

Perfluorinated Pyridinium and Imidazolium Ionic Liquids

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Graphical Abstract

Key topic: Fluorinated Ionic Liquids



Pyridinium and imidazolium ionic liquids with perfluorinated side chains and different anions were prepared.

Abstract: Ionic liquids with perfluorinated side chains are prepared as hybrid materials for surface impregnation. For the cationic part, methyl and ethyl pyridinium as well as imidazolium scaffolds are used. The anions are hydroxide, acetate, trifluoroacetate, triflate, triflimide, chloride, bromide, iodide, hydrogensulfate, and perfluoro-dodecanoate. The key feature of this investigation are relatively short perfluorohexyl residues as the fluorinated part of the salts, making the target compounds beneficial alternatives to established products because of their lower bioaccumulativity. One compound yielded single crystals suitable for X-ray structure analysis revealing a layered structure with relatively well-resolved, hard ionic domains alternating with disordered, soft perfluorinated layers. The wettability of all 30 materials was investigated

by water contact angle measurements of a thin film on a glass surface. In two cases, promising contact angles (130° and 140°) were observed indicating, that the products might be suitable candidates for the impregnation of surfaces.

Keywords: Ionic Liquids, Fluorine compounds, Wettability, Pyridine derivatives, Imidazole derivatives.

Introduction

lonic liquids^[1] and perfluorinated solvents^[2] are neoteric solvents, which are often associated with sustainable processes and green chemistry,^[3] although their benefits are sometimes critically discussed.^[4] The combination of both, i.e. ionic liquids with perfluorinated side chains,^[5] has been realized in a few cases. Most of them utilize perfluorocarboxylic acids as anions,^[6] but also perfluorinated cations have been reported.^[7] Fluorinated quaternary phosphonium salts were reported to be super-hydrophobic materials^[8] with contact angles up to 168°.^[9]

As a manufacturer of water repellent textile coatings, the latter materials property attracted our particular attention, since we are aiming at identifying new compounds with shorter perfluoroalkyl side chains. The compounds used in this field of application so far, perfluoroalkyl carboxylic and sulfonic acids with longer carbon chains $(C_nF_{2n+1}CO_2H \text{ and } C_nF_{2n+1}SO_3H \text{ with } n > 6)$ and derivatives thereof, came into the focus of environmental concerns. The most prominent representatives of these compound classes are PFOA (C7F15CO2H) and PFOS (C8F17SO3H), which have found ubiquitous applications for surface treatment of textiles, leathers, cardboard, paper, polymeric materials, metals etc.^[10] Especially so called fluorocarbon resins are widely in use as impregnation materials for industrial as well as consumer^[11] applications. Although PFOA and PFOS itself are quite harmless since chemically inert, they are for the same reason persistent, they pollute the environment and are accumulated in the biosphere. Meanwhile they are detectable ubiquitously in the abiotic environment^[12] as well as in animals and humans^[13] and have thus attracted attention as global contaminants. These compounds were consequently listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009.^[14] 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).^[15] The chemical industry started off several initiatives for identifying replacements for perfluoroalkyl materials.^[16] 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. We propose that both features could be addressed by pyridinium and imidazolium ionic liquids with perfluorohexyl chains (nC_6F_{13}). Whereas the pyridinium scaffold has so far not been equipped with fluorinated residues, the imidazolium core has been with targeting the development of new fluorinated *N*-heterocyclic carbene ligands for homogeneous catalysis.^[17] Herein we wish to disclose the synthesis of a small series of 30 fluorinated ionic liquids based on the two pyridinium cations **1** and **2** as well as the imidazolium cation^[18] **3** (Figure 1). In order to access a rather divers set of compounds for screening the material properties, we have focused on the exchange of anions.^[19]





Results and Discussion

Pyridinium Cations. The synthesis of pyridinium compounds proceeded from the acid chloride, which was obtained from 3,5-pyridine dicarboxylic acid **4** with an excess of SOCl₂. Conversion with $R_FCH_2CH_2OH$ ($R_F = nF_{13}C_6$) without additional solvent furnished the fluorinated diester **5** in 93%, as reported before (Scheme 1).^[20] The alkylation with an excess of MeI and EtI, resp., required relatively high concentration (1 mol/L in acetone) and temperature (150°C), therefore, the reaction was performed in a tightly closed reaction vial. The pyridinium iodides **1a** and **2a** were obtained in 89% and 74% yields, resp., after crystallization from MTBE (*tert*-butyl-methylether). These two compounds were fully characterized. Efforts to prepare the *N*-butyl congener from *n*Bul were less successful (10% yield after crystallization),





Scheme 1. Preparation of pyridinium salts. Reagents and conditions: (a) 1. xs. SOCl₂, cat. DMF, 90°C, 16 h; 2. 2.2 equiv. nF₁₃C₆CH₂CH₂OH, 90°C, 96 h; (b) 14 equiv. Mel or 11 equiv. Etl, acetone, 150°C, 3 h; (c) hydroxide loaded resin Lewatit Mono MP Plus 800; (d) + 1.0 equiv. HX in MeOH, anions X: AcO (c), CF₃CO₂ (d), TfO (e), Tf₂N (f), Cl (g), Br (h), HSO₄ (i), CF₃(CF₂)₁₀CO₂ (j).

lodide ions from salts **1a** and **2a** were changed to hydroxide by using a column of hydroxide-loaded ion exchange resin. First of all, the hydroxides **1b** and **2b** were obtained after elution from the column with MeOH and evaporation of their solutions; yields of anhydrous materials were quantitative (98–100%). All other salts **1c–1j** and **2c–2j** were prepared from the MeOH solutions of hydroxides **1b** and **2b** with a stoichiometric amount of the respective Brønsted acids HX as MeOH solutions (except Tf₂NH, which was used neat), as were AcOH (**c**), CF₃CO₂H (**d**), TfOH (**e**), Tf₂NH (**f**), HCl (**g**), HBr (**h**), H₂SO₄ (0.50 equiv.) (**i**). Furthermore, the perfluorodode-canoic acid, CF₃(CF₂)₁₀CO₂H (**j**), was used, also in neat form. In all 16 cases, the products **1c–1j** and **2e–2j** were obtained in 96–100% yields as analytically pure materials, except compounds **2c** (81%) and **2d** (83%), which required recrystallization from MTBE to obtain analytically pure materials. Compounds **1b–1j** and **2b–2j** gave the same NMR and mass spectra as their parent iodides **1a** and **2a**, therefore, only

IR data and combustional analyses are given in the experimental section.

Although perfluorinated compounds are generally regarded to be difficult to crystallize, we were able to obtain single crystals of compound **2a** suitable for X-ray structure determination at T = 170 K.^[21] Compound **2a** crystallized in the monoclinic space group P2₁/n with *a* = 750.40(2) pm, *b* = 4784.12(15) pm, *c* = 967.17(3) pm, *α* = 90°, β = 93.3645(15)°, γ = 90°. An ORTEP representation of the molecular structure is given in Figure 2. Whereas the pyridinium part of the molecular cation appears well resolved, the anisotropic atomic displacement parameters become larger towards the end of the fluorinated chain. In addition, the perfluoroalkyl chains are disordered as shown in Figure 3, a clear indication of the PTFE-like nature of the perfluoroalkyl chains which originates from the extraordinarily weak intermolecular forces.



Figure 2. ORTEP-representation of the X-ray structure of compound **2a** in the solid state, ellipsoids at the 50% probability level, H atoms and disor-dered atoms were omitted for clarity; color code: carbon gray, fluorine green, iodine violet, nitrogen blue, oxygen red.



Figure 3. Structure of compound **2a** including the disorder of the ethyl group and of the perfluoroalkyl chains.

Figure 4 shows the crystal packing of compound **2a**. The unit cell is depicted with black lines (Z = 4); view along the *a*-axis; the horizontal edge is the *b*-axis. The compound exhibits a layered structure of alternating ionic and fluorinated domains in the ac-plane. The pyridinium iodide units define the "hard" ionic domains, which are well resolved. In contrast, the "soft" fluorinated domains show large displacement parameters and disorder (cf. Figure 3).



Figure 4. ORTEP-representation of the packing of compound 2a in the unit cell.

Imidazolium Cation. In order to access a perfluoroalkylated imidazolium derivative^[18] we first tried to dialkylate imidazole 8 with the triflate 7, derived from the alcohol $nF_{13}C_6CH_2CH_2OH$ according to a known procedure,^[22] but we failed. We then turned to 1-trimethylsilylimidazole (6), which was reported to give superior results in alkylation reactions,^[23] and we were indeed able to isolate the triflate salt **3e** in 35% yield after recrystallization. Apart from the higher costs of the TMS-derivative 6, this method did not convince us due to the relatively low yield. Therefore, we investigated the alkylation with iodo compound 9 as starting material, and indeed imidazole 8 could be alkylated twice and the iodide 3a was obtained in 44% yield after crystallization. The anion exchange was performed as established for the synthesis of the pyridinium derivatives: After procuring the hydroxide 3b, and respective MeOH solution was neutralized with the respective Brønsted acids HX yielding the compounds 3c-3j all in quantitative yields (96-100%) and analytically pure materials, except the triflate 3e, which was obtained in 35% yield after recrystallization (IR and combustion analysis are given in the experimental section). The NMR and mass spectra of all compounds 3a-3j appear equal; respective data for compound 3e are given in the experimental section.



Scheme 2. Preparation of imidazolium salts. Reagents and conditions: (a) 2.5 equiv. $nF_{13}C_6CH_2CH_2OTf$, 60°C, 24 h; (b) 2.2 equiv. $nF_{13}C_6CH_2CH_2I$, toluene, 110°C, 24 h; (c) hydroxide loaded resin Lewatit Mono MP Plus 800; (d) + 1.0 equiv. HX in H₂O, anions X: AcO (c), CF₃CO₂ (d), TfO (e), Tf₂N (f), Cl (g), Br (h), HSO₄ (i), CF₃(CF₂)₁₀CO₂ (j).

Physical Properties. In order to obtain a first impression of water repellency of the new products we have investigated the wettability of a thin film spread on a glass surface by measuring the water contact angle.^[8] Figure 5 shows a representative photograph of the droplet on the surface impregnated with compound 1a. Table 1 lists the average of left and right angle together with the melting point and the calculated fluorine content. Obviously, no correlation can be derived from the angles and the two other pieces of data. A great influence has of course the anion of the respective salt as well as the constitution of the cation. Even small changes like methyl replaced by ethyl results in significant changes of the contact angle, as is particularly obvious by comparison of compounds 1a and 2a (140° and 62°, resp.). Actually, compound 1a (Figure 5) is the only example which fulfilled out expectations completely. All other compounds with perfluorohexyl moieties showed contact angles below 110°. Higher values were obtained with the perfluorododecanoate anion (series j), however, the aim of our efforts is to abolish such compounds from future applications. Anyhow, with methylpyridinium compound **1a** we have a promising candidate for a material suitable for textile impregnation in our hand, which is expected to be - as a benefit of shorter perfluoroalkyl chains - bio-degradable. We are presently investigating its application, in particular the question whether an iodide salt shows long term stability under aerobic conditions.

	Methylpyridinium cation 1			Ethylpyridinium cation 2			Imidazolium cation 3		
Anion	mp./°C	F/% w/w	Θ/°	mp./°C	F/% w/w	Θ/°	mt	F/% w/w	Θ/°
$ \begin{array}{c} {\sf I}^- ({\bm a}) \\ {\sf HO}^- ({\bm b}) \\ {\sf AcO}^- ({\bm c}) \\ {\sf CF}_3 {\sf CO}_2^- ({\bm d}) \\ {\sf TfO}^- ({\bm e}) \\ {\sf Tf}_2 {\sf N}^- ({\bm f}) \\ {\sf CI}^- ({\bm g}) \end{array} $	193 79 135 157 122 66 151	49.3 55.4 52.9 55.8 53.8 52.7 54.3	$140.5\pm0.1 \\ _^{[a]} \\ 38.5\pm1.1 \\ 42.4\pm3.2 \\ 79.3\pm2.2 \\ 95.8\pm0.2$	182 57 132 152 136 51 141	48.7 54.6 52.1 55.0 53.1 52.0 53.5	$\begin{array}{c} 62.4{\pm}0.3\\ _^{[b]}\\ 24.7{\pm}0.9\\ 91.0{\pm}0.0\\ 87.6{\pm}0.3\\ 101.6{\pm}0.4\end{array}$	anuscrip	55.6 63.5 60.2 64.2 60.6 58.4 62.0	$127.9\pm0.0\\98.8\pm2.3_^{[b]}\\8.8\pm0.6\\69.6\pm1.1\\88.7\pm1.7\\69.4\pm1.1$
Br ⁻ (h) HSO ₄ ⁻ (i) CF ₃ (CF ₂) ₁₀ CO ₂ ⁻ (j)	161 126 81	51.8 53.6 62.6	80.2±1.8 31.8±0.3 109.7±0.1	154 112 59	51.0 50.1 62.0	108.3±0.3 _ ^[b] 113.8±0.0	Σ	58.7 57.6 67.7	94.0±0.5 _ ^[b] 115.9±0.1

Table 1. Selected properties of fluorinated compounds 1a-1j, 2a-2j and 3a-3j: Melting points (mp.), fluorine content (F/% w/w; calculated) and water contact angles (Θ) (the average value between left and right angle together with its span width is given).

[a] dissolves in water, [b] the angles are less 5° due to good wettability of the surface, [c] not a solic

nbient temperature.



Figure 5. Shape of a water droplet on a glass surface coated with compound **1a**; contact angles are 140.4° and 140.6°, resp.

Summary. In the course of our efforts to develop perfluorinated compounds for textile impregnation as alternatives to PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$), we have prepared 30 (three series of 10 compounds each) new hybrid materials as ionic liquids with perfluoro-*n*-hexyl moieties. In the first and second series, bis(tridecafluorohexyl) 3,5-pyridine dicarboxylate (**5**) was alkylated with MeI and EtI to yield the respective pyridinium iodides **1a** (89%) and **2a** (74%). For the third series, imidazole (**8**) was alkylated twice with $nC_6F_{13}CH_2CH_2I$ (**9**) to furnish the respective imidazolium iodide **3a** (44%). All three compounds **1a**, **2a**, and **3a** were then submitted to anion exchange on a hydroxide-loaded Lewatit Mono MP Plus 800 resin to give the respective hydroxide salts **1b**, **2b**, and **3b**, all with quantitative yields. These hydroxides were then neutralized with the Brönsted acids AcOH (**c**), CF_3CO_2H (**d**), TfOH (**e**), Tf_2NH (**f**), HCI (**g**), HBr (**h**), H_2SO₄ (**i**), $CF_3(CF_2)_{10}CO_2H$ (**j**) to furnish the exceptions) and as analytically pure materials (combustion analysis). Compounds **2c**

(81%), **2d** (83%), and **3e** (35%) required recrystallization to achieve analytical purity. Ethylpyridinium iodide **2a** is a crystalline compound and was suitable for single crystal X-ray structure analysis, which is unusual for perfluorinated compounds. As shown in the ORTEP plots, the crystallinity originates from ionic interactions within the pyridinium iodide part of the compound and is well resolved. The perfluorohexyl side chains are highly disordered and exhibit large anisotropic displacement parameters indicating the expected weak intermolecular forces. In the solid state, compound **2a** forms a layered structure within the crystal where the well-resolved ionic sides alternate with the disordered perfluorinated side chains.

As a first survey of their property profile, we have investigated the wettability of all 30 compounds **1a–1j**, **2a–2j**, and **3a–3j** by water contact angle measurements of a thin film on a glass surface. In two cases, promising contact angles were observed (140° for compound **1a**, 130° for compound **3a**) indicating, that the products might be suitable candidates for the impregnation of surfaces. Further studies are in progress in our laboratories, in particular, studies on the biodegradability of the new compounds. The latter shall actually be the key property of the new materials. With their relatively short perfluoroalkyl side chains and therefore low bioaccumulativity, the target compounds might be beneficial alternatives to established products, like PFOA and PFOS.

Experimental Section

General: ¹H-. ¹⁹F- and ¹³C-NMR spectra were recorded on a Bruker Avance DRX 500 instrument. Multiplicities of carbon signals were determined with DEPT experiments. MS and HRMS spectra of products were obtained with a Waters Q-TOF Premier (ESI) 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. Diester $5^{[20]}$ and $nC_6F_{13}CH_2CH_2OTf$ (7)^[22] were prepared according to literature protocols. All other starting materials were commercially available. In particular, $nC_6F_{13}CH_2CH_2I$ was purchased from Apollo, $nC_6F_{13}CH_2CH_2OH$ from DuPont, and $CF_3(CF_2)_{10}CO_2H$ from Matrix Scientific.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium iodide (1a). A solution of MeI (10 mL, 22.8 g, 161 mmol, 14 equiv.) and pyridine dicarboxylate 5 (9.67 g, 11.3 mmol, 1.0 equiv.) in acetone (10 mL) was stirred in a tightly closed reaction tube for 3 h at 150°C. After evaporation of the volatiles, the residue was recrystallized from tert-butylmethylether (MTBE) (20 mL) to furnish the product **1a** (10.0 g, 9.98 mmol, 89%) as yellow solid, mp. 193°C. ¹H-NMR (500 MHz, CD₃OD): δ = 2.86 (tt, J = 19.0 Hz, J = 6.2 Hz, 4H), 4.59 (s, 3H), 4.82 (t, J = 6.0 Hz, 4H), 9.34 (t, J = 1.6 Hz, 1H), 9.74 (d, J = 1.6 Hz, 2H) ppm. ${}^{13}C{}^{1}H$ -NMR (125 MHz, CD_3OD): $\delta = 31.07$ (2 CH_2), 49.90 (CH_3), 60.22 (2 CH_2), 131.85 (2 C), 145.49 (CH), 151.29 (2 CH), 161.72 (2 C) ppm. ¹⁹F-NMR (470 MHz, CD₃OD): δ = -82.43 (tt, J = 3.0 Hz, J = 10.4 Hz, 6F), (-114.45)-(-114.62) (m, 4F), (-122.59)-(-122.97) (m, 4F), (-123.72)-(-123.98 (m, 4F), (-124.36)-(-124.59) (m, 4F), (-127.14)-(-127.38) (m, 4F) ppm. IR (ATR): nu(tilde) = 2994 (w), 2932 (w), 1742 (s), 1647 (w), 1608 (w), 1500 (w), 1470 (w), 1350 (m), 1322 (m), 1233 (s), 1191 (s), 1143 (s), 1078 (s), 1006 (m), 844 (m), 740 (s), 699 (s), 656 (s) cm⁻¹. HR-MS (ESI, pos. mode): calcd. 874.0502 (for $C_{24}H_{14}F_{26}NO_4$), found 874.0512 [M⁺ – I]. $C_{24}H_{14}F_{26}INO_4$ (1001.24): calcd. C 28.79%, H 1.41%, N 1.40%; found C 29.04%, H 1.28%, N 1.46%.

General procedure: Exchange of Anions. A column of ion-exchange resin Lewatit Mono MP Plus 800 (Lanxess, capacity ca. 0.95 mmol/g) (20 g) was regenerated prior to each use by the following sequential washings: (1) with hydrochloric acid (10 mL, 2 mol L⁻¹) until to pH = 1 of the eluent, (2) with water until pH = 7, (3) with aq. NaOH (10 mL, 2 mol L⁻¹) until pH = 13–14 and finally (4) again with water to pH = 7. A solution of the iodide salts **1a**, **2a** (0.50 mmol, 500 mg or 507 mg, resp.) in 5 mL MeOH (ca. 60°C warm) or **3a** (1.00 mmol, 888 mg) in 10 mL MeOH (ambient temperature) was transferred on top of the column and the hydroxide salts **1b**, **2b** or **3b**

rature) was transferred on top of the column and the hydroxide salts **1b**, **2b** or **3b** eluted with methanol, until to pH = 7 of the eluent; the eluted volume ranged between 5 mL and 50 mL.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

hydroxide (1b). lodo compound 1a (500 mg, 0.50 mmol) was converted according to the General Procedure to furnish compound 1b (437 mg, 0.49 mmol, 98%) after eva-

poration of the solvent as colorless solid, mp. 79°C. IR (ATR): nu(tilde) = 3434 (w), 2972 (w), 1669 (m), 1620 (m), 1546 (w), 1322 (w), 1201 (s), 1169 (s), 1081 (s), 1034 (w), 993 (m), 842 (m), 748 (m), 698 (m) cm⁻¹. $C_{24}H_{15}F_{26}NO_5$ (891.34): calcd. C 32.34%, H 1.70%, N 1.57%; found C 32.69%, H 1.74%, N 1.54%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

acetate (1c). A solution of compound **1b** in MeOH obtained from iodo compound **1a** (500 mg, 0.50 mmol) according to the General Procedure was neutralized with acetic acid (0.50 mL of a 1 mol L⁻¹ solution in MeOH) to furnish acetate **1c** (458 mg, 0.49 mmol, 98%) after evaporation of the solvent as a colorless solid, mp. 135°C. IR (ATR): nu(tilde) = 3082 (w), 1732 (m), 1685 (s), 1341 (m), 1233 (m), 1180 (s), 1141 (s), 1122 (s), 1079 (s), 997 (m), 828 (m), 696 (m) cm⁻¹. C₂₆H₁₇F₂₆NO₆ (933.38): calcd. C 33.46%, H 1.84%, N 1.50%; found C 33.31%, H 2.04%, N 1.73%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium trifluoroacetate (1d). A solution of compound 1b in MeOH obtained from iodo compound 1a (500 mg, 0.50 mmol) according to the General Procedure was neutralized with trifluoroacetic acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH) to furnish trifluoroacetate 1d (484 mg, 0.50 mmol, 100%) after evaporation of the solvent as a light yellow solid, mp. 157°C. IR (ATR): nu(tilde) = 3027 (w), 1752 (m), 1739 (s), 1685 (s), 1467 (w), 1384 (w), 1342 (m), 1322 (w), 1232 (s), 1188 (vs), 1142 (vs), 1124 (s), 1078 (s), 842 (m), 821 (m), 747 (m), 735 (m), 697 (s), 651 (m) cm⁻¹. C₂₆H₁₄F₂₉NO₆ (971.35): calcd. C 31.63%, H 1.43%, N 1.42%; found C 31.41%, H 1.45%, N 1.56%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium trifluoromethanesulfonate (1e). A solution of compound 1b in MeOH obtained from iodo compound 1a (500 mg, 0.50 mmol) according to the General Procedure was neutralized with trifluoromethanesulfonic acid (0.5 mL of a 1 mol L⁻¹ in solution in MeOH) to furnish triflate 1e (511 mg, 0.50 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 122°C. IR (ATR): nu(tilde) = 3011 (w), 1750 (m), 1737 (m), 1657 (w), 1685 (w), 1385 (w), 1342 (m), 1272 (s), 1253 (s), 1227 (s), 1191 (vs), 1142 (vs), 1124 (vs), 1078 (s), 1032 (s), 736 (m), 697 (s), 639 (s) cm⁻¹. C₂₅H₁₄F₂₉NO₇S (1023.40): calcd. C 29.34%, H 1.38%, N 1.37%, S 3.13%; found C 29.10%, H 1.44%, N 1.39%, S 3.23%. 1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium bis-(trifluoromethanesulfonyl)amide (1f). A solution of compound 1b in MeOH obtained from iodo compound 1a (500 mg, 0.50 mmol) according to the General Procedure was neutralized with bis(trifluoromethanesulfonyl)imide (140 mg, 0.50 mmol) to furnish the triflimide 1f (564 mg, 0.49 mmol, 98%) after evaporation of the solvent as a colorless solid, mp. 66°C. IR (ATR): nu(tilde) = 3098 (w), 1741 (m), 1346 (m), 1231 (m), 1182 (vs), 1133 (s), 1059 (s), 842 (m), 740 (m), 651 (m), 616 (m) cm⁻¹. $C_{26}H_{14}F_{32}N_2O_8S_2$ (1154.47): calcd. C 27.05%, H 1.22%, N 2.43%, S 5.55%; found C 27.03%, H 1.52%, N 2.69%, S 5.22%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium chloride (1g). A solution of compound **1b** in MeOH obtained from iodo compound **1a** (500 mg, 0.50 mmol) according to the General Procedure was neutralized with hydrochloric acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH containing some water) to furnish the chloride **1g** (456 mg, 0.50 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 151°C. IR (ATR): nu(tilde) = 1736 (s), 1610 (w), 1339 (m), 1320 (m), 1231 (s), 1189 (vs), 1141 (vs), 1076 (s), 991 (w), 914 (w), 842 (w), 812 (w), 782 (w), 746 (m), 731 (s), 697 (s), 650 (s), 602 (m) cm⁻¹. C₂₄H₁₄CIF₂₆NO₄ (909.79): calcd. C 31.68%, H 1.55%, N 1.54%; found C 31.56%, H 1.73%, N 1.83%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium bromide (1h). A solution of compound 1b in MeOH obtained from iodo compound 1a (500 mg, 0.50 mmol) according to the General Procedure was neutralized with hydrobromic acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH containing some water) to furnish the bromide 1h (467 mg, 0.49 mmol, 98%) after evaporation of the solvent as a colorless solid, mp. 161°C. IR (ATR): nu(tilde) = 1724 (s), 1345 (m), 1318 (m), 1235 (s), 1188 (vs), 1141 (vs), 1077 (s), 1038 (w), 1001 (w), 956 (w), 841 (m), 782 (w), 744 (m), 734 (m), 699 (m), 638 (s) cm⁻¹. C₂₄H₁₄BrF₂₆NO₄ (954.24): calcd. C 30.21%, H 1.48%, N 1.47%; found C 30.15%, H 1.87%, N 1.64%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

hydrogensulfate (1i). A solution of compound 1b in MeOH obtained from iodo compound 1a (500 mg, 0.50 mmol) according to the General Procedure was neutralized

with sulfuric acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH) to furnish the hydrogensulfate **1h** (484 mg, 0.50 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 126°C. IR (ATR): nu(tilde) = 3094 (w), 1750 (m), 1734 (m), 1461 (w), 1346 (m), 1320 (m), 1229 (vs), 1183 (vs), 1143 (vs), 1124 (vs), 1078 (s), 1041 (s), 1016 (m), 993 (m), 840 (m), 748 (m), 734 (m), 697 (s), 648 (s) cm⁻¹. C₂₄H₁₅F₂₆NO₈S (971.40): calcd. C 29.68%, H 1.56%, N 1.44%, S 3.30%; found C 29.64%, H 1.55%, N 1.38%, S 3.04%.

1-Methyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

perfluorododecanoate (1j). A solution of compound **1b** in MeOH obtained from iodo compound **1a** (4.00 g, 4.00 mmol) according to the General Procedure was neutralized with perfluorododecanoic acid (2.46 g, 4.00 mmol) to furnish the compound **1j** (5.95 g, 4.00 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 81°C. IR (ATR): nu(tilde) = 1742 (m), 1685 (m), 1342 (m), 1191 (vs), 1142 (vs), 1080 (m), 1001 (w), 842 (w), 809 (w), 746 (m), 697 (s), 652 (s) cm⁻¹. $C_{36}H_{14}F_{49}NO_6$ (1487.43): calcd. C 29.07%, H 0.95%, N 0.94%; found C 29.06%, H 0.84%, N 1.04%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium iodide (2a). A solution of Etl (5.0 mL, 9.7 g, 62 mmol, 11 equiv.) and pyridine dicarboxylate 5 (5.00 g, 5.82 mmol, 1.0 equiv.) in acetone (5 mL) was stirred in a tightly closed reaction tube for 3 h at 150°C. After evaporation of the volatiles, the residue was recrystallized from MTBE (15 mL) to furnish the product **2a** (4.36 g, 4.29 mmol, 74%) as yellow solid, mp. 182°C. ¹H-NMR (500 MHz, acetone-d₆): δ = 1.81 (t, J = 7.4 Hz, 3H), 3.00 (tt, J = 19.3 Hz, J = 6.2 Hz, 4H), 4.87 (t, J = 6.0 Hz, 4H), 5.23 (q, J = 7.3Hz, 2H), 9.36 (t, J = 1.6 Hz, 1H), 10.15 (d, J = 1.6 Hz, 2H) ppm. ¹³C{¹H}-NMR (125) MHz, CD₃OD): δ = 16.75 (CH₃), 31.08 (t, J = 21.2 Hz, 2 CH₂), 59.79 (CH₂), 60.20 (2 CH₂),132.39 (2 C), 145.67 (CH), 150.21 (2 CH), 161.76 (2 C) ppm. ¹⁹F-NMR (470 MHz, acetone-d₆): δ = 50.63–50.86 (m, 4F), 53.41–53.61 (m, 4F), 54.02–54.21 (m, 4F), 55.00–55.26 (m, 4F), 63.46–63.48 (m, 4F), 95.78 (tt, J = 2.6 Hz, J = 10.4 Hz, 6F) ppm. IR (ATR): nu(tilde) = 3016 (w), 2978 (w), 2937 (w), 1733 (s), 1335 (m), 1233 (s), 2281 (vs), 1141 (vs), 1077 (s), 842 (m), 811 (m), 739 (s), 697 (s) cm⁻¹. HR-MS (ESI, pos. mode): calcd. 888.0659 (for $C_{25}H_{16}F_{26}NO_4$), found 888.0698 [M⁺ - I]. C₂₅H₁₆F₂₆INO₄ (1015.27): calcd. C 29.58%, H 1.59%, N 1.38%; found C 29.69%, H 1.67%, N 1.57%.

Single crystal X-ray data for 2a were measured on a Bruker AXS Apex II diffractometer (Mo-K α radiation, $\lambda = 0.71073$ Å, Kappa 4 circle goniometer, Bruker Apex II detector) at T = 170 K. Compound **2a** crystallizes in the monoclinic space group $P2_1/n$ with a = 7.5040(2), b = 47.8412(15), c = 9.6717(3) Å, $\beta = 93.3645(15)^\circ$, V = 3466.16(18) Å³, Z = 4. A numerical absorption correction followed by a correction based on symmetry-related measurements (multi-scan) was performed with SADABS.^[24] The structure was solved with the program SHELXS^[25] and refined with SHELXL.^[25] Non-H atoms were refined anisotropically, non-H atoms involved in disorder were partially refined isotropically. H atoms were located from the difference Fourier maps but subsequently fixed to geometric positions using appropriate riding models. Refinement parameters: 90723 reflections measured, 7656 unique ($R_{int} = 0.0287$), 6876 observed [I > 2sig(I)], R1 for the observed data = 0.0572, wR2 = 0.1362, R1 for all data = 0.0625, wR2 = 0.1390, GooF = 1.196, maximum and minimum difference density = 0.939 and -1.855 e Å⁻¹.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

hydroxide (2b). lodo compound **2a** (507 mg, 0.50 mmol) was converted according to the General Procedure to furnish compound **2b** (456 mg, 0.50 mmol, 100%) after evaporation of the solvent as a light yellow colorless solid, mp. 57°C. IR (ATR): nu(tilde) = 3421 (w), 2974 (w), 1702 (m), 1678 (s), 1615 (m), 1541 (m), 1461 (m), 1358 (w), 1335 (m), 1321 (m), 1231 (s), 1202 (s), 1162 (s), 1122 (s), 1081 (s), 1035 (s), 1006 (m), 950 (w), 866 (m), 696 (m), 643 (m) cm⁻¹. C₂₅H₁₇F₂₆NO₅ (905.37): calcd. C 33.17%, H 1.89%, N 1.55%; found C 33.21%, H 2.07%, N 1.58%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium acetate (2c). A solution of compound 2b in MeOH obtained from iodo compound 2a (507 mg, 0.50 mmol) according to the General Procedure was neutralized with acetic acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH) to furnish acetate 2c (384 mg, 0.41 mmol, 81%) after evaporation of the solvent and recrystallization from MTBE (20 mL) as a light yellow colorless solid, mp. 132°C. IR (ATR): nu(tilde) = 3035 (w), 1965 (w), 1735 (s), 1650 (m), 1610 (m), 1450 (w), 1351 (m), 1311 (m), 1275 (m), 1234 (m), 1187 (s), 1142 (s), 1124 (s), 1078 (m), 841 (m), 651 (s) cm⁻¹. C₂₇H₁₉F₂₆NO₆ (947.41): calcd. C 34.23%, H 2.02%, N 1.48%; found C 34.52%, H 2.36%, N 1.81%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium trifluoroacetate (2d). A solution of compound 2b in MeOH obtained from iodo compound 2a (507 mg, 0.50 mmol) according to the General Procedure was neutralized with trifluoroacetic acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH) to furnish trifluoroacetate 2d (410 mg, 0.42 mmol, 83%) after evaporation of the solvent and recrystallization from MTBE (10 mL) as a light yellow colorless solid, mp. 152°C. IR (ATR): nu(tilde) = 3099 (w), 3056 (w), 3046 (w), 3022 (w), 1753 (m), 1739 (m), 1685 (m), 1343 (m), 1232 (m), 1188 (s), 1141 (vs), 1124 (s), 1078 (s), 746 (m), 697 (m), 651 (m) cm⁻¹. C₂₇H₁₆F₂₉NO₆ (985.38): calcd. C 31.63%, H 1.43%, N 1.42%; found C 31.41%, H 1.45%, N 1.56%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium trifluoromethanesulfonate (2e). A solution of compound 2b in MeOH obtained from iodo compound 2a (507 mg, 0.50 mmol) according to the General Procedure was neutralized with trifluoromethanesulfonic acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH) to furnish triflate 2e (511 mg, 0.49 mmol, 99%) after evaporation of the solvent as an orange solid, mp. 136°C. IR (ATR): nu(tilde) = 3084 (w), 3039 (w), 1741 (m), 1380 (w), 1342 (m), 1322 (w), 1258 (s), 1239 (s), 1178 (s), 1141 (vs), 1124 (s), 1079 (m), 1031 (m), 1005 (w), 842 (w), 747 (m), 697 (m), 638 (s) cm⁻¹. C₂₆H₁₆F₂₉NO₇S (1037.43): calcd. C 30.10%, H 1.35%, N 1.55%, S 3.09%; found C 30.13%, H 1.17%, N 1.51%, S 2.75%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium bis(trifluoromethanesulfonyl)amide (2f). A solution of compound **2b** in MeOH obtained from iodo compound **2a** (507 mg, 0.50 mmol) according to the General Procedure was neutralized with bis(trifluoromethanesulfonyl)imide (140 mg, 0.50 mmol) to furnish the triflimide **2f** (563 mg, 0.48 mmol, 96%) after evaporation of the solvent as a colorless solid, mp. 51°C. IR (ATR): nu(tilde) = 3087 (w), 1746 (m), 1347 (m), 1234 (m), 1179 (vs), 1133 (s), 1055 (s), 740 (m), 652 (m), 618 (m) cm⁻¹. C₂₇H₁₆F₃₂N₂O₈S₂ (1168.50): calcd. C 27.75%, H 1.38%, N 2.40%, S 5.49%; found C 27.41%, H 1.66%, N 2.58%, S 5.10%. **1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium** chloride (2g). A solution of compound 2b in MeOH obtained from iodo compound 2a (507 mg, 0.50 mmol) according to the General Procedure was neutralized with hydrochloric acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH containing some water) to furnish the chloride 2g (461 mg, 0.50 mmol, 100%) after evaporation of the solvent as a yellow solid, mp. 141°C. IR (ATR): nu(tilde) = 2897 (w), 1735 (s), 1646 (w), 1335 (m), 1234 (s), 1180 (vs), 1079 (s), 1050 (m), 1011 (m), 843 (w), 812 (w), 752 (m), 698 (m), 680 (m), 651 (m) cm⁻¹. C₂₅H₁₆ClF₂₆NO₄ (923.82): calcd. C 32.50%, H 1.75%, N 1.52%; found C 32.31%, H 2.12%, N 1.70%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium bromide (2h). A solution of compound 2b in MeOH obtained from iodo compound 2a (507 mg, 0.50 mmol) according to the General Procedure was neutralized with hydrobromic acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH containing some water) to furnish the bromide 2h (484 mg, 0.50 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 154°C. IR (ATR): nu(tilde) = 3102 (w), 2966 (w), 1748 (m), 1735 (m), 1333 (w), 1262 (m), 1174 (s), 1123 (s), 1076 (m), 1048 (m), 1007 (m), 749 (m), 695 (m), 649 (m) cm⁻¹. C₂₅H₁₆BrF₂₆NO₄ (968.27): calcd. C 31.01%, H 1.67%, N 1.40%; found C 31.34%, H 1.97%, N 1.78%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

hydrogensulfate (2i). A solution of compound **2b** in MeOH obtained from iodo compound **2a** (507 mg, 0.50 mmol) according to the General Procedure was neutralized with sulfuric acid (0.5 mL of a 1 mol L⁻¹ solution in MeOH) to furnish the hydrogensulfate **2h** (487 mg, 0.49 mmol, 99%) after evaporation of the solvent as a light yellow colorless solid, mp. 112°C. IR (ATR): nu(tilde) = 2989 (w), 1744 (m), 1232 (m), 1171 (s), 1140 (s), 1083 (s), 1006 (m), 890 (m), 812 (m), 745 (m), 698 (m), 648 (m) cm⁻¹. C₂₅H₁₇F₂₆NO₈S (985.43): calcd. C 30.47%, H 1.74%, N 1.42%, S 3.25%, found C 30.20%, H 1.90%, N 1.65%, S 3.45%.

1-Ethyl-3,5-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoyl)pyridinium

perfluorododecanoate (2j). A solution of compound 2b in MeOH obtained from iodo compound 2a (5.71 g, 5.62 mmol) according to the General Procedure was neutralized with perfluorododecanoic acid (3.45 g, 5.62 mmol) to furnish the compound 2j (8.21 g, 5.47 mmol, 97%) after evaporation of the solvent as a colorless solid, mp. 59°C. IR (ATR): nu(tilde) = 1735 (w), 1690 (w), 1667 (w), 1393 (w), 1328 (w), 1214 (m), 1179 (vs), 1140 (s), 1077 (m), 811 (m), 750 (m), 698 (m), 678 (m), 652 (m) cm⁻¹. $C_{37}H_{16}F_{49}NO_6$ (1501.46): calcd. C 29.60%, H 1.07%, N 0.93%; found C 29.48%, H 1.38%, N 0.85%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium iodide (3a). A mixture of perfluorinated iodoalkane 9 (5.21 g, 11.0 mmol, 2.20 equiv.) and imidazole (340 mg, 5.00 mmol, 1.00 equiv.) in toluene (5 ml) was stirred in a tighly closed tube at 110°C for 24 h. After evaporation of excess volatile materials, the mixture was dissolved in MTBE (20 mL) and washed with water (2 x 20 mL). The organic layer was dried (MgSO₄) and evaporated after filtration. The title compound **3a** (1.86 g, 2.09 mmol, 44%) was obtained after recrystallization from EtOAc/hexane (1 / 10, 50 mL) as a colorless solid, mp. >300°C. ¹H-NMR (500 MHz, DMSO-d₆): δ = 3.00 (tt, J = 19.2 Hz, J = 6.4 Hz, 4H), 4.61 (t, J = 6.5 Hz, 4 H), 7.93 (s, 2H), 9.40 (s, 1H) ppm. ¹³C{¹H}-NMR (125 MHz, DMSO-d₆): δ = 29.91 (2 CH₂), 41.49 (2 CH₂), 122.78 (2 CH), 137.36 (CH) ppm. ¹⁹F-NMR (470 MHz, DMSO-d₆): δ = -80.50 (tt, J = 2.5 Hz, J = 9.6 Hz, 6F), (-113.16)-(-113.48) (m, 4F), (-121.73)-(-121.99) (m, 4F), (-122.59)-(-122.92) (m, 4F), (-123.07)-(-123.31) (m, 4F), (-125.69)-(-126.16) (m, 4F) ppm. IR (ATR): nu(tilde) = 3122 (w), 3055 (w), 1575 (m), 1321 (w), 1235 (s), 1180 (s), 1142 (s), 1121 (s), 1077 (s), 1040 (m), 743 (m), 691 (m), 632 (m), 616 (s) cm⁻¹. HR-MS (ESI, pos. mode): calcd. 761.0502 (for $C_{19}H_{11}F_{26}N_2^+$), found 761.0497 [M⁺ – I]. C₁₉H₁₁F₂₆IN₂ (888.17): calcd. C 25.69%, H 1.25%, N 3.15%; found C 25.93%, H 1.12%, N 3.55%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium hydroxide (3b). lodo compound **3a** (888 mg, 1.00 mmol) was converted according to the General Procedure to furnish compound **3b** (778 mg, 1.00 mmol, 100%) after evaporation of the solvent as a brown liquid. IR (ATR): nu(tilde) = 3106 (w), 1647 (w), 1570 (w), 1365 (w), 1321 (w), 1232 (s), 1187 (s), 1141 (vs), 1123 (s), 1077 (m), 735 (m), 700 (m), 644 (m) cm⁻¹. $C_{19}H_{12}F_{26}N_2O$ (778.28): calcd. C 29.32%, H 1.55%, N 3.60%; found C 29.35%, H 1.25%, N 3.45%. **1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium acetate (3c).** A solution of compound **3b** in MeOH obtained from iodo compound **3a** (888 mg, 1.00 mmol) according to the General Procedure was neutralized with acetic acid (1.0 mL of a 1 mol L⁻¹ solution in MeOH) to furnish acetate **3c** (820 mg, 1.00 mmol, 100%) after evaporation of the solvent as a colorless liquid. IR (ATR): nu(tilde) = 3152 (w), 3106 (w), 3065 (w), 1711 (m), 1569 (w), 1412 (w), 1364 (w), 1232 (s), 1190 (s), 1122 (s), 1078 (m), 1008 (m), 708 (m), 700 (m), 647 (m) cm⁻¹. C₂₁H₁₄F₂₆N₂O₂ (820.32). calcd. C 30.75%, H 1.75%, N 3.42%; found C 30.87%, H 1.74%, N 3.65%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium trifluoroactate (3d). A solution of compound 3b in MeOH obtained from iodo compound 3a (888 mg, 1.00 mmol) according to the General Procedure was neutralized with trifluoroacetic acid (1.0 mL of a 1 mol L⁻¹ solution in MeOH) to furnish trifluoroacetate 3d (849 mg, 0.99 mmol, 99%) after evaporation of the solvent as a colorless liquid. IR (ATR): nu(tilde) = 3152 (w), 3097 (w), 3066 (w), 1779 (m), 1570 (w), 1166 (s), 1140 (s), 1078 (m), 809 (m), 706 (m) cm⁻¹. C₂₁H₁₁F₂₉N₂O₂ (858.28): calcd. C 29.39%, H 1.29%, N 3.26%; found C 28.99%, H 0.96%, N 3.38%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium trifluoromethanesulfonate (3e). Under exclusion of moisture (N₂ atmosphere), a mixture of perfluorinated triflate **7** (2.50 g, 5.04 mmol, 2.5 equiv.) and trimethylsilylimidazole (280 mg, 2.02 mmol, 1.0 equiv.) was stirred for 24 h at 60°C. Subsequently, the mixture was dissolved in MTBE (20 mL) and washed with water (2 x 20 mL). The organic layer was dried (MgSO₄) and evaporated after filtration. The title compound (651 mg, 0.720 mmol, 35%) was received after recrystallization from CH_2CI_2 (50 mL) as a colorless solid, mp. 163°C. IR (ATR): nu(tilde) = 3155 (w), 3124 (w), 3082 (w), 1573 (w), 1366 (w), 1321 (w), 1251 (s), 1226 (s), 1179 (s), 1142 (vs), 1125 (s), 1080 (m), 1029 (s), 995 (w), 848 (w), 747 (m), 636 (s) cm⁻¹. $C_{20}H_{11}F_{29}N_2O_3S$ (910.33): calcd. C 26.39%, H 1.22%, N 3.08%, S 3.52%; found C 26.53%, H 1.56%, N 3.30%, S 3.25%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium bis(trifluoromethanesulfonyl)amide (3f). A solution of compound 3b in MeOH obtained from iodo compound 3a (888 mg, 1.00 mmol) according to the General Procedure was neutralized with bis(trifluoromethanesulfonyl)imide (281 mg, 1.00 mmol) to furnish the triflemide **3f** (1.02 g, 0.98 mmol, 98%) after evaporation of the solvent as a colorless solid, mp. 54°C. IR (ATR): nu(tilde) = 3089 (w), 1683 (m), 1570 (w), 1350 (w), 1182 (s), 114 (vs), 1081 (m), 1055 (m), 701 (m), 641 (m), 617 (m) cm⁻¹. $C_{21}H_{11}F_{32}N_3O_4S_2$ (1041.40): calcd. C 24.22%, H 1.06%, N 4.04%, S 6.16%; found C 24.18%, H 1.37%, N 4.27%, S 6.48%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium chloride (3g). A solution of compound **3b** in MeOH obtained from iodo compound **3a** (888 mg, 1.00 mmol) according to the General Procedure was neutralized with hydrochloric acid (1.0 mL of a 1 mol L⁻¹ solution in MeOH containing some water) to furnish the chloride **3g** (789 mg, 0.99 mmol, 99%) after evaporation of the solvent as a yellow solid, mp. 172°C. IR (ATR): nu(tilde) = 3092 (w), 3064 (w), 3010 (w), 2990 (w), 1569 (w), 1365 (w), 1321 (w), 1231 (s), 1188 (s), 1168 (s), 1124 (s), 1075 (m), 840 (m), 699 (m), 643 (m) cm⁻¹. C₁₉H₁₁ClF₂₆N₂ (796.72): calcd. C 28.64%, H 1.39%, N 3.52%; found C 28.45%, H 1.29%, N 3.49%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium bromide (3h). A solution of compound **3b** in MeOH obtained from iodo compound **3a** (888 mg, 1.00 mmol) according to the General Procedure was neutralized with hydrobromic acid (1.0 mL of a 1 mol L⁻¹ solution in MeOH containing some water) to furnish the bromide **3h** (790 mg, 0.96 mmol, 96%) after evaporation of the solvent as a colorless solid, mp. 249°C. IR (ATR): nu(tilde) = 3063 (w), 2988 (w), 2964 (w), 1573 (w), 1366 (w), 1320 (w), 1232 (s), 1181 (s), 1141 (vs), 1122 (s), 1077 (m), 700 (m), 639 (m), 622 (m) cm⁻¹. C₁₉H₁₁BrF₂₆N₂ (822.18): calcd. C 27.13%, H 1.32%, N 3.33%; found C 27.38%, H 1.05%, N 3.35%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium hydrogensulfate

(3i). A solution of compound **3b** in MeOH obtained from iodo compound **3a** (888 mg, 1.00 mmol) according to the General Procedure was neutralized with sulfuric acid (1.0 mL of a 1 mol L⁻¹ solution in MeOH) to furnish the hydrogensulfate **3h** (863 mg, 1.00 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 83°C. IR (ATR): nu(tilde) = 3308 (s), 3174 (m), 3121 (s), 2967 (m), 2754 (s), 2642 (s), 1919 (w), 1660 (w), 1595 (s), 1462 (m), 1316 (m), 1201 (w), 1050 (vs), 979 (vs), 901 (vs),

901 (vs), 870 (vs), 798 (vs), 628 (vs) cm⁻¹. $C_{19}H_{12}F_{26}N_2O_4S$ (858.33): calcd. C 26.59%, H 1.41%, N 3.26%, S 3.74%; found C 26.80%, H 1.61%, N 3.05%, S 3.92%.

1,3-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)imidazolium perfluorododecanoate (3j). A solution of compound **3b** in MeOH obtained from iodo compound **3a** (500 mg, 0.56 mmol) according to the General Procedure was neutralized with perfluorododecanoic acid (346 mg, 0.56 mmol) to furnish the compound **3j** (770 mg, 0.56 mmol, 100%) after evaporation of the solvent as a colorless solid, mp. 125°C. IR (ATR): nu(tilde) = 3087 (w), 3063 (w), 2988 (w), 1682 (m), 1571 (w), 1367 (w), 1195 (s), 1142 (vs), 1080 (m), 709 (m), 643 (m) cm⁻¹. C₃₁H₁₁F₄₉N₂O₂ (1374.36): calcd. C 27.09%, H 0.81%, N 2.04%; found C 27.42%, H 0.63%, N 2.24%.

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