delta$ 142.34, 69.57 (m), 51.48, 26.24 (m) ppm. <sup>19</sup>F NMR ([D<sub>6</sub>]acetone):  $\delta$  = 85.06 (m, 1 F), 64.29, 2 H (d, m, 4 F) ppm. C<sub>5</sub>H<sub>10</sub>ClF<sub>5</sub>N<sub>4</sub>O<sub>4</sub>S (352.67): calcd. C 17.03, H 2.86, N 15.89; found C 16.90, H 2.93, N 15.53.

**4-Amino-1-[3-(pentafluorosulfanyl)propyl]triazolium Dinitramide (4c):** Yield 78% (0.280 g). IR (KBr pellet):  $\tilde{\nu}$  = 3317, 3133, 1708, 1632, 1521, 1434, 1379, 1187, 1074, 1016, 833, 759, 621, 563, 484 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 8.88 (s, 1 H), 8.69 (s, 1 H), 4.55 (t,  $J$  = 4.56 Hz, 2 H), 3.98 (m, 2 H), 2.64 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  = 146.46, 68.91 (m), 51.35, 26.07 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 85.05 (m, 1 F), 64.25, (d, m, 4 F) ppm. C<sub>5</sub>H<sub>10</sub>F<sub>5</sub>N<sub>7</sub>O<sub>4</sub>S (359.23): calcd. C 16.72, H 2.81, N 27.29; found C 16.97, H 2.97, N 27.05.

**4-Amino-1-[3-(pentafluorosulfanyl)propyl]triazolium Pentafluorosulfanylnitramide (4d):** Yield 70% (0.308 g). IR (KBr pellet):  $\tilde{\nu}$  = 3289, 3133, 3021, 2959, 2362, 1803, 1623, 1455, 1371, 1327, 1298, 1178, 1039, 992, 824, 736, 622, 565, 481 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 10.71 (s, 1 H), 9.1 (s, 1 H), 4.83 (t,  $J$  = 4.56 Hz), 4.19 (m, 2 H), 2.73 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  = 144.66, 69.54 (m), 50.92, 26.45 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 91.75 (m, 1 F) 84.84 (m, 1 F), 64.13 (d, m, 4 F), 64.09 (m, 4 F) ppm. C<sub>5</sub>H<sub>10</sub>F<sub>10</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub> (440.29): calcd. C 13.64, H 2.29, N 19.09; found C 13.78, H 2.45, N 18.68.

**1-[3-(Pentafluorosulfanyl)propyl]pyridinium Bromide (6):** Yield 78% (0.256 g). IR (KBr pellet):  $\tilde{\nu}$  = 3475, 3402, 3120, 3042, 3022, 2960, 2052, 1629, 1484, 1213, 1180, 874, 827, 785, 690, 630, 557, 493, 454 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 8.89 (d, 2 H  $J$  = 3.78 Hz), 8.60 (t,  $J$  =

5.25 Hz, 1 H), 8.12 (t,  $J$  = 4.84 Hz, 2 H), 4.75 (t,  $J$  = 5.12 Hz), 4.60 (m, 2 H), 2.72 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  =  $\delta$ 147.15, 145.34, 129.48, 68.62 (m), 60.31, 28.32 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 85.02 (m, 1 F), 64.82 (d, m, 4 F) ppm. C<sub>8</sub>H<sub>11</sub>BrF<sub>5</sub>NS (328.14): calcd. C 29.28, H 3.38, N 4.27; found C 29.43, H 3.23, N 4.10.

**1-[3-(Pentafluorosulfanyl)propyl]pyridinium Dinitramide (6a):** Yield 89% (0.315 g). IR (KBr pellet):  $\tilde{\nu}$  = 3540, 3138, 3065, 2358, 2331, 1637, 1519, 1486, 1424, 1310, 1183, 1015, 814, 772, 753, 686, 626 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  = 9.27 (d,  $J$  = 3.62 Hz), 8.75 (t,  $J$  = 5.25 Hz), 8.30 (t,  $J$  = 4.79 Hz), 5.03 (t,  $J$  = 5.11 Hz), 4.20 (m, 2 H), 2.90 (m, 2 H) ppm. <sup>13</sup>C NMR:  $\delta$  = 147.11, 146.10, 129.59, 68.18 (m), 60.27, 28.86 (m) ppm. <sup>19</sup>F NMR:  $\delta$  = 84.66 (m, 1 F), 64.35 (d, m, 4 F) ppm. C<sub>8</sub>H<sub>11</sub>F<sub>5</sub>N<sub>4</sub>O<sub>4</sub>S (354.25): calcd. C 27.12, H 3.13, N 15.82; found C 27.30, H 3.03, N 15.56.

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