Synthesis and Sorption Analysis of Task-specific Fluorous Ionic Liquids

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Six 1-alkyl-4-tridecafluorooctyl-1,2,4-triazolium triflimides **2a**–**f** and 4-amino-1-tridecafluoro-octyl-1,2,4-triazolium triflimide (**4**) were prepared from the respective iodides **1a**–**f** (**1a**, **2a**: *n*-propyl; **1b**, **2b**: *n*-butyl; **1c**, **2c**: *n*-hexyl; **1d**, **2d**: *n*-heptyl; **1e**, **2e**: *n*-octyl; **1f**, **2f**: *n*-decyl) and iodide **3** by ion metathesis. Compounds **2a** and **4** are liquid at room temperature. Two liquid fluorous imidazolium salts bearing functionalized polar substituents were synthesized in an analogous manner, namely 1-(2-(diethylamino)ethyl)-3-(heptadecafluorodecyl)imidazolium triflimide (**5b**) and 1-(2-hydroxyethyl)-3-(heptadecafluorodecyl)imidazolium triflimide (**6b**) from the respective bromides **5a** and **6a**. The bis(triflimide) **5c** has a melting point slightly above room temperature. Three fluorous ionic liquids (ILs; **2a**, **5b**, and **6b**) were subjected to vapor sorption analysis at 25 °C and exhibited dual affinity to water and, even much more pronounced, to methoxynonafluorobutane (hydrofluoroether HFE-7100). Thus, IL **6b** absorbed 3.2 % (by weight) water and 200 % HFE, whereas ILs **2a** and **5b** absorbed 0.4 and 0.5 % water, but 300 and 1200 % HFE, respectively. Commercial 1-butyl-2,3-dimethyl-imidazolium triflimide and 1-ethyl-3-methyl-imidazolium triflimide were used as reference compounds and absorbed 0.9 and 2.2 % water, respectively, but only 17 % HFE.

Key words: Fluorous, Hydrofluoroether, Imidazole, Ionic Liquid, Sorption, Triazole

Introduction

Due to their extraordinary chemical properties, organofluorine compounds [1] have significantly impacted many aspects of the chemical industry, human health, and environment [2 – 5]. Partially fluorinated solvents such as hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) are fluids with excellent chemical stability, yet short atmospheric life span [6], designed to replace chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and perfluorocarbons (PFCs) in various applications because of their significantly reduced environmental impact relative to CFCs, particularly due to their zero ozone-depletion potential (ODP) and minimum greenhouse warming potential (GWP) compared to PFCs [7]. Especially hydrofluoroethers (HFEs) such as HFE-7100 ($C_4F_9OCH_3$) and HFE-7200 ($C_4F_9OC_2H_5$) have been developed as alternatives for the ecologically harmful halons, freons and related ozone depleters [8]. HFEs are ideally suited for use in technical processes such as vapor degreasing, particulate removal, rinsing, and displacement drying. Meanwhile they find use in applications such as the precision cleaning of electronic equipment, spot-free dewatering of optical parts, dielectric heat transfer agents in refrigeration systems, solvents for coating materials, or as fire extinguishing media [9]. In addition, some specialty applications include their use in co-solvent systems. Coupled with fluorous functional materials [10, 11], HFEs as orthogonal solvents (*i. e.*, solvents that do not dissolve or adversely affect an organic layer) open new frontiers for "green" materials processing that can be readily adopted by industry [11].

Ionic liquids (ILs) with fluorine-containing cations [12, 13] are known to facilitate the emulsification of fluoroalkanes when added to conventional ILs [14]. Solubilities of fluorinated gases in ILs with non-fluorous cations were also determined [15]. Dedicated fluorous imidazolium salts [16] and the

corresponding Pd-*N*-heterocyclic carbene (NHC) complexes [17, 18] display unique mutual solubility patterns with fluoroorganic solvents. For an analogous series of 1,2,4-triazolium-based ILs, miscibility data have been reported only for common organic solvents [19, 20]. Phase equilibria between the common hydrophobic IL 1-ethyl-3-methyl-imidazolium triflimide and HFE [21], halocarbon isomers [22], and (refrigerant) fluorocarbons [23, 24] have been studied, revealing large differences in the solubilities. Based on this unique phase behavior of fluorocarbons in RTILs, they have been proposed as extractants for separation and purification. Fluorous ILs, predominantly polyfluoroalkyl- and polyfluoroalkyl ether-substituted azolium salts are used in optoelectronic applications [25] and in dye sensitized solar cells [26, 27]. For other related fluoro-substituted imidazolium salts [16] and their corresponding Ag-*N*-heterocyclic carbene (NHC) complexes [28] striking differences in fluorophilicity were observed depending on the type of polyfluorinated substituents. The compounds bearing a polyfluoroalkyl ponytail displayed moderate fluorophilicities, whereas the presence of fluorinated polyether chains resulted in much higher fluorophilicity. Mutual solubility data of a number of mixtures of commonly used ILs with partially fluorinated *n*-alkanols (C_7 to C_{10}) or perfluoroheptane have been determined as well [29].

Because the effect of the hydrophobic triflimide anion on the hydrophobicity of ILs can be overridden by hydroxylation of the organic cation [30 – 34] and, on the other hand, the separability of ILs from aqueous matrixes [35] can easily be adjusted by partial chlorination or fluorination of the cation, a versatile toolbox for tailoring even multi-functional task-specific ILs (TSILs) is within reach of routine organic chemistry. The principles of balanced amphiphilicity [36] suggest that a wide range of orthogonal affinity profiles are feasible, as applied in surfactants design [37]. The general concepts of potential recycling of anthropogenic fluorous pollutants using fluorophilic ILs have been reviewed very recently [38]. Based on above considerations, the aim of this work [39] was to devise a TSIL for the efficient recovery of the expensive and volatile HFEs from industrial effluents and exhaust gas streams. In addition, an agent for spotless cleaning/dewatering of high-precision optical glass was desired. This preferably inexpensive liquid should exhibit a challenging feature, namely a dual affinity to
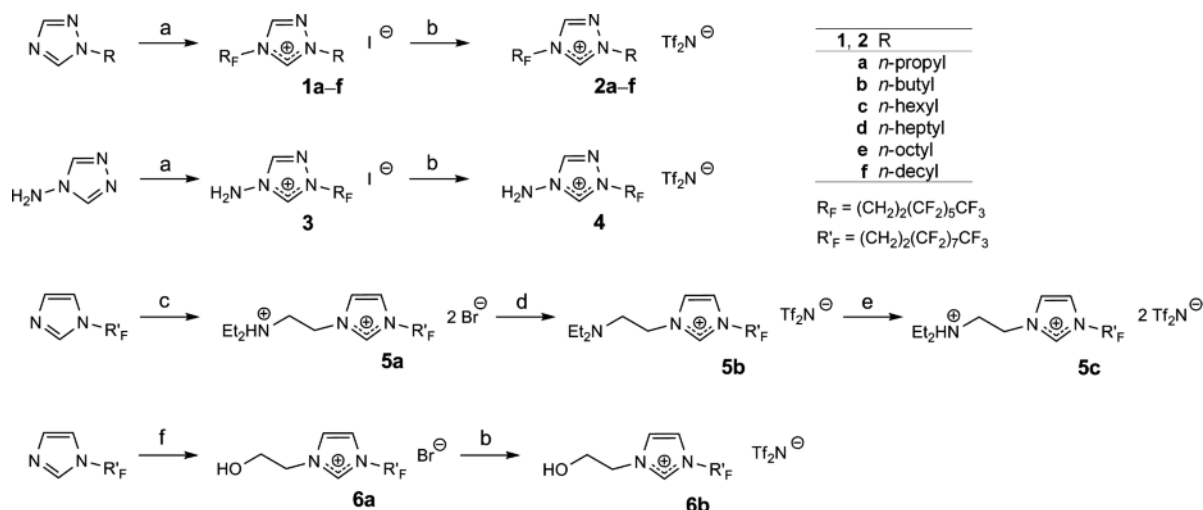
HFE and water, but should be largely immiscible with water, yet completely rinseable by HFEs.

Results and Discussion

Synthetic considerations

Asymmetry of cations, charge delocalization, and conformational freedom of long side chains have been provided as criteria for low-melting salts [40, 41]. The bis(trifluoromethanesulfonyl)imide ('triflimide') anion [42] has been widely used for the synthesis of hydrophobic ILs, including degradable and patent-free representatives [43, 44]. The absence of strong interactions between anions and cations may explain the low melting points of these salts [45]. Therefore, we decided to use the triflimide anion as an advantageous building block for our fluorous triazolium and imidazolium salts. Introduction of polyfluoroalkyl chains (in this case, octyl and decyl) bearing a non-fluorinated ethylene spacer into 1-alkyl-1,2,4-triazoles was straightforward, giving **1a–f**, followed by ion metathesis yielding fluorous ionic liquids (FILs) **2a–f** (Scheme 1).

From the literature, 1-heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium triflimide (**2d**) [20] was identified as a possible candidate to serve as a starting point. Contrary to the literature, we followed the known quaternization-deamination protocol [46] for the synthesis of the requisite 1-alkyl-1,2,4-triazoles to obtain isomer-free products. Consequently, we found higher melting points for the quaternary salts **2b** and **2d** than previously reported [20]. In fact, we recently published the crystal structure of **2d** [47] which had been described as liquid (reported melting point of 22 °C) [20]. In an attempt to obtain FILs with a polar functional group, 4-amino-1,2,4-triazolium salts **3** and **4** were synthesized, although in disappointing yield. Therefore, other polar group-bearing substituents, such as hydroxyethyl or diethylaminoethyl (Scheme 1), were introduced by quaternization of polyfluorodecyl-imidazole [18] to give **5a** and **6a** in good yields. Again, ion metathesis yielded liquid salts **5b** and **6b**. The protic dicationic salt **5c**, prepared from **5b** and bis(trifluoromethanesulfonyl)imide, was envisioned to exhibit increased affinity to water due to hydrogen bonding [48], but had a melting point slightly above room temperature, 33 °C. So far, our efforts produced many ILs, but only three room-temperature ILs in acceptable yields.

Scheme 1. a) $I(CH_2)_2(CF_2)_5CF_3$, CH_3CN; b) Tf_2NLi, H_2O; c) $Et_2N(CH_2)_2Br \cdot HBr$, CH_3CN; d) Tf_2NLi, NaOH; e) Tf_2NH; f) $HO(CH_2)_2Br$, toluene.

Sorption studies

The absorption of water and HFE-7100 vapor by these azolium-based RTILs was studied and the results compared to the sorption behavior of two commercial reference triflimides, EMIm and BMMIm (Table 1). Although the ILs form two phases with water, a significant mass increase due to moisture sorption could be determined. A biphasic first-order curve was fitted to the time-dependent sorption data points (Eq. 1). The parameters of the sorption curves are summarized in Table 2.

$$\Delta m/m = A\left(1 - e^{-Bt}\right) + C\left(1 - e^{-Dt}\right) \tag{1}$$

The results showed that the water uptake of the two new ILs, **2a** and **5b**, was much lower than that of the non-fluorous reference ILs (Fig. 1). This can be explained by the fluorinated substituents which lower the
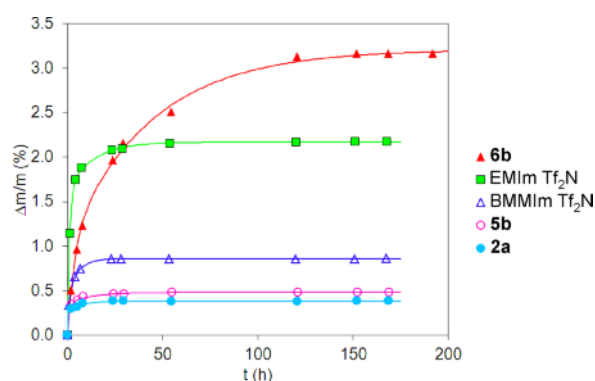

Fig. 1 (color online). Mass increase caused by water sorption of the dry ILs plotted against time.

affinity to water. However, **6b** exhibited the highest water uptake (3.16 %) due to the hydroxy-functionalized substituent, which is capable of forming hydrogen bonds. On the other hand, the new ILs exhibited a much higher HFE affinity than the hydrophobic reference ILs (Fig. 2), showing a relative mass increase of nearly 200 % (for **6b**), 300 % (for **2a**), and even 1200 % (for **5b**). The latter value was derived by extrapolation of the curve as calculated from Eq. 1.

The reference ILs absorbed only 17 % HFE. This result confirms the importance of the fluorinated substituents of the cation. In contrast, the HFE sorption of the reference ILs, low as it is, can be attributed to the fluorinated triflimide anion only. Water-saturated ILs

Table 1. Results of H_2O and HFE-7100 sorption analysis at 25 °C, $\Delta m/m$ (%).

Ionic liquid	H_2O	H_2O^a	HFE	HFE^b
2a	0.38	0.23	298	193
5b	0.48	0.24	1191[c]	1013[c]
6b	3.16	1.80	199	142
BMMIm Tf_2N	0.86	0.48	17	15
EMIm Tf_2N	2.17	0.75	17	14

[a] After HFE sorption, calculated for pure IL; [b] after H_2O sorption, calculated for dry IL; [c] extrapolated.

Table 2. Parameters for the biphasic first-order model for the sorption curves of H_2O and HFE in ionic liquids [a].

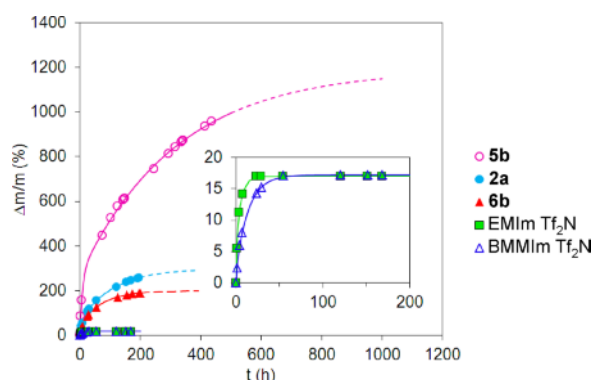| Ionic liquid	H_2O				HFE				H_2O/HFE			
	A	B	C	D	A	B	C	D	A	B	C	D
2a	0.27	7.29	0.11	0.15	63.5	0.14	234.5	0.009	75	0.16	117	0.014
5b	0.36	1.01	0.12	0.08	271	0.13	920	0.0031	189	0.16	823	0.004
6b	1.02	0.28	2.19	0.023	42.6	0.15	156.5	0.014	67.5	0.15	74.6	0.019
BMMIm Tf$_2$N	0.44	1.19	0.42	0.19	1.87	0.7	15.34	0.07	15.3	0.16	0	0
EMIm Tf$_2$N	1.64	0.94	0.53	0.074	5.0	1.6	12.0	0.19	9.9	0.53	3.86	0.13

[a] Squared correlation coefficients $r^2 > 0.993$.

Fig. 2 (color online). Mass increase caused by HFE sorption of the dry ILs plotted against time.

showed a similar HFE sorption profile but the amount of absorbed solvent is clearly smaller than in the dry ILs (Table 1). Karl-Fischer titrations revealed that also the amount of water in the water-saturated ILs decreased when stored in a saturated HFE atmosphere, indicating that the HFE displaced some of the water which was associated with the polar moieties of the ILs. Thus, the newly developed ILs in fact exhibit dual affinity, a remarkable property.

Conclusions and Outlook

This study [39] introduces novel ionic liquids with an affinity for both water and apolar hydrofluoroethers. The sorption behavior of the ILs was tuned by the incorporation of both polar and fluorophilic moieties as substituents in the azolium-based cation. Due to their extremely high HFE sorption ability, the new task-specific RTILs are promising materials for technical applications such as scrubbing liquids for exhaust air containing HFEs and related HFC-based blowing agents, aerosol propellants [49, 50] and inhalation anesthetics [51]. Apart from recovering expensive and volatile hydrofluoroethers, the ILs themselves can be easily recycled by applying gentle heating under reduced pressure. Mutual affinity profiles between fluorous organics and task specific ILs and characterization of new fluorous/organic biphasic and ternary systems [52], achievable by co-solute and solvent tuning [53], are challenging topics of the future. The results presented herein will hopefully stimulate further research towards technical applications of FILs in combination with neutral polyfluorinated compounds.

Experimental Section

1-Propyl-1,2,4-triazole [54, 55], 1-butyl-1,2,4-triazole [20], 1-hexyl-1,2,4-triazole (no spectroscopic data) [56 – 58], 1-heptyl-1,2,4-triazole [20], 1-octyl-1,2,4-triazole (incomplete NMR data) [59], 1-decyl-1,2,4-triazole [20] were synthesized by deamination [46] of the respective 1-alkyl-4-amino-1,2,4-triazolium bromides [60, 61]. The missing spectroscopic data are disclosed here. 1-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl)imidazole [18] was prepared by a published method. Reference ILs 1-butyl-2,3-dimethyl-imidazolium (BMMIm) Tf$_2$N and 1-ethyl-3-methyl-imidazolium (EMIm) triflimides were purchased from IoLiTec, Germany. Commercial HFE-7100, a mixture of nonafluoro-*n*-butyl methyl ether and nonafluoro-*iso*-butyl methyl ether, was obtained from 3M, Germany. The three RTILs **2a**, **5b**, and **6b** as well as the two reference ILs were exposed to a relative humidity of 98 % generated by a saturated aqueous solution of K_2SO_4 or HFE-7100 at 25 °C, respectively. The sample was placed over the saturated solution or solvent. The resulting water or solvent uptake was monitored until an equilibrium state was achieved [62]. HFE sorption was also carried out with water-saturated ILs. The water content resulting after the exposure to a saturated HFE atmosphere was determined by the Karl Fischer method using a Mettler DL 37 KF coulometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum GX FT-IR instrument in ATR mode. Mass spectra were measured on a Bruker micrOTOF-QII spectrometer.

1-Hexyl-1,2,4-triazole [63936-00-5]

$n_\text{D}^{20} = 1.4611$. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.80$ (t, 3H, $J = 6.8$ Hz), 1.20 (m, 6H), 1.74 (m, 2H, $J = 7.0$ Hz), 4.14 (t, 2H, $J = 7.0$ Hz), 7.92 (s, 1H), 8.49 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 13.8$, 21.9, 25.4, 29.2, 30.6, 48.5, 143.9, 151.3 ppm. – IR (neat): $\nu = 3107$, 2955, 2928, 2858, 1505, 1466, 1437, 1379, 1346, 1272, 1205, 1139, 1012, 958 cm^{-1}.

1-Octyl-1,2,4-triazole [105279-46-7]

$n_\text{D}^{20} = 1.4621$. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.80$ (t, 3H, $J = 6.8$ Hz), 1.29 (m, 10H), 1.74 (m, 2H, $J = 7.0$ Hz), 4.14 (t, 2H, $J = 7.0$ Hz), 7.91 (s, 1H), 8.48 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 13.8$, 22.1, 25.8, 28.4, 28.6, 29.3, 31.2, 48.5, 143.8, 151.2 ppm. – IR (neat): $\nu = 3108$, 2952, 2924, 2855, 1505, 1486, 1437, 1377, 1345, 1272, 1205, 1140, 1010, 958 cm^{-1}.

*General procedure for the preparation of 1-alkyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodides **1a–f***

A solution of 1-alkyl-1,2,4-triazole (7.0 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (7.0 mmol) in anhydrous CH$_3$CN (7 mL) was heated in a microwave reactor for 2 h at 160 °C. The product precipitated and was collected by filtration. From the filtrate another crop was harvested after addition of Et$_2$O. The colorless solid was washed with Et$_2$O and dried.

*4-(1H,1H,2H,2H-Perfluorooctyl)-1-propyl-1,2,4-triazolium iodide (**1a**)*

Yield: 74%. Sublimation at 285 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.88$ (t, 3H, $J = 7.3$ Hz), 1.87 (m, 2H, $J = 7.2$ Hz), 3.09 (m, 2H), 4.36 (t, 2H, $J = 6.9$ Hz), 4.65 (t, 2H, $J = 7.3$ Hz), 9.30 (s, 1H), 10.22 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 10.3$, 21.5, 29.7 (t, $J = 20$ Hz), 40.0, 53.2, 142.9, 145.0 ppm. – IR (neat): $\nu = 3106$, 3015, 2975, 2888, 1580, 1464, 1366, 1319, 1232, 1186, 1143, 1122, 1079, 994 cm^{-1}.

*1-Butyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodide (**1b**) [490024-73-2]*

Yield: 60%. M. p. 274 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.90$ (t, 3H, $J = 7.3$ Hz), 1.87 (m, 2H, $J = 7.2$ Hz), 3.09 (m, 2H), 4.36 (t, 2H, $J = 6.9$ Hz), 4.65 (t, 2H, $J = 7.3$ Hz), 9.30 (s, 1H), 10.22 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 13.2$, 18.6, 29.7 (t, $J = 20$ Hz), 30.0, 40.0, 51.4, 142.9, 145.0 ppm. – IR (neat): $\nu = 3107$, 3016, 2943, 2881, 1578, 1466, 1365, 1318, 1232, 1186, 1144, 1123, 1079, 995 cm^{-1}.

*1-Hexyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodide (**1c**)*

Yield: 59%. M. p. 276–277 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.84$ (t, 3H, $J = 6.4$ Hz), 1.26 (m, 6H), 1.83 (m, 2H, $J = 6.5$ Hz), 3.08 (m, 2H), 4.39 (t, 2H, $J = 6.9$ Hz), 4.65 (t, 2H, $J = 7.1$ Hz), 9.28 (s, 1H), 10.19 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 13.8$, 21.8, 25.0, 28.0, 29.7 (t, $J = 20$ Hz), 30.5, 39.9, 51.7, 142.9, 145.0 ppm. – IR (neat): $\nu = 3103$, 3016, 2966, 2939, 2879, 1579, 1365, 1318, 1232, 1185, 1144, 1123, 1079, 995 cm^{-1}.

*1-Heptyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodide (**1d**) [490024-74-3]*

Yield: 71%. M. p. 277 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.84$ (t, 3H, $J = 6.9$ Hz), 1.25 (m, 8H), 1.83 (m, 2H, $J = 7.0$ Hz), 3.09 (m, 2H), 4.39 (t, 2H, $J = 6.9$ Hz), 4.65 (t, 2H, $J = 7.1$ Hz), 9.29 (s, 1H), 10.21 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 13.9$, 21.9, 25.3, 28.0 (2C), 29.7 (t, $J = 20$ Hz), 31.0, 40.0, 51.7, 142.9, 145.0 ppm. – IR (neat): $\nu = 3107$, 3017, 2967, 2936, 2862, 1579, 1469, 1365, 1318, 1234, 1185, 1144, 1122, 1079, 992 cm^{-1}.

*1-Octyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodide (**1e**)*

Yield: 70%. M. p. 264–265 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.83$ (m, 3H), 1.23 (m, 10H), 1.83 (m, 2H), 3.08 (m, 2H), 4.39 (t, 2H, $J = 6.7$ Hz), 4.65 (t, 2H, $J = 6.9$ Hz), 9.29 (s, 1H), 10.21 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 13.9$, 22.0, 25.3, 28.0, 28.3, 28.5, 29.7 (t, $J = 20$ Hz), 31.1, 40.0, 51.7, 142.9, 145.0 ppm. – IR (neat): $\nu = 3105$, 3016, 2965, 2932, 2859, 1579, 1467, 1365, 1318, 1235, 1185, 1144, 1122, 1079, 994 cm^{-1}.

*1-Decyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodide (**1f**)*

Yield: 49%. M. p. 260–261 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.84$ (t, 3H, $J = 6.9$ Hz), 1.22 (m, 14H), 1.82 (m, 2H), 3.08 (m, 2H), 4.39 (t, 2H, $J = 6.9$ Hz), 4.64 (t, 2H, $J = 7.2$ Hz), 9.28 (s, 1H), 10.19 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 14.0$, 22.1, 25.3, 28.0, 28.4, 28.7, 28.9, 29.7 (t, $J = 20$ Hz), 31.3, 40.0, 51.7, 142.9, 145.1 ppm. – IR (neat): $\nu = 3108$, 3030, 2961, 2922, 2855, 1582, 1469, 1366, 1318, 1231, 1186, 1145, 1123, 1080, 997 cm^{-1}.

*General procedure for the preparation of 1-alkyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imides **2a–f***

1-Alkyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1*H*-1,2,4-triazolium iodide (1.60 mmol) was dissolved in H$_2$O (10 mL)

and CH_2Cl_2 (10 mL). A solution of Tf_2NLi (1.76 mmol, 1.1 equiv.) in H_2O (2 mL) was added, and the mixture was stirred at 35 °C for 15 h. The organic phase was separated, washed repeatedly with H_2O, and dried with Na_2SO_4. The solvent was removed under reduced pressure, and the residue was dried to constant weight.

4-(1H,1H,2H,2H-Perfluorooctyl)-1-propyl-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*2a*)

Viscous, tan liquid. Yield: 90%. – $n_D^{20} = 1.3803$. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.88$ (t, 3H, $J = 7.4$ Hz), 1.86 (m, 2H, $J = 7.2$ Hz), 3.07 (m, 2H), 4.36 (t, 2H, $J = 6.9$ Hz), 4.64 (t, 2H, $J = 7.3$ Hz), 9.28 (s, 1H), 10.17 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 10.3$, 21.6, 29.7 (t, $J = 20$ Hz), 39.9, 53.2, 119.5 (q, $J = 320$ Hz), 142.9, 145.0 ppm. – IR (neat): $\nu = 3141$, 3087, 2981, 2949, 2888, 1579, 1466, 1347, 1328, 1231, 1183, 1133, 1055, 995 cm^{-1}. – MS (ESI): $m/z = 458.10$ (calcd. 458.09 for $C_{13}H_{13}F_{13}N_3$, [M]$^+$).

1-Butyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*2b*) [490024-95-8]

Colorless, waxy product. Yield: 60%. M. p. 36 °C (lit. 28 °C [20]). – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.90$ (t, 3H, $J = 7.3$ Hz), 1.29 (m, 2H, $J = 7.5$ Hz), 1.82 (m, 2H, $J = 7.4$ Hz), 3.07 (m, 2H), 4.39 (t, 2H, $J = 7.0$ Hz), 4.63 (t, 2H, $J = 7.3$ Hz), 9.27 (s, 1H), 10.17 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 13.2$, 18.6, 29.7 (t, $J = 20$ Hz), 30.0, 39.9, 51.4, 119.5 (q, $J = 320$ Hz), 142.9, 145.0 ppm. – IR (neat): $\nu = 3145$, 3091, 2971, 2944, 2883, 1580, 1469, 1348, 1328, 1234, 1184, 1135, 1056, 997 cm^{-1}.

1-Hexyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*2c*)

Colorless, waxy product. Yield: 88%. M. p. 63 – 64 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.84$ (m, 3H), 1.26 (m, 6H), 1.83 (m, 2H), 3.07 (m, 2H), 4.38 (t, 2H, $J = 7.0$ Hz), 4.64 (t, 2H, $J = 7.2$ Hz), 9.27 (s, 1H), 10.17 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 13.7$, 21.9, 25.0, 28.0, 29.7 (t, $J = 20$ Hz), 30.5, 40.0, 51.7, 119.5 (q, $J = 320$ Hz), 142.9, 145.0 ppm. – IR (neat): $\nu = 3143$, 3091, 2963, 2936, 2865, 1581, 1470, 1348, 1328, 1234, 1185, 1135, 1056, 998 cm^{-1}.

1-Heptyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*2d*) [490024-97-0]

Colorless, waxy product. Yield: 94%. M. p. 65 – 66 °C (lit. 22 °C [20]). – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.84$ (t, 3H, $J = 6.9$ Hz), 1.25 (m, 8H), 1.83 (m, 2H, $J = 7.0$ Hz), 3.06 (m, 2H), 4.38 (t, 2H, $J = 7.0$ Hz), 4.64 (t, 2H, $J = 7.2$ Hz), 9.27 (s, 1H), 10.18 (s, 1H) ppm. – ^{13}C NMR

(75 MHz, [D_6]DMSO): $\delta = 13.8$, 22.0, 25.3, 28.0 (2C), 29.7 (t, $J = 20$ Hz), 31.0, 39.9, 51.7, 119.5 (q, $J = 320$ Hz), 142.9, 145.0 ppm. – IR (neat): $\nu = 3144$, 3092, 2961, 2934, 2863, 1581, 1470, 1347, 1330, 1235, 1185, 1137, 1055, 997 cm^{-1}.

1-Octyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*2e*)

Colorless, waxy product. Yield: 98%. M. p. 69 – 71 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.84$ (t, 3H, $J = 6.9$ Hz), 1.23 (m, 10H), 1.83 (m, 2H), 3.07 (m, 2H), 4.39 (t, 2H, $J = 6.9$ Hz), 4.64 (t, 2H, $J = 7.2$ Hz), 9.27 (s, 1H), 10.17 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 13.9$, 22.0, 25.3, 28.0, 28.3, 28.4, 29.7 (t, $J = 20$ Hz), 31.1, 40.0, 51.7, 119.5 (q, $J = 320$ Hz), 142.9, 145.0 ppm. – IR (neat): $\nu = 3142$, 3094, 2962, 2934, 2863, 1583, 1471, 1346, 1330, 1235, 1185, 1143, 1056, 997 cm^{-1}.

1-Decyl-4-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*2f*)

Colorless, waxy product. Yield: 81%. M. p. 82 – 83 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.84$ (t, 3H, $J = 6.8$ Hz), 1.22 (m, 14H), 1.83 (m, 2H), 3.07 (m, 2H), 4.39 (t, 2H, $J = 6.9$ Hz), 4.64 (t, 2H, $J = 7.2$ Hz), 9.28 (s, 1H), 10.18 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 13.9$, 22.1, 25.3, 28.0, 28.3, 28.7, 28.8, 28.9, 29.7 (t, $J = 20$ Hz), 31.3, 40.0, 51.7, 119.5 (q, $J = 320$ Hz), 142.9, 145.0 ppm. – IR (neat): $\nu = 3146$, 3092, 2959, 2927, 2858, 1581, 1469, 1348, 1328, 1235, 1186, 1135, 1057, 997 cm^{-1}.

4-Amino-1-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium iodide (*3*)

A solution of 4-amino-1,2,4-triazole (0.50 g, 5.88 mmol) and $1H,1H,2H,2H$-perfluorooctyl iodide (2.91 g, 5.88 mmol) in anhydrous CH_3CN (20 mL) was refluxed for 24 h. The solvent was evaporated, and the residue was washed with H_2O and Et_2O and dried *in vacuo*. Yield: 0.40 g (12%). M. p. 146 °C. – ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 3.03$ (m, 2H), 4.73 (t, $J = 6.4$ Hz, 2H), 7.03 (s, 2H), 9.26 (s, 1H), 10.22 (s, 1H) ppm. – IR (neat): $\nu = 3282$, 3205, 3020, 1685, 1630, 1615, 1556, 1524, 1422, 1405, 1367, 1320, 1283, 1235, 1202, 1181, 1172, 1141, 1123, 1080, 1074, 1034, 1004, 975 cm^{-1}.

4-Amino-1-(1H,1H,2H,2H-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (*4*)

3 (330 mg, 0.59 mmol) was dissolved in H_2O (10 mL) and CH_2Cl_2 (10 mL). A solution of Tf_2NLi (340 mg, 1.3 mmol, 2.2 equiv.) in H_2O (3 mL) was added, and the mixture was stirred at 35 °C for 24 h. The organic phase was separated and washed repeatedly with H_2O. The solvent was removed under reduced pressure, and the resulting viscous, tan liquid

was dried *in vacuo* to constant weight. Yield: 220 mg (52 %). – $n_D^{20} = 1.3859$. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta =$ 3.03 (m, 2H), 4.73 (t, $J = 6.7$ Hz, 2H), 7.03 (s, 2H), 9.25 (s, 1H), 10.22 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 28.9$ (t, $J = 20$ Hz), 44.2, 119.5 (q, $J = 321$ Hz), 143.3, 145.3 ppm. – IR (neat): $\nu = 3556, 3252, 3141, 2967, 1705, 1636, 1567, 1459, 1408, 1346, 1231, 1183, 1130, 1054, 1005, 982, 951$ cm^{-1}.

1-(2-(Diethylamino)ethyl)-3-(1H,1H,2H,2H-perfluorodecyl)imidazolium bromide hydrobromide (5a)

A solution of 2-(diethylamino)ethyl bromide hydrobromide (6.22 g, 23.33 mmol) and 1-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)imidazole (12.00 g, 23.33 mmol) in anhydrous CH$_3$CN (120 mL) was refluxed for 24 h. The mixture was allowed to cool, and the resulting colorless precipitate was collected by filtration and washed with CH$_3$CN and Et$_2$O. Yield: 12.54 g (69 %). M. p. 244–245 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.23$ (t, 6H, $J = 7.0$ Hz), 3.05 (m, 2H), 3.22 (m, 4H), 3.63 (m, 2H), 4.59 (t, 2H, $J = 7.1$ Hz), 4.70 (m, 2H), 7.95 (s, 2H), 9.45 (s, 1H), 9.77 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 8.4$ (2C), 30.0 (t, $J = 20$ Hz), 41.4 (t, $J = 5$ Hz), 43.2, 46.9 (2C), 49.4, 122.7, 122.9, 137.8 ppm. – IR (neat): $\nu = 3469, 3395, 3070, 2987, 2944, 2637, 1567, 1451, 1371, 1333, 1197, 1175, 1148, 1134, 1115, 1027, 1004, 953$ cm^{-1}.

1-(2-(Diethylamino)ethyl)-3-(1H,1H,2H,2H-perfluorodecyl)imidazolium bis(trifluoromethanesulfonyl)imide (5b)

A mixture of **5a** (8.70 g, 11.22 mmol), NaOH (450 mg, 1.0 equiv.), and Tf$_2$NLi (3.54 g, 1.1 equiv.) in H$_2$O (100 mL) was stirred for 15 h at 35 °C. CH$_2$Cl$_2$ was added, and the phases were separated. The organic phase was repeatedly washed with H$_2$O and dried with Na$_2$SO$_4$. The volatiles were removed under reduced pressure, and the resulting tan liquid was dried *in vacuo* to constant weight. Yield: 8.75 g (87 %). – $n_D^{20} = 1.3886$. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.81$ (t, 6H, $J = 7.1$ Hz), 2.42 (q, 4H, $J = 7.1$ Hz), 2.68 (t, 2H, $J = 5.6$ Hz), 2.96 (m, 2H), 4.19 (t, 2H, $J = 5.5$ Hz), 4.58 (t, 2H, $J = 6.6$ Hz), 7.76 (s, 1H), 7.85 (s, 1H), 9.18 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 11.5$ (2C), 30.0 (t, $J = 20$ Hz), 41.2, 46.1 (2C), 47.7, 51.8, 119.5 (q, $J = 320$ Hz), 122.2, 122.9, 137.0 ppm. – IR (neat): $\nu = 3152, 3119, 2976, 2822, 1565, 1462, 1349, 1330, 1186, 1143, 1133, 1055, 996$ cm^{-1}. – MS (ESI): $m/z = 614.17$ (calcd. 614.15 for C$_{19}$H$_{21}$F$_{17}$N$_3$ [M]$^+$).

1-(2-(Diethylammonio)ethyl)-3-(1H,1H,2H,2H-perfluorodecyl)imidazolium bis(bis(trifluoromethanesulfonyl)imide) (5c)

A mixture of **5b** (1.64 g, 1.83 mmol) and excess Tf$_2$NH was stirred under Ar at 80 °C for 15 h. The volatiles were

removed *in vacuo*, and the resulting tan solid was washed with CH$_2$Cl$_2$. Yield: 1.83 g (85 %). M. p. 33 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.20$ (t, 6H, $J = 7.1$ Hz), 2.98 (m, 2H), 3.19 (m, 4H), 3.56 (m, 2H), 4.60 (m, 4H), 7.86 (s, 1H), 7.93 (s, 1H), 9.29 (s, 2H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 8.4$ (2C), 30.0 (t, $J = 20$ Hz), 41.3, 43.2, 47.1 (2C), 49.2, 119.4 (q, $J = 322$ Hz), 122.8, 122.9, 137.5 ppm. – IR (neat): $\nu = 3156, 1568, 1471, 1339, 1182, 1129, 1053, 993, 975$ cm^{-1}.

1-(2-Hydroxyethyl)-3-(1H,1H,2H,2H-perfluorodecyl)-imidazolium bromide (6a)

A mixture of 2-bromoethanol (2.97 g, 22.56 mmol) and 1-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)imidazole (11.60 g, 22.56 mmol) in toluene (25 mL) was refluxed for 24 h. The resulting precipitate was collected by filtration, washed with toluene and Et$_2$O, and dried. Yield: 13.82 g (95 %). M. p. 111–112 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.01$ (m, 2H), 3.71 (m, 2H), 4.23 (t, $J = 4.8$ Hz, 2H), 4.58 (t, $J = 7.0$ Hz, 2H), 5.17 (t, $J = 5.0$ Hz, 1H), 7.77 (s, 1H), 7.90 (s, 1H), 9.27 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 30.0, 41.1, 51.8, 59.2, 122.4, 122.9, 137.0$ ppm. – IR (neat): $\nu = 3276, 3153, 3051, 2946, 1573, 1334, 1198, 1179, 1146, 1134, 1116, 1071, 1059, 1025, 997, 956$ cm^{-1}.

1-(2-Hydroxyethyl)-3-(1H,1H,2H,2H-perfluorodecyl)-imidazolium bis(trifluoromethanesulfonyl)imide (6b)

A suspension of **6a** (6.60 g, 10.32 mmol) in H$_2$O (30 mL) was ultrasonicated, and Tf$_2$NLi (3.26 g, 11.35 mmol, 1.1 equiv.) in H$_2$O (5 mL) was added. The mixture was stirred for 15 h at 35 °C. The lower phase was separated, dissolved in EtOAc, washed repeatedly with H$_2$O, dried with Na$_2$SO$_4$, and filtered through charcoal and celite. The solvent was removed under reduced pressure, and the resulting viscous liquid was dried *in vacuo* to constant weight. Yield: 8.2 g (95 %). – $n_D^{20} = 1.3810$. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 2.96$ (m, 2H), 3.73 (t, $J = 5.0$ Hz, 2H), 4.22 (t, $J = 4.9$ Hz, 2H), 4.56 (t, $J = 7.2$ Hz, 2H), 7.75 (m, 1H), 7.86 (m, 1H), 9.24 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 30.2$ (t, $J = 20$ Hz), 41.2, 51.9, 59.3, 119.6 (q, $J = 322$ Hz), 122.5, 123.0, 137.1 ppm. – IR (neat): $\nu = 3521, 3157, 3121, 2956, 2891, 1567, 1347, 1184, 1132, 1505, 997$ cm^{-1}. – MS (ESI): $m/z = 559.09$ (calcd. 559.07 for C$_{15}$H$_{12}$F$_{17}$N$_2$O, [M]$^+$).

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