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Perfluorinated 1,2,3- and 1,2,4-Triazolium Ionic Liquids

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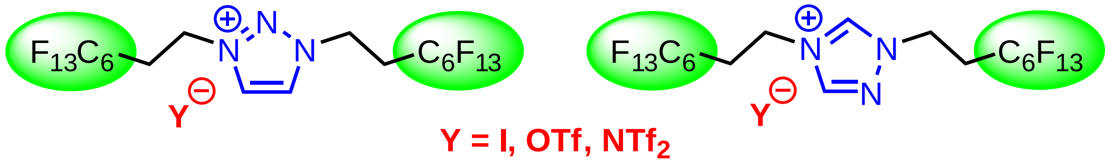
Graphical Abstract

Key topic: Fluorinated Ionic Liquids



Dialkyl 1,2,3- and 1,2,4-triazolium triflimides with perfluorinated side chains were prepared by copper-catalyzed alkyne azide cycloaddition or alkylation reactions. The products shall serve as hydrophobic ionic liquids for surface impregnation.

Abstract. Dialkyl triazolium triflimides with perfluorinated side chains were prepared as hydrophibic ionic liquids (ILs) for surface impregnation. The key feature of the new materials are relatively short perfluorohexyl residues ($n$$C_6F_{13}$ = R_F) as the fluorinated part of the cations, making the target compounds beneficial alternatives to established products because of their enhanced degradability and therefore lower bioaccumulativity. As heterocyclic scaffold, either 1,2,3-triazole or 1,2,4-triazole were chosen. As the two alkyl moieties, either two $R_FCH_2CH_2$ groups or one $R_FCH_2CH_2$ and one Et residue were applied. The diethyl congeners were also prepared. Fluorinated starting materials were $R_FCH_2CH_2OTf$ as alkylating reagent or $R_FCH_2CH_2N_3$ as 1,3-dipole for a copper catalyzed cycloaddition (CuAAC) with trimethylsilyl acetylene. After sequential CuAAC and alkylation reactions, the triflimide salts were finally obtained from the intermediate iodides or triflates with the aid of an ion exchange resin. Out of 14 triazolium salts prepared, four compounds have finally been identified as hydrophobic ILs (contact angles between 85° and 100° with mp. < 100°C), being promising materials for surface impregnation: the 1,2,3-triazolium triflate and triflimide with two fluorinated alkyl residues, and the 1,2,4-triazolium triflimides (two regioisomers) with one fluorinated alkyl residues and one ethyl group.

Keywords: Ionic Liquids; Fluorine compounds; Heterocyclic Compounds; Triazoles, Click Chemistry; Triflimide

Introduction

Ionic liquids (ILs)[1] represent a prominent class of organic materials. Due to their wide temperature range of the liquid state, associated with a low vapor pressure, high thermal stability and good recyclability,[2] ILs are often associated with sustainable processes and green chemistry,[3] although their benefits are sometimes critically discussed.[4] With respect to the cations, this compound class is dominated by imidazolium, phosphonium, pyridinium and quaternary ammonium salts.[5] 1,2,3- and 1,2,4-triazolium based ILs, however, are reported more rarely.[6] As the prototypic representative of "click chemistry",[7] the copper-catalyzed Huisgen 1,3-dipolar cycloaddition[8] of an alkyne with an organic azide (CuAAC) developed very rapidly during the past two decades. For this reason, 1,2,3-triazoles became one of the most popular classes of heterocyclic compounds in Life Sciences[9] as well as Materials Science.[10] In contrast to the paramount prominence of 1,2,3-triazoles, the constitutionally isomeric 1,2,4-triazole motif is, of course, far less represented in the literature, although many biologically relevant compounds carry this heterocycle. Most of them show significant antifungal activity and are applied as active pharmaceutical ingredients for human therapy[11] or for agricultural antifungal treatments.[12]

Perfluorinated carboxylic and sulfonic acids ($C_nF_{2n+1}CO_2H$ and $C_nF_{2n+1}SO_3H$ with n > 6) are ubiquitously applied for surface impregnation of paper, cardboard, textiles, leathers, polymeric materials, metals etc.[13] Especially so called fluorocarbon resins are widely used as materials for industrial as well as consumer[14] applications, firefighting foams, aviation hydraulic fluids, pesticides and paints.[15] The most prominent representatives of this compound class are PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$).[16] Although PFOA and PFOS itself are quite harmless since chemically inert, they are for the same reason persistent and came into the focus of environmental concerns. In particular, they are accumulated in the biosphere and are not affectted by biodegradation or photodegradation.[17] Meanwhile, they are detectable ubiquitously in the abiotic environment[18] as well as in animals and humans[19] and have thus attracted attention as global contaminants. Especially PFOA, because of its water solubility, was found in animal serum as well as in fat and it was shown that PFOA could bind to proteins.[20] These compounds were consequently listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009.[21] Furthermore, the European Chemicals Agency lists PFOA on the SVHC Candidate List as a CMR-substance (SVHC = substance of very high concern; CMR = carcinogenic, mutagenic, or toxic for reproduction).[22] The chemical industry currently makes efforts for identifying replacements for perfluoroalkyl materials with C_8F_{17} chains or higher.[23] A reasonable alternative are shorter chain compounds with C_6F_{13} or C_4F_9 residues, which on the one hand could address the same outstanding material properties, but on the other hand do not accumulate in the environment due to their increased degradability.

As a manufacturer of water repellent textile coatings, we are aiming at identifying new compounds, which can be used as replacements for commonly used long chained perfluorinated substances.[24] Our idea was to develop fluorinated ILs, which has been realized in a few cases before.[25] Most of the literature reports utilize perfluorocarboxylic acids as anions,[26] but also perfluorinated cations have been published.[27] Among the perfluorinated cations, imidazolium,[28] quaternary ammonium[29] and quaternary phosphonium species[30] have been reported. Fluorinated 1,2,3- and 1,2,4-triazolium salts were rarely reported so far; all of them carry only one perfluorinated side chain.[31] Fluorinated 1,2,3-triazolium cations without substituents in the 4- and 5-position are completely unknown. Herein we wish to disclose the synthesis of a small series of fluorinated ILs based on 1,2,3- and 1,2,4-triazoles with double (products **1** and **4**) or single (products **2**, **5**, **6**) perfluoroalkylation at nitrogen and no substituents at the carbon atoms (Figure 1). As fluorinated side chains R_F, perfluorohexyl residues were applied. Furthermore, we have prepared the triazoles **3** and **7** with two ethyl residues as reference materials. As anions Y, iodide or triflate (OTf^-) originated from the synthesis of intermediate products, but were both exchanged by triflimide [NTf_2^-, bis(trifluoromethylsulfonyl)imide anion].

1, R^1, R^2 = $(CH_2)_2R_F$,
2, R^1 = Et, R^2 = $(CH_2)_2R_F$,
3, R^1, R^2 = Et,

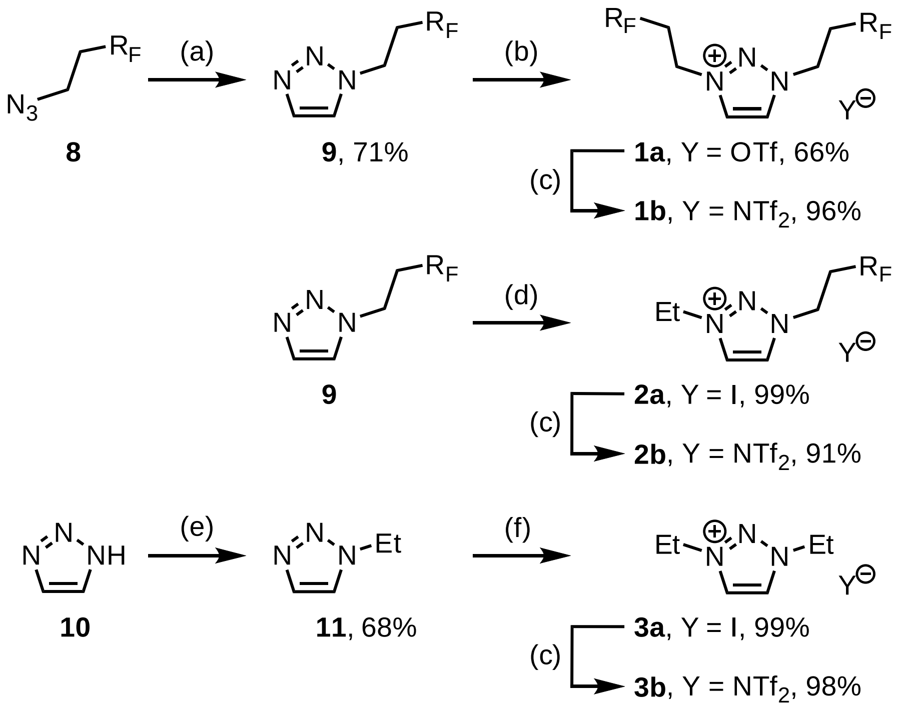
Y = I, OTf, NTf_2,
R_F = nC_6F_{13}

4, R^1, R^2 = $(CH_2)_2R_F$,
5, R^1 = Et, R^2 = $(CH_2)_2R_F$,
6, R^1 = $(CH_2)_2R_F$, R^2 = Et,
7, R^1, R^2 = Et,

Figure 1. Target compounds of this study.

Results and Discussion

1,2,3-Triazolium Salts. For the preparation of 1-alkyl 1,2,3-triazoles **9** and **11** we envisioned the CuAAC of TMS-acetylene with alkyl azides which subsequent protodesilylation of the TMS-group with fluoride, as was reported before by Ryu and coworker.[6a] For this purpose, we first prepared perfluorinated azide **8** from the respective iodide $R_FCH_2CH_2I$ following the procedure of Read *et al*.[31c] Conversion of azide **8** with TMSC≡CH in the presence of $CuSO_4$ and sodium ascorbate was directly followed by treatment of the reaction mixture with TBAF (Scheme 1). Compound **9** was obtained in 71% yield after chromatography.[32] Initial attempts of alkylation 1,2,3-triazole (**10**) with $R_FCH_2CH_2I$ failed, whereas the use of $R_FCH_2CH_2OTf$ (prepared from the respective alcohol $R_FCH_2CH_2OH$ ("6:2 FTOH") according to a literature procedure)[33] as alkylating reagent gave compound **9** in 10% yield. Thus, the CuAAC reaction is in this case the method of choice. The next steps towards triazolium salts **1a** and **2a** were alkylations of compound **9** with $R_FCH_2CH_2OTf$ or EtI, which were performed in acetone at 130°C in a sealed reaction vial. The bis(perfluoroalkyl) triflate **1a** was obtained in 66% yield, the mono(perfluoroalkyl) congener **2a** was obtained as the iodide in almost quantitative yield, both after recrystallization from MTBE.

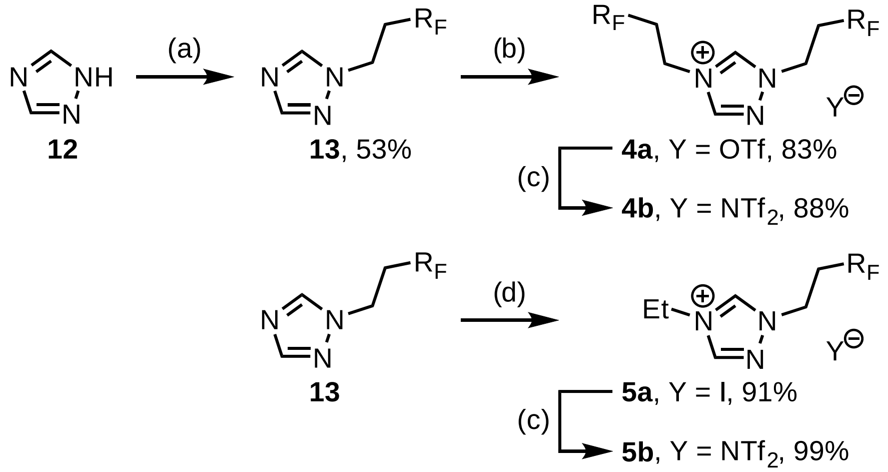


Scheme 1. Preparation of 1,2,3-triazolium salts **1a**,**b–3a**,**b**; reagents and conditions: (a) 1. 0.02 equiv. $CuSO_4$, 0.2 equiv. sodium ascorbate, 1.5 equiv. TMSC≡CH, THF, 23°C, 16 h; 2. 3.0 equiv. TBAF, THF, 23°C, 6 h; (b) 2.0 equiv. $R_FCH_2CH_2OTf$, acetone, 130°C, 3 h; (c) 1. column of hydroxide loaded Lewatit Mono MP Plus 800, 2. 1.0 equiv. $HNTf_2$; (d) 4.0 equiv. EtI, acetone, 130°C, 3 h; (e) 2.0 equiv. EtI, 1.0 equiv. **10**, 2.0 equiv. K_2CO_3, THF, 23°C, 25 h; (f) 2.0 equiv. EtI, acetone, 130°C, 3 h.

The diethyl-substituted compound **3a** was prepared as reference material. In a first approach, compound **11** was prepared by CuAAC from NaN_3, EtI and TMS-acetylene. However, the overall yield after cleavage of the TMS group remained low (26%). Therefore, the alkylation of 1,2,3-triazole (**10**) with EtI was chosen to access compound **11**, which was obtained in 68% after distillation. Interestingly, no competing alkylation at the 2-position of the triazole **10** was found, as was reported in the literature by others.[34] Alkylation of triazole **11** with EtI proceeded straightforwardly in acetone at 130°C to give iodide salt **3a** in quantitative yield after recrystallization from MTBE.

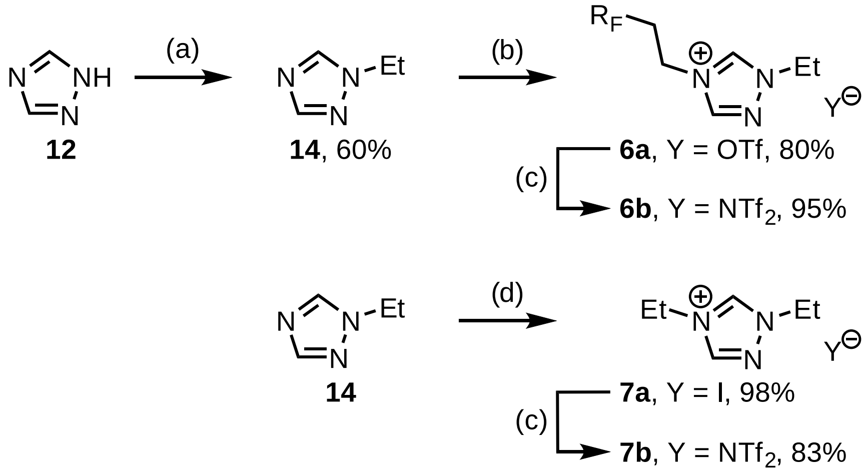
Finally, the triflate (from **1a**) and iodide ions (from **2a** and **3a**) were changed to triflimide (NTf_2^-). First, the triazolium hydroxides were obtained from a column of hydroxide loaded anion exchange resin, which were then neutralized with the acid $HNTf_2$. After evaporation and recrystallization from MTBE, the yields of the triflimide salts **1a**–**3a** were very good (91–98%); their purity was confirmed by elemental combustion analysis. The anion exchange did not lead to differences of the NMR spectra of the cations.

1,2,4-Triazolium salts. The twofold perfluoroalkylated 1,2,4-triazolium salt **4a** was obtained in two steps from the parent heterocycle **12**. The first alkylation with $R_FCH_2CH_2OTf$ was achieved at ambient temperature and proceeded regioselectively at the 1-position, which is clearly indicated by the NMR-spectra of this unsymmetric compound **13**. The second alkylation required, as in the 1,2,3-triazole series, elevated temperature (130°C in acetone) and led to bis(perfluoroalkyl) triflate **4a** in 83% yield after recrystallization from MTBE. The mixed ethyl-perfluoroalkyl compound **5a** was respectively accessed from compound **13** with EtI. The iodide salt **5a** was obtained in 91% yield after recrystallization from MTBE. Although the 1,4-dialkyl constitution of compound **5a** is already determined by the constitution of the starting material, it was double checked by 2D NMR experiments. In particular, the methylene ^1H resonance of the ethyl group at N-4 (q at 4.32 ppm) shows HMBC ^3J-crosspeaks to both aromatic ^{13}C CH resonances (C-5 at 143.15 ppm and C-3 at 144.15 ppm), whereas the α-CH_2 moiety of the fluorinated residue (t at 4.78 ppm) shows a HMBC ^3J-crosspeak to only one aromatic CH (C-5 at 143.15 ppm). The exchange of OTf^- (from **4a**) and I^- (from **5a**) proceeded as in the 1,2,3-triazolium series *via* the hydroxide salts. The triflimides **4a** (88%) and **5b** (99%) were obtained after recrystallzation from MTBE; their purity was confirmed by elemental combustion analysis. Again, NMR spectra of the cations remain the same.



Scheme 2. Preparation of 1,2,4-triazolium salts **4a**,**b** and **5a**,**b**; reagents and conditions: (a) 2.0 equiv. $R_FCH_2CH_2OTf$, 2.0 equiv. K_2CO_3, acetone, 23°C, 24 h; (b) 2.0 equiv. $R_FCH_2CH_2OTf$, acetone, 130°C, 3 h; (c) 1. column of hydroxide loaded Lewatit Mono MP Plus 800, 2. 1.0 equiv. $HNTf_2$; (d) 2.0 equiv. EtI, acetone, 130°C, 3 h.

The mono-perfluoroalkyl 1,2,4-triazolium salt **6a** regioisomeric to compound **4a** was obtained by double alkylation with inverted use of the electrophiles. First, 1,2,4-triazole (**12**) was alkylated with EtI at ambient temperature furnishing compound **14** (60%), which is again exclusively formed as the 1-regioisomer. This compound was reported before (39% yield).[35] The perfluoroalkyl residue was then introduced at 130°C in acetone; compound **6a** was obtained in 90% yield after recrystallization from MTBE. As for compound **5a**, the constitution of compound **6a** as double checked by a HMBC experiment: The ethyl CH_2 resonance (q at 4.42 ppm) shows only one ^3J-crosspeak to C-5 at 142.65 ppm, whereas the α-CH_2 resonance of the fluorinated residue (t at 4.64 ppm) shows ^3J-crosspeaks to both aromatic CH signals (C-5 at 142.65 ppm and C-3 at 144.91 ppm). Again, as a reference compound, the diethyl congener **7a** was prepared, which actually literature known.[36] In both cases, the OTf^- and I^- were exchange to NTf_2^- *via* the hydroxides as reported above. Compounds **6b** (95%) and **7b** (83%) were obtained after recrystallization from MTBE; their purity was confirmed by elemental combustion analysis. Also in these cases, the NMR spectra of the cations did not change.



Scheme 3. Preparation of 1,2,4-triazolium salts **6a**,**b** and **7a**,**b**; reagents and conditions: (a) 2.0 equiv. EtI, 2.0 equiv. K_2CO_3, acetone, 23°C, 21 h; (b) 2.0 equiv. $R_FCH_2CH_2OTf$, acetone, 130°C, 3 h; (c) 1. column of hydroxide loaded Lewatit Mono MP Plus 800, 2. 1.0 equiv. $HNTf_2$; (d) 2.0 equiv. EtI, acetone, 130°C, 3 h.

Physical properties. All triazolium salts carrying at least one fluorinated residue, **1a**,**b**–**2a**,**b** and **4a**,**b**–**6a**,**b**, are unsoluble in water and hexanes, but sparely soluble in MTBE, CH_2Cl_2 and $CHCl_3$ at ambient temperature. They show solubility in MeOH, DMSO or acetone, which is sufficient to obtain NMR-spectra in these solvents. The diethyl congeners **3a**,**b** and **7a**,**b** are well soluble in water, CH_2Cl_2, $CHCl_3$, MeOH and acetone and poorly in hexanes and MTBE.

Some of the compounds (**1a**,**b**–**7a**,**b**) are solids and their melting points are listed in Table 1. It is noticable that all triflimides can be regarded as ILs, with low melting points up to 51°C (for **6b**). All other triflimide salts melt at lower temperatures and some of them (**2b**, **3b**, **4a**, **7b**) could be even regarded as RTILs (room temperature ILs). The triflates or iodides **1a**–**7a** generally show a higher melting point compared to their respective triflimides **1b**–**7b**. Only compounds **1a**, **3a**, and **7a** could be regarded as IL by definition. Compound **3a** is a RTIL. Regarding the differences between the isosteric 1,2,3- and 1,2,4-triazolium series, it is interesting to observe a high melting point difference of about 100 K between compounds **1a** (99°C) and **4a** (196°C). A similar phenomenon is observed for compounds **3a** (liquid) and **7a** (84°C). The difference could be explained by lack of symmetry for the 1,2,4-trizaolium motif leading to a higher dipole moment, thus, better crystallinity compared to their 1,2,3-isosters.

In order to obtain a first impression of water repellency of the new compounds, we have investigated the wettability of a thin film spread on a glass surface by measuring the water contact angle.[30] This investigation was actually only possible for solid compounds. They were spread by melting them on a hot glass plate. Table 1 lists the average of left and right angle. All compounds are far from being "superhydrophobic". Water soluble compound **7a** could actually being regarded as hydrophilic (contact angle 26.4°). Reasonable hydrophobicity was observed for compound **4a** (113.1°), which is actually no IL, and compounds **1b** (97.1°) and **6b** (100.2°).

Table 1. Selected properties of products **1a**,**b**–**7a**,**b**: Melting points and water contact angles (the average value between left and right angle together with its span width is given).

Compound	R^1	R^2	Y	mp.	Contact angle
1a	$(CH_2)_2R_F$	$(CH_2)_2R_F$	OTf	99°C	85.3±1.5°
2a	$(CH_2)_2R_F$	Et	I	148°C	46.9±0.0°
3a	Et	Et	I	liquid	–
4a	$(CH_2)_2R_F$	$(CH_2)_2R_F$	OTf	196°C	113.1±0.0°
5a	Et	$(CH_2)_2R_F$	I	208°C	64.1±0.6°
6a	$(CH_2)_2R_F$	Et	OTf	152°C	65.1±2.5°
7a	Et	Et	I	84°C	26.4±0.1°
1b	$(CH_2)_2R_F$	$(CH_2)_2R_F$	NTf_2	41°C	97.1±0.1°
2b	$(CH_2)_2R_F$	Et	NTf_2	liquid	–
3b	Et	Et	NTf_2	liquid	–
4b	$(CH_2)_2R_F$	$(CH_2)_2R_F$	NTf_2	liquid	–
5b	Et	$(CH_2)_2R_F$	NTf_2	50°C	89.0±1.2°
6b	$(CH_2)_2R_F$	Et	NTf_2	51°C	100.2±0.1°
7b	Et	Et	NTf_2	liquid	–

Summary. In the course of efforts to replace PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$) as surface active materials many industrial manufacturers started off investigations on alternative resins with shorter perfluorinated alkyl chains, to achieve enhanced biodegradability and therefore lower bioaccumulativity. Our contribution to this field is the development of novel ionic liquids with triazolium cations carrying perfluorinated hexyl residues ($n$$C_6F_{13}$, "$R_F$"), which were introduced by $R_FCH_2CH_2OTf$ as alkylating reagent or $R_FCH_2CH_2N_3$ as 1,3-dipole in a cycloaddition reaction.

In particular, we have prepared 1,3-dialkylated 1,2,3-triazolium and 1,4-dialkylated 1,2,4-triazolium triflimides, with either two perfluorinated residues or one perfluoroalkyl and ethyl residue.

In the 1,2,3-triazolium series, perfluorinated triazole **9** was obtained by CuAAC of TMS-acetylene with $R_FCH_2CH_2N_3$ **8** (71% yield). This intermediate product **9** was alkylated by $R_FCH_2CH_2OTf$ or EtI to give triflate **1a** (66%) and iodide **2a** (99%). Furthermore, the diethyl triazolium iodide **3a** (99%) was prepared. The anions of all

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three compounds **1a**, **2a**, and **3a** were changed with the aid of an ion exchange resin to the hydroxide, and these products were then neutralized with Tf_2NH to furnish the respective triflimide salts **1b** (96%), **2b** (91%), and **3b** (98%).

In the second series, 1,2,4-triazole was alkylated regioselectively in the 1-position with either $R_FCH_2CH_2OTf$ or EtI to give two intermediate products **13** (53%) and **14** (60%), which were both submitted to a second alkylation with again $R_FCH_2CH_2OTf$ or EtI. Thus, four 1,2,4-triazolium salts with either triflate or iodide anion, **4a** (83%), **5a** (91%), **6a** (80%), and **7a** (98%) were obtained. As above, the anions of all four compounds **4a**–**7a** were changed to the respective triflimide salts **4b** (88%), **5b** (99%), **6b** (95%), and **7b** (83%).

The melting points of triflates and iodides **1a**–**7a** are higher (some even above 100°C) than their respective triflimide congeners **1b**–**7b**. The latter can all be regarded as ILs (mp. < 100°C), some are even RTILs. The water contact angles were investigated. Four materials (compounds **1a**, **1b**, **5b**, and **6b**) were identified as hydrophobic ILs (contact angles >90° with mp. <100°C), being promising materials for surface impregnation.

Experimental Section

General: Preparative column chromatography was carried out using Merck SiO_2 (35–70 µm, type 60 A) with hexanes (bp 40–60°C) and *tert*-butyl methyl ether (MTBE) as eluents. TLC was performed on aluminum plates coated with SiO_2 F_{254}. ^{1}H-, ^{19}F- and ^{13}C-NMR spectra were recorded on Bruker Avance 500 MHz and 300 MHz instruments. Multiplicities of carbon signals were determined with DEPT experiments. ^{13}C-signals of CF_2 and CF_3 moieties (including OTf and NTf_2) could not be individually distinguished due to extended overlapping. MS and HRMS spectra of products were obtained with an Thermo Fischer DFS (EI) or a Waters Q-TOF Premier (ESI, positive mode) spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond ATR unit. Elemental analyses were determined with a Euro EA-CHNS instrument from HEKAtech. Melting points were obtained with a Gallenkamp device; values are uncorrected. Contact angle measurements were performed with a Contact Angle System OCA, model 15plus from dataphysics and a Teli ccd camera, model CS8620C1. The droplet volume was 9 µL and photograph was taken after 2 s. The perfluorinated starting materials

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$R_FCH_2CH_2N_3$[31c] (**8**) and $R_FCH_2CH_2OTf$[33] were prepared according to literature procedures. All other starting materials were commercially available. In particular, $n C_6F_{13}CH_2CH_2OH$ was purchased from DuPont.

General procedure: Exchange of anions with $HNTf_2$. A column of ion-exchange resin Lewatit Mono MP Plus 800 (20 g, Lanxess, capacity ca. 0.95 mmol/g) was regenerated prior to each use by the following sequential washings: (1) with hydrochloric acid (10 mL, 2 mol/L) until to pH = 1 of the eluent, (2) with water until pH = 7, (3) with aq. NaOH (10 mL, 2 mol/L) until pH = 13–14 and finally (4) again with water to pH = 7.

A solution of the triflate salts **1a**, **4a**, or **6a** (0.33–0.84 mmol) or iodide salts **2a**, **3a**, **5a** or **7a** (0.241–1.98 mmol) in 5 mL MeOH was applied to the column and the hydroxide salts eluted with methanol, until pH = 7 of the eluent; the eluted volume was about 100–200 mL each time. The hydroxide salts were not isolated, but its solutions in MeOH were treated with $HNTf_2$ (1.0 equiv.), the resulting mixtures were evaporated and the residues recrystallized from MTBE to furnish the triflimide salts **1b**–**7b**.

1-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-1,2,3-triazole (9). A solution of $R_FCH_2CH_2N_3$ (**8**) (1.01 g, 2.60 mmol, 1.0 equiv.), sodium ascorbate (52 mg, 0.26 mmol, 0.1 equiv.), $CuSO_4$ (0.026 mmol, 10 mL of a $2.6 \cdot 10^{-3}$ mol/L aqueous solution, 0.01 equiv.) and TMSC≡CH (383 mg, 3.90 mmol, 1.5 equiv.) in THF (15 mL) was stirred for 7 h at 23°C. More sodium ascorbate (52 mg, 0.26 mmol, 0.1 equiv.) and $CuSO_4$ (0.026 mmol, 10 mL of a $2.6 \cdot 10^{-3}$ mol/L aqueous solution, 0.01 equiv.) was added and it was stirred for additional 16 h at 23°C. TBAF (2.5 g, 7.8 mmol, 3.0 equiv.) was then added to the reaction mixture and it was stirred for additional 6 h at 23°C. Subsequently, MTBE (50 mL) was added and the solution was washed with water (3 x 20 mL). The organic layer was dried ($MgSO_4$) and evaporated after filtration. Product **9** (769 mg, 1.85 mmol, 71%) was obtained after chromatography (SiO_2, hexanes/MTBE 1:7, R_f = 0.13) as colorless solid, mp. 90°C. ^{1}H-NMR (300 MHz, CD_3OD): δ = 2.95 (tt, *J* = 7.2 Hz, *J* = 18.8 Hz, 2H), 4.82 (t, *J* = 7.0 Hz, 2H), 7.75 (s, 1H), 8.09 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, CD_3OD): δ = 32.29 (t, *J* = 21.7 Hz, CH_2), 43.28 (CH_2), 126.32 (CH), 134.55 (CH) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, CD_3OD): δ = –80.78 (tt, *J* = 2.4 Hz, *J* = 9.9 Hz), (–113.39)–(–113.60) (m), (–121.69)–(–121.93) (m), (–122.70)–(–122.90) (m), (–123.44)–(–123.61) (m), (–125.99)–(–126.18) (m) ppm. IR (ATR): nu(tilde) = 3099 (w), 1232 (s), 1186 (vs), 1140 (vs), 1124 (s), 1080 (s), 825 (s), 726 (s), 708 (s), 634 (s), 566 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 415.0354 (for $C_{10}H_6F_{13}N_3^+$), found 415.0356 [M^+]. $C_{10}H_6F_{13}N_3$ (415.05).

1,3-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,3-triazolium trifluoromethanesulfonate (1a). A solution of $R_FCH_2CH_2OTf$ (1.91 g, 3.85 mmol, 2.0 equiv.) and triazole **9** (800 mg, 1.93 mmol, 1.0 equiv.) in acetone (2 mL) was stirred in a tightly closed reaction tube for 3 h at 130°C. After evaporation of the volatiles, the residue was recrystallized from MTBE (20 mL) to furnish product **1a** (1.16 g, 1.28 mmol, 66%) as colorless solid, mp. 99°C. ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 2.99–3.26 (m, 4H), 5.09 (t, *J* = 6.1 Hz, 4H), 9.06 (s, 2H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, DMSO-d_6): δ = 29.28 (t, *J* = 21.8 Hz, CH_2), 45.92 (CH_2), 131.82 (2 CH) ppm. ^{19}F{^{1}H}-NMR (470 MHz, DMSO-d_6): δ = –77.84 (s), –80.69 (tt, *J* = 10.3 Hz, *J* = 2.6 Hz), (–113.56)–(–113.81) (m), (–121.91)–(–122.17) (m), (–122.87)–(–123.08) (m), (–123.26)–(–123.40) (m), (–126.06)–(–126.26) (m) ppm. IR (ATR): nu(tilde) = 2354 (m), 2330 (m), 2195 (m), 2172 (m), 2067 (m), 1982 (m), 1141 (s), 640 (s), 615 (m), 594 (s), 560 (vs) cm^{-1}. HRMS (EI, 70 eV): calcd. 762.0454 (for $C_{18}H_{10}F_{26}N_3^+$), found 762.0426 [M – OTf^-]. $C_{19}H_{10}F_{29}N_3O_3S$ (911.32).

1,3-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide (1b). Triflate salt **1a** (500 mg, 0.55 mmol) was converted with $HNTf_2$ (154 mg, 0.55 mmol) according to the general procedure to give compound **1b** (557 mg, 0.530 mmol, 96%) after recrystallization from MTBE (10 mL) as colorless solid, mp. 41°C. IR (ATR): nu(tilde) = 3170 (w), 3154 (w), 1361 (m), 1347 (m), 1231 (m), 1176 (s), 1125 (s), 1098 (m), 1058 (s), 810 (m), 698 (m) cm^{-1}. $C_{20}H_{10}F_{32}N_4O_4S_2$ (1042.39): calcd. C 23.05%, H 0.97%, N 5.37%, S 6.15%; found C 23.09%, H 1.30%, N 5.55%, S 6.51%.

1-Ethyl-3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,3-triazolium iodide (2a). A solution of EtI (526 mg, 3.37 mmol, 4.0 equiv.) and triazole **9** (350 mg, 0.84 mmol, 1.0 equiv.) in acetone (2 mL) was stirred in a tightly closed reaction tube for 3 h at 130°C. After evaporation of the volatiles, the residue was recrystallized from MTBE (20 mL) to furnish product **2a** (474 mg, 0.83 mmol, 99%) as colorless solid, mp. 148°C. ^{1}H-NMR (300 MHz, CD_3OD): δ = 1.69 (t, *J* = 7.3 Hz, 3H), 3.18 (tt, *J* = 18.6 Hz, *J* = 7.2 Hz, 2H),

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4.77 (q, *J* = 7.4 Hz, 2H), 5.12 (t, *J* = 7.0 Hz, 2H), 8.86 (s, 1H), 8.92 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, CD_3OD): δ = 14.66 (CH_3), 31.30 (t, *J* = 21.6 Hz, CH_2), 47.31 (CH_2), 50.96 (CH_2), 131.76 (CH) 132.56 (CH) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, CD_3OD): δ = –82.39 (tt, *J* = 10.5 Hz, *J* = 2.5 Hz), (–114.61)–(–115.33) (m), (–122.38)–(–123.06) (m), (–123.49)–(–124.02) (m), (–124.24)–(–124.72) (m), (–127.01)–(–127.62) (m) ppm. IR (ATR): nu(tilde) = 3124 (w), 3103 (w), 2969 (w), 2955 (w), 1531 (w), 1369 (w), 1321 (w), 1306 (w), 1240 (m), 1221 (m), 1183 (s), 1141 (s), 1123 (s), 1075 (m), 1026 (w), 820 (m), 702 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 444.0740 (for $C_{12}H_{11}F_{13}N_3^+$), found 444.0744 [M – I^-]. $C_{12}H_{11}F_{13}IN_3$ (571.12).

1-Ethyl-3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide (2b). Iodide salt **2a** (300 mg, 0.532 mmol) was converted with $HNTf_2$ (93 mg, 0.532 mmol) according to the general procedure to give compound **2b** (352 mg, 0.486 mmol, 91%) after washing with MTBE (5 mL) as colorless oil. IR (ATR): nu(tilde) = 3144 (w), 1708 (w), 1348 (m), 1181 (s), 1133 (s), 1055 (s), 791 (m), 616 (m) cm^{-1}. $C_{14}H_{11}F_{19}N_4O_4S_2$ (724.36): calcd. C 23.21%, H 1.53%, N 7.73%, S 8.85%; found C 23.21%, H 1.54%, N 7.66%, S 8.89%.

1-Ethyl-1,2,3-triazole (11). A solution of EtI (4.51 g, 29.0 mmol, 2.0 equiv.), K_2CO_3 (4.00 g, 29.0 mmol, 2.0 equiv.) and 1,2,3-triazole **10** (1.00 g, 14.5 mmol, 1.0 equiv.) in THF (20 mL) was stirred at 23°C for 25 h. The suspension was filtered and all volatiles were removed under reduced pressure. Product **11** (954 mg, 9.82 mmol, 68%) was obtained after distillation (bp. 58°C at 0.33 mbar) as colorless oil. ^1H-NMR (300 MHz, $CDCl_3$): δ = 1.55 (t, *J* = 7.4 Hz, 3H), 4.44 (q, *J* = 7.4 Hz, 2H), 7.55 (s, 1H), 7.69 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): δ = 15.65 (CH_3), 45.23 (CH_2), 122.71 (CH), 133.94 (CH) ppm. IR (ATR): nu(tilde) = 3448 (w), 3122 (w), 2985 (w), 1647 (w), 1223 (s), 1209 (s), 1117 (s), 1068 (s), 788 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 98.0713 (for $C_4H_8N_3^+$), found 98.0715 [M + H^+]. $C_4H_7N_3$ (97.12).

1,3-Diethyl-1,2,3-triazolium iodide (3a). A solution of EtI (1.61 g, 10.3 mmol, 2.0 equiv.) and ethyltriazole **11** (500 mg, 5.15 mmol, 1.0 equiv.) in acetone (2 mL) was stirred in a tightly closed reaction tube for 3 h at 130°C. After evaporation of the volatiles, the residue was washed with MTBE (10 mL) to furnish product **3a** (1.29 g, 5.09 mmol, 99%) as yellowish liquid. ^1H-NMR (300 MHz, DMSO-d_6): δ = 1.53 (t, *J* = 7.3

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Hz, 6H), 4.65 (q, *J* = 7.3 Hz, 4H), 8.94 (s, 2H) ppm. $^{13}C\{^1H\}$-NMR (75 MHz, DMSO-d_6): δ = 14.12 (2 CH_3), 48.66 (2 CH_2), 130.33 (2 CH) ppm. IR (ATR): nu(tilde) = 3451 (s), 3091 (m), 2986 (s), 1450 (s), 1201 (s), 1085 (s), 804 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 126.1026 (for $C_6H_{12}N_3^+$), found 126.1031 [M – I^-]. $C_6H_{12}IN_3$ (253.09).

1,3-Diethyl-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide (3b). Iodide salt **3a** (500 mg, 1.98 mmol) was converted with $HNTf_2$ (555 mg, 1.98 mmol) according to the general procedure to give compound **3b** (785 mg, 1.93 mmol, 98%) after washing with MTBE (10 mL) as yellowish oil. IR (ATR): nu(tilde) = 3146 (w), 3088 (w), 2995 (w), 2953 (w), 2849 (w), 1583 (m), 1450 (m), 1342 (s), 1335 (s), 1171 (s), 1132 (s), 1040 (s), 617 (s) cm^{-1}. $C_8H_{12}F_6N_4O_4S_2$ (406.02): calcd. C 23.65%, H 2.98%, N 13.79%, S 15.78%; found C 23.94%, H 3.05%, N 13.70%, S 15.69%.

1-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-1,2,4-triazole (13). A solution of $R_FCH_2CH_2OTf$ (1.80 g, 3.62 mmol, 1.0 equiv.), K_2CO_3 (1.00 g, 7.24 mmol, 2.0 equiv.) and triazole **12** (250 mg, 3.62 mmol, 1.0 equiv.) in acetone (6 mL) was stirred in at 23°C for 24 h. MTBE (30 mL) was added and the mixture was washed with water (3 x 50 mL). The organic layer was dried ($MgSO_4$) and evaporated after filtration. Product **13** (354 mg, 0.853 mmol, 53%) was obtained after chromatography (SiO_2, hexanes/MTBE 1:7, R_f = 0.15) as colorless solid, mp. 61°C. ^1H-NMR (300 MHz, DMSO-d_6): δ = 2.88 (tt, *J* = 6.7 Hz, *J* = 19.7 Hz, 2H), 4.56 (t, *J* = 6.8 Hz, 2H), 8.01 (s, 1H), 8.60 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, DMSO-d_6): δ = 29.96 (t, *J* = 20.8 Hz, CH_2), 40.81–40.92 (m, CH_2), 144.53 (CH), 151.69 (CH) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, DMSO-d_6): δ = (–80.34 (tt, *J* = 10.2 Hz, *J* = 2.6 Hz), (–113.45)–(–113.43) (m), (–121.62)–(–121.98) (m), (–122.54)–(–122.86) (m), (–123.14)–(–123.44) (m), (–125.72)–(–126.04) (m) ppm. IR (ATR): nu(tilde) = 1187 (s), 1170 (s), 1138 (s), 1078 (s), 709 (s), 687 (s), 639 (s), 612 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 415.0354 (for $C_{10}H_6F_{13}N_3^+$), found 415.0358 [M^+]. $C_{10}H_6F_{13}N_3$ (415.05).

1,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium trifluoromethanesulfonate (4a). A solution of $R_FCH_2CH_2OTf$ (717 mg, 1.45 mmol, 2.0 equiv.) and triazole **13** (300 mg, 0.723 mmol, 1.0 equiv.) in acetone (2 mL) was stirred in a tightly closed reaction tube for 3 h at 130°C. After evaporation of the volatiles, the residue was re-crystallized from MTBE (10 mL) to furnish product **4a** (545 mg, 0.598 mmol, 83%) as colorless solid, mp. 196°C. ^{1}H-NMR (500 MHz, acetone-d$_6$): δ = 3.13–3.45 (m, 4H), 4.99–5.22 (m, 4H), 9.45 (s, 1H), 10.49 (s, 1H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, acetone-d$_6$): δ = 41.78 (CH_2), 45.82 (CH_2), 145.07 (CH), 146.28 (CH) ppm. ^{19}F{^{1}H}-NMR (470 MHz, acetone-d$_6$): δ = –79.42 (s), –82.01 (tt, *J* = 10.4 Hz, *J* = 2.6 Hz), –114.51 (dm), (–122.52)–(–122.78) (m), (–123.53)–(–123.79) (m), (–124.21)–(–124.42) (m), (–126.91)–(–127.13) (m) ppm. IR (ATR): nu(tilde) = 3131 (w), 3083 (w), 1585 (w), 1229 (s), 1201 (s), 1185 (s), 1143 (vs), 1080 (m), 1030 (s), 1009 (m), 707 (m), 695 (m), 638 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 762.0454 (for $C_{18}H_{10}F_{26}N_3^+$), found 762.0474 [M – OTf$^-$]. $C_{19}H_{10}F_{29}N_3O_3S$ (911.32).

1,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (4b). Triflate salt **4a** (301 mg, 0.329 mmol) was converted with $HNTf_2$ (93 mg, 0.329 mmol) according to the general procedure to give compound **4b** (301 mg, 0.289 mmol, 88%) after washing with MTBE (10 mL) as colorless oil. IR (ATR): nu(tilde) = 3245 (w), 3099 (w), 3062 (w), 3037 (w), 1704 (m), 1345 (m), 1321 (m), 1233 (m), 1187 (s), 1142 (s), 1128 (s), 1058 (m), 1058 (m), 708 (m), 697 (m) cm^{-1}. $C_{20}H_{10}F_{32}N_4O_4S_2$ (1042.39): calcd. C 23.05%, H 0.97%, N 5.37%, S 6.15%; found C 22.77%, H 1.31%, N 5.16%, S 6.41%.

4-Ethyl-1-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium iodide (5a). A solution of EtI (751 mg, 4.81 mmol, 4.00 equiv.) and perfluoroalkyltriazole **13** (500 mg, 1.20 mmol, 1.0 equiv.) in acetone (2 mL) was stirred in a tightly closed reaction tube for 3 h at 130°C. After evaporation of the volatiles, the residue was recrystallized from MTBE (30 mL) to furnish product **7a** (624 mg, 1.09 mmol, 91%) as colorless solid, mp. 208°C. ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ = 1.46 (t, *J* = 7.3 Hz, 3H), 3.03 (tt, *J* = 19.5 Hz, *J* = 7.0 Hz, 2H), 4.32 (q, *J* = 7.3 Hz, 2H), 4.78 (t, *J* = 6.9 Hz, 2H), 9.32 (s, 1H), 10.24 (s, 1H) ppm. ^{13}C{^{1}H}-NMR (75 MHz, DMSO-d$_6$): δ = 14.52 (CH_3), 29.05 (t, *J* = 20.1 Hz, CH_2), 43.25 (CH_2), 43.96 (t, *J* = 4.1 Hz, CH_2), 143.15 (CH) 144.67 (CH) ppm. ^{19}F{^{1}H}-NMR (470 MHz, DMSO-d$_6$): δ = –82.39 (tt, *J* = 10.3 Hz, *J* = 2.4 Hz), (–114.81)–(–115.07) (m), (–122.69)–(–122.97) (m), (–123.71)–(–122.96) (m), (–124.30)–(–124.51) (m), (–127.19)–(–127.42) (m) ppm. IR (ATR): nu(tilde) = 3045 (m), 1586 (m), 1235 (s), 1201 (vs), 1180 (vs), 1080 (s), 1010 (s), 693 (s), 652 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 444.0740 (for $C_{12}H_{11}F_{13}N_3^+$), found 444.0736 [M – I$^-$]. $C_{12}H_{11}F_{13}IN_3$ (571.12).

4-Ethyl-1-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (5b). Iodide salt **5a** (500 mg, 0.875 mmol) was converted with $HNTf_2$ (237 mg, 0.84 mmol) according to the general procedure to give compound **5b** (625 mg, 0.863 mmol, 99%) after recrystallization from MTBE (10 mL) as colorless solid, mp. 50°C. IR (ATR): nu(tilde) = 3146 (w), 3098 (w), 1585 (w), 1352 (m), 1321 (m), 1231 (m), 1183 (s), 1058 (s), 1010 (m), 609 (m) cm^{-1}. $C_{14}H_{11}F_{19}N_4O_4S_2$ (724.36): calcd. C 23.21%, H 1.53%, N 7.73%, S 8.85%; found C 23.51%, H 1.67%, N 7.47%, S 8.61%.

1-Ethyl-1,2,4-triazol (14). A solution of EtI (4.52 g, 29.0 mmol, 2.0 equiv.), K_2CO_3 (4.01 g, 29.0 mmol, 2.0 equiv.) and 1,2,4-triazole (**12**) (1.00 g, 14.5 mmol, 1.0 equiv.) in acetone (10 mL) was stirred at 23°C for 21 h. The suspension was filtered and all volatiles were removed under reduced pressure. Product **14** (851 mg, 8.76 mmol, 60%) was obtained after distillation (40 mbar, 86°C) as colorless oil. ^1H-NMR (500 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7.3 Hz, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 7.82 (s, 1H), 7.98 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 14.95 (CH_3), 44.51 (CH_2), 142.13 (CH), 151.72 (CH) ppm. IR (ATR): nu(tilde) = 3474 (w), 3396 (w), 3119 (w), 2989 (w), 1648 (w), 1509 (vs), 1274 (vs), 1207 (s), 1140 (vs), 1012 (s), 959 (s), 682 (vs), 671 (vs), 645 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 98.0713 (for $C_4H_8N_3^+$), found 98.0720 [M + H^+]. $C_4H_7N_3$ (97.12).

1-Ethyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium trifluoromethanesulfonate (6a). A solution of $R_FCH_2CH_2OTf$ (2.04 g, 4.12 mmol, 2.0 equiv.) and ethyltriazole **14** (200 mg, 2.06 mmol, 1.0 equiv.) in acetone (5 mL) was stirred in a tightly closed reaction tube for 3 h at 130°C. After evaporation of the volatiles, the residue was recrystallized from MTBE (50 mL) to furnish product **6a** (972 mg, 1.64 mmol, 80%) as colorless solid, mp. 152°C. ^1H-NMR (300 MHz, DMSO-d_6): δ = 1.47 (t, *J* = 7.3 Hz, 3H), 2.90–3.21 (m, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.64 (t, *J* = 7.6 Hz, 2H), 9.26 (s, 1H), 10.17 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (75 MHz, DMSO-d_6): δ = 13.57 (CH_3), 29.81 (t, *J* = 20.5 Hz, CH_2), 39.56 (CH_2), 47.27 (CH_2), 120.67 (q, *J* = 322.1 Hz; CF_3), 142.65 (CH) 144.91 (CH) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, DMSO-d_6): δ = –78.03 (s), –82.56 (tt, *J* = 10.1 Hz, *J* = 2.6 Hz), (–113.00)–(–113.50) (m), (–121.58)–(–122.06) (m), (–122.56)–(–123.07) (m), (–123.28)–(–123.64) (m), (–125.82)–(–126.32) (m) ppm. IR

(ATR): nu(tilde) = 3135 (w), 3080 (w), 2998 (w), 1585 (m), 1364 (m), 1242 (s), 1226 (s), 1188 (s), 1168 (s), 1081 (m), 1031 (s), 997 (m), 694 (m) cm^{-1}. HRMS (ESI, pos. mode): calcd. 444.0740 (for $C_{12}H_{11}F_{13}N_3^+$), found 444.0741 [M – OTf$^-$]. $C_{13}H_{11}F_{16}N_3O_3S$ (593.28).

1-Ethyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (6b). Triflate salt **6a** (500 mg, 0.84 mmol) was converted with $HNTf_2$ (237 mg, 0.84 mmol) according to the general procedure to give compound **6b** (580 mg, 0.80 mmol, 95%) after recrystallization from MTBE (10 mL) as colorless solid, mp. 51°C. IR (ATR): nu(tilde) = 3146 (w), 3099 (w), 1586 (m), 1352 (m), 1321 (m), 1183 (s), 1057 (s), 1009 (m), 652 (m) cm^{-1}. $C_{14}H_{11}F_{19}N_4O_4S_2$ (724.36): calcd. C 23.21%, H 1.53%, N 7.73%, S 8.85%; found C 23.59%, H 1.82%, N 7.54%, S 8.72%.

1,4-Diethyl-1,2,4-triazolium iodide (7a). A solution of EtI (643 mg, 4.12 mmol, 2.0 equiv.) and ethyltriazole **14** (200 mg, 2.06 mmol, 1.0 equiv.) in acetone (12 mL) was stirred in a tightly closed reaction tube for 2 h at 130°C. After evaporation of the volatiles, the residue was recrystallized from hexanes/MTBE (1:1, 10 mL) to furnish product **7a** (280 mg, 2.20 mmol, 54%) as colorless solid, mp. 84°C. ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ = 1.46 (t, *J* = 7.2 Hz, 6H), 4.26 (q, *J* = 7.3 Hz, 2H), 4.38 (q, *J* = 7.3 Hz, 2H), 9.23 (s, 1H), 10.13 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, DMSO-d$_6$): δ = 13.64 (CH_3), 14.46 (CH_3), 42.99 (CH_2), 47.08 (CH_2), 141.89 (CH), 144.34 (CH) ppm. IR (ATR): nu(tilde) = 3031 (m), 2998 (s), 2980 (s), 2882 (w), 1776 (w), 1579 (s), 1340 (s), 1172 (s), 997 (s), 966 (s), 702 (s), 626 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 126.1026 (for $C_6H_{12}N_3^+$), found 126.1030 [M – I$^-$]. $C_6H_{12}IN_3$ (253.09).

1,4-Diethyl-1,2,4-triazolium bis(trifluoromethanesulfonyl)imide (7b). Iodide salt **7a** (61 mg, 0.241 mmol) was converted with $HNTf_2$ (68 mg, 0.241 mmol) according to the general procedure to give compound **7b** (81 mg, 0.199 mmol, 83%) after washing with MTBE (5 mL) as colorless oil. IR (ATR): nu(tilde) = 3143 (w), 3090 (w), 2995 (w), 2954 (w), 2922 (w), 2853 (w), 1580 (m), 1454 (m), 1347 (s), 1329 (s), 1179 (s), 1132 (s), 1051 (s), 790 (m), 741 (m), 612 (s) cm^{-1}. $C_8H_{12}F_6N_4O_4S_2$ (406.02): calcd. C 23.65%, H 2.98%, N 13.79%, S 15.78%; found C 23.41%, H 2.96%, N 13.71%, S 15.95%.

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