

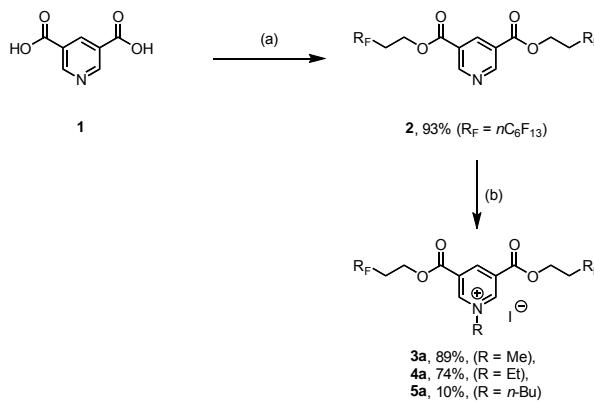
Perfluorinated pyridinium based ionic liquids were synthesized by esterification of pyridine dicarboxylic acid followed by quaternarization of the nitrogen atom. Subsequent exchange of anions delivered a variety of different ionic liquids.

Introduction

Perfluorinated compounds, such as perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$) and perfluoroalkyl sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$) have been found ubiquitous in applications for surface treatment of textiles, leathers, metals etc. Due to the persistency and bioaccumulativity, they have attracted much attention as contaminants in the natural environment.^[1] As a replacement we decided to combine the outstanding characteristics of ionic liquids (ILs) like thermal stability, low melting points, zero flammability and their practically non-volatile nature with the characteristics of shorter chain perfluoroalkyl materials, which included also high hydrophobicity and high lipophobicity.^[2] As a scaffold we suggested to use pyridinium based ionic liquids, because contiguous to imidazolium ionic liquids, these are the most common ILs.

Preparation of pyridinium based ionic liquids

As a starting material we used 3,5-pyridine dicarboxylic acid **1** which can be easily converted by esterification to the corresponding perfluorinated ester **2** in 93% yield. For quaternarization of the nitrogen atom we used the three alkyl iodides MeI, EtI and *n*-BuI, to receive the ILs **3a–5a** as iodide salts in 10–89% yield. The optimal reaction conditions are high temperatures, short reaction times, an excess of alkyl iodides, as well as high concentration in the solvent acetone.



Scheme 1. Synthesis of perfluorinated ionic liquids **3**. (a) 1. xs. $SOCl_2$, 90°C, 3 h; 2. 2.2 eq. $C_6F_{13}(CH_2)_2OH$, 90°C, 3 h; (b) xs. RI, 150°C, 1–3 h, acetone.

Acknowledgement

We are grateful to the Ferdinand Eimermacher GmbH & Co. KG, Nordwalde for generous support of this project.

X-Ray structure of perfluorinated ionic liquid

Although perfluorinated compounds are not easy to crystallize, we could get an X-ray structure of compound **4a**.

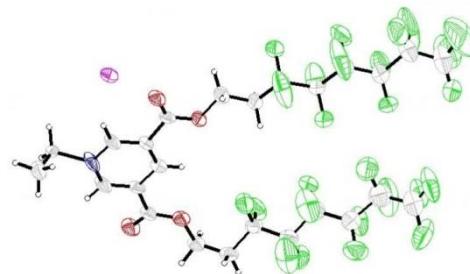


Figure 1. ORTEP representation of compound **4a**.

Exchange of Anions

Subsequently, we tried to access a small library of compounds by exchanging the corresponding anions. Therefore we used an ion exchange resin to receive the hydroxy ionic liquid, which can be neutralized with Brønsted acids into the corresponding ionic liquids. So we received 22 compounds, which are characterized by melting points depicted below (Table 1). Nine of them fit into the specification of ionic liquids with a melting point lower than 100°C and compound **4g** is an example of a room temperature IL.

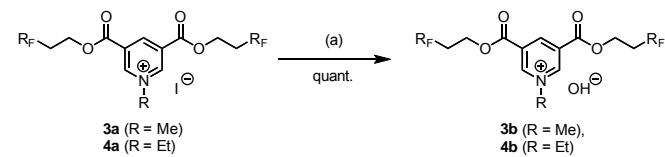


Table 1. Melting points of compounds **3a-k**, **4a-k**

	X	3	4
a	I^-	193°C	182°C
b	OH^-	79°C	57°C
c	$CF_3CO_2^-$	157°C	152°C
d	AcO^-	135°C	132°C
e	Br^-	161°C	154°C
f	Cl^-	151°C	141°C
g	SO_4^{2-}	126°C	liquid
h	TfO^-	122°C	136°C
i	Tf_2N^-	66°C	51°C
j	$CF_3(CF_2)_{10}COO^-$	81°C	59°C
k	$CF_3(CF_2)_{15}COO^-$	85°C	119°C

X = $CF_3CO_2^-$, AcO^- , Br^- , Cl^- , SO_4^{2-} , TfO^- , Tf_2N^- , $CF_3(CF_2)_{10}COO^-$, $CF_3(CF_2)_{15}COO^-$

Scheme 2. Reagents and conditions. (a) Ion exchange resin Lewatit Mono MP 800 Plus; (b) several Brønsted acids HX (1.0 eq.).

[1] Z. Wang, I. T. Cousins, M. Scheringer, K. Hungerbühler, *Environment International* **2013**, *60*, 242–248.

[2] A. Pereiro, J. M. Araujo, S. Martinho, F. Alves, S. Nunes, A. Matias, C. Duarte, L. Rebelo, I. Marrucho, *ACS Sustainable Chem. Eng.* **2013**, *1*, 427–439.