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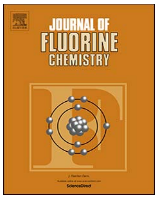

Catalyst retention utilizing a novel fluorinated phosphonium ionic liquid in Heck reactions under fluorous biphasic conditions

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ABSTRACT

A novel ionic liquid based on a highly fluorinated phosphonium cation was synthesized and its physicochemical properties were compared to its semi- and non-fluorinated analogue. The fluorinated ionic liquid was found to show a thermomorphic mixing behavior with organic solvents so that it could be applied as a substitute for volatile perfluorinated solvents in fluorous biphasic catalysis to achieve the recovery of perfluoro-tagged catalysts. Efficient immobilization of a perfluoro-tagged palladium catalyst in the fluorous ionic liquid phase was demonstrated for the Heck reaction as a model reaction of the widely applied Pd-catalysed C—C coupling reactions. The reaction of iodobenzene and methyl acrylate resulted in 83% yield after 20 runs proofing the efficient immobilization in the fluorophilic ionic liquid.

1. Introduction

Ionic liquids (ILs) and fluorous solvents are both regarded as “neoteric solvents” in the context of a greener, more sustainable chemistry since they share the potential to facilitate recycling procedures and reduce waste material as well as energy consumption [1–4]. However their physicochemical properties vary considerably. While ionic liquids have a negligible vapor pressure, polar structural motifs and are often hydrophilic, fluorous solvents show a significant vapor pressure and are highly apolar. Furthermore perfluoroalkyl groups show an even greater hydrophobicity than hydrocarbons through the reduced polarizability resulting from the high electronegativity of the fluorine atoms. The behavior of the perfluorocarbons of being hydro- and lipophobic at the same time is referred to as flurorophilicity [5]. Many fluorous and organic solvents are known to show a thermomorphic mixing behavior, forming a biphasic system at room temperature and a homogenous phase at elevated temperatures. This thermoregulated effect allows the specific separation and immobilization of components in liquid–liquid multiphasic systems and orthogonal chemistry in the separated phases [6]. A famous concept for thermoregulated chemistry is the fluorous biphasic catalysis (FBC) to achieve the recovery of perfluoro-tagged transition metal catalysts [7–10]. Important drawbacks of conventional fluorous solvents are their limited tuneability and relatively high vapor pressure, which restricts the useable temperature range. Furthermore bioaccumulation, persistence and the global warming potential of the volatile fluorous solvents can pose serious environmental problems [11,12]. The use of highly fluorinated ionic liquids [13] combines the advantages of fluorous solvents for efficient extraction and immobilization with non-volatility and a high degree of flexibility (through the task-specific and tailored designs) of ionic liquids. In this way it is possible to combine the benefits of these two neoteric solvents classes for effective and environmentally friendly reagent immobilization strategies. The use of fluorous groups in ionic liquids allows the implementation of fluorophilicity to the broad field of possible modifications beside the choices for anion and cation. This task-specific tuning allows new possible applications or the improvement of existing techniques [14]. It thus becomes feasible to modify the properties of liquid multiphasic systems in a wide range using non-volatile, modifiable fluorinated ILs as fluorous phase. The search for effective and reusable catalyst systems for multiphasic homogenous catalysis is an important issue in green chemistry since it saves energetic and chemical input [15,16]. ILs with perfluoroalkyl substituents have found numerous applications in many scientific fields like the use as surfactants [17], coating material [18] or liquid crystals [19,20], highly hydrophobic extraction agents [21], as well as for gas separation and gas dissolution [22,23] to name only a few. Furthermore fluorinated ILs are intensively investigated because of their unique microscopic heterogeneous structuring leading to a triphilic organization in ionic, hydrocarbon and fluorous domains driven by solvophobic interactions comparable to the macroscopic solvent behavior observed in limited miscibility and phase separation [24–27].

In this work we describe a new highly fluorinated phosphonium

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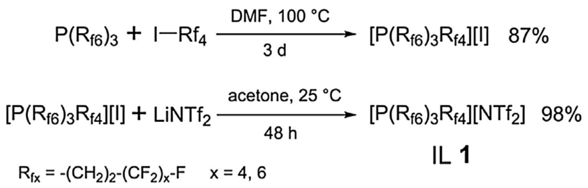
ionic liquid $[P(R_{f6})_3R_{f4}][NTf_2]$ (**1**) having four perfluoroalkyl chains ($R_{fx} = (CH_2)_2(CF_2)_xF$; x = 4, 6) in the cation combined with the bis (trifluoromethanesulfonyl)imide (NTf_2^-) anion. The application of this "building-block"-approach [28] for the synthesis of perfluoroalkyl substituted ILs allows the synthesis under laboratory conditions with easily adjustable structures. To investigate the effect of fluorination on important physicochemical properties and mixing behavior with organic solvents, IL **1** was compared to the non-fluorinated analogues hexyltrioctylphosphonium bis(trifluoromethanesulfonyl)imide $[P(oct)_3hex][NTf_2]$, the semifluorinated IL $[P(oct)_3R_{f4}][NTf_2]$ and the commonly used 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide $[BMIM][NTf_2]$. The highly fluorinated IL **1** shows a low solubility and thermomorphic phase-mixing behavior with many organic solvents as it is commonly found for perfluorinated molecular solvents. The combination of the perfluorinated IL **1** and DMF was found to be an effective liquid–liquid system for immobilization of a palladium catalyst with highly fluorinated ligands [29] in Heck reactions [30]. Van Koten and coworkers already reported the use of a highly fluorinated IL for the retention of a perfluoro-tagged rhodium catalyst in a hydrosilylation [13]. Since the palladium catalyzed C—C bond formation is of high interest for laboratory and industrial preparations we wanted to demonstrate the application of this concept to the cross coupling reactions utilizing a Pd-catalyst immobilized in a fluorous ionic liquid phase. As a model reaction for palladium catalysis we chose the widely used Heck reaction for the cross coupling reaction of iodobenzene with either methyl acrylate or styrene. The Heck reaction is one of the most important reactions for C-C-bond formation, but in most reports the catalyst is lost during work-up and cannot be recovered. Creating an efficient recycling protocol for the Heck cross coupling is found to be a tough challenge because of the instable catalytic cycle and the use of multiple reagents and products which are changing the system properties and may have a disturbing or inactivating effect on the catalyst [31].

2. Experimental

2.1. Synthesis of the ionic liquids

The investigated ILs were synthesized by modified quaternization reactions of the corresponding phosphines with 1-bromohexane or 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide in acetonitrile or DMF under inert gas atmosphere at elevated temperatures [32]. Tris(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phosphine was synthesized following literature protocols [18,33]. The halide ILs were then converted to the corresponding NTf_2-ILs by anion metathesis reaction with $LiNTf_2$ in acetone. The exemplary synthesis of the fluorous IL **1** via quarternization of the fluorinated phosphine followed by anion metathesis is sketched in Scheme 1. Purity of the obtained ILs was checked by multinuclear NMR-spectroscopy and ESI–MS. The absence of halide ions was confirmed using methanolic $AgNO_3$ solution. Further details about the applied materials, synthesis conditions and multinuclear NMR-spectra are given in the Supporting information. $[BMIM][NTf_2]$ was prepared following literature reports [34].



Scheme 1. Synthesis of the fluorinated ionic liquid **1** via quaternization of ternary phosphine and 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide followed by anion metathesis reaction with $LiNTf_2$.

2.2. Thermal properties

Melting, glass transition and cold crystallization points were determined by differential scanning calorimetry (DSC) using a DSC 1 STARe System (Mettler Toledo, Gießen, Germany) equipped with liquid nitrogen cooling. For the measurements about 20 mg sample were weighted into aluminum crucibles and hermetically sealed. The temperature program started with a heating rate of +5 °C/min to 100 °C followed by 30 min isothermal step at 100 °C to remove thermal history. Afterwards a dynamic step with cooling rate of −1 °C/min to -120 °C was applied. The temperature was held constant at −120 °C for 10 min, followed by a heating step (+1 °C/min) to 120 °C and then returned to the initial conditions. Decomposition temperatures were determined by thermogravimetric analysis (TGA) using a TG 209 F1 Iris (Netzsch, Selb, Germany) and Al_2O_3 crucibles. The temperature program was set from 20 °C to 600 °C applying a heating rate of 10 °C/min and a nitrogen flow of 20 mL/min. Decomposition temperatures were determined as extrapolated onset temperatures.

2.3. Polarity determination using the solvatochromic dye Nile Red

To 0.5 g of the ILs was added a solution of 0.5 mL Nile Red (NR) in acetone ($c(NR) = 3.0 \times 10^{-3}\ mol\ L^{-1}$) and stirred until the solution became homogenous. In case of IL 1 an additional milliliter acetone was added to ensure full dissolution. The solvent was then removed by drying in oil-pump vacuum for two days and the Nile Red solutions of the ILs were transferred to a quartz cuvette of 1 mm diameter to record a transmission UV/Vis spectrum. In case of 1 the UV/Vis-measurement was performed on a thin film of the sample in supercooled state as this IL showed a widely suppressed crystallization (see DCS results in Section 3.1). For each IL ten measurements were performed, the wavelength of the absorption maxima detected and the results averaged. The E_{NR} values were calculated after Eq. (1).

$$E_{NR} = hcN_A\,\lambda_{max}^{-1} \times 10^{-6} \tag{1}$$

with:

h: Planck's constant
c: speed of light
N_A: Avogadro's constant
λ_{max}: wavelength of the maximum absorbance (in nm)

2.4. Crystal structure determination of IL 1

Single crystal X-ray diffraction data were collected on a X8 Apex II diffractometer (Bruker AXS, Karlsruhe, Germany) at −121 °C using Mo-Kα radiation (λ = 0.71073 Å) in theta range from 0.607° to 27.811° collecting 88389 reflections in total. Crystal data: $C_{30}H_{16}F_{48}P^+$, $C_2F_6NO_4S_2^-$: $M_r = 1599.55$, triclinic, P-1, a = 9.1235(6) Å, b = 9.6920(6) Å, c = 33.677(2) Å, α = 86.357(3)°, β = 85.533(4)°, γ = 63.392(3)°, V = 2653.0(3) Å^3, Z = 2, $\rho_r = 2.002\ g\ cm^{-3}$. The refinement using full-matrix least-squares on F^2 resulted in 12220 independent reflections, 381 restraints, 822 parameters, $R[F^2 > 2\sigma(F^2)] = 0.1245$, $wR(F^2) = 0.3897$.

2.5. Determination of ionic liquid solubility/miscibility in organic solvents

Solubilities or miscibilities of the phosphonium ILs with a range of organic solvents were determined by preparing saturated solutions of the ILs and 3.000 mL of purified and dried organic solvents under argon by stirring for at least 3 h in a thermostated bath keeping the temperature at 25 °C until a two phase system remained. Then the solution was allowed to settle for 16 h after which a completely homogenous upper phase was observed. A 2.000 mL sample of the organic phase was carefully taken and the solvent removed in oil pump vacuum by drying for at least one day until the mass remained constant. By weighting the remaining IL the solubility per liter could be calculated. If no second phase was formed with varying the amount of organic solvent the IL was stated as miscible. Experiments were performed in triple and the results averaged. The phase diagram of IL 1 and DMF was constructed by inserting a molten sample of the IL into a graduated cylinder. Known volumes of DMF were added, the cylinder sealed and slowly heated with stirring until the phases became homogenous. The temperature at this point is the mixing temperature T_{mix} for the given volume fraction. After cooling to ambient temperature further volumes of DMF were added and the process repeated to construct the phase diagram.

2.6. Heck reactions under fluorous biphasic conditions using the fluorous IL

All reactions were carried out under inert atmosphere of argon. 1.00 g of IL 1 was degassed in vacuum and flushed with argon for 3 times. Then the IL-phase was saturated with DMF (about 0.2 mL) to obtain a slightly viscous, fluorous phase. In case of the cross coupling reactions performed at 85 °C, 8.0 mg of the catalyst $[Pd(P(m\text{-}C_6H_4\text{-}(CH_2)_2\text{-}(CF_2)_8\text{-}F)_3)_2Cl_2]$ (2.37×10^{-3} mmol, 0.80 mol%) was added. For the coupling reaction carried out at 70 °C 10.0 mg of the catalyst (2.96×10^{-3} mmol, 1.00 mol%) was added. The catalyst was then dissolved under slight heating and 0.400 mL of a 0.740 mol L^{-1} iodobenzene stock solution in DMF (0.296 mmol 1.00 eq.), 0.400 mL of a 0.888 mol L^{-1} olefin stock solution in DMF (0.355 mmol, 1.20 eq.) and 0.200 mL of a 1.78 mol L^{-1} stock solution of triethylamine in DMF (0.355 mmol, 1.20 eq.) were added. The mixture was stirred and heated to 85 °C resp. 70 °C for 16 h (unless noted otherwise) and then cooled down to −18 °C. The upper organic phase was carefully removed and the fluorous phase extracted with 0.2 mL of DMF. The combined DMF-phases were filled up to 100 mL with acetonitrile and a sample was analyzed with high performance liquid chromatography (HPLC). The HPLC system consisted of ASI-100 automated sample injector, Degasys DG-1210 solvent degasser, P680 HPLC Pump, TCC100 Thermostated Column Compartment and UVD3404 UV/Vis detector (all from Dionex, Sunnyvale, USA). The used column was a Hibar 150 × 4 mm C18/5 µm (Merck, Darmstadt, Germany). The column temperature was controlled by a column oven at 25 °C. Gradient program with a total flow of 1.000 mL/min using water and acetonitrile started with 100% water at $t = 0$ min to 100% MeCN at $t = 20$ min. Wavelength for UV/Vis detection was set to 254 nm. Retention times of the fully resolved peaks were 13.8 min for methyl cinnamate, 17.8 min for stilbene, 15.8 min for iodobenzene and 15.0 min for styrene. The amount of product was calculated by integration of the product peak in comparison with calibration curves. For each sample at least three runs were performed and the results averaged. Facile product isolation for six times was proven in a separate experiment for the reaction of iodobenzene with methyl acrylate at reaction times of 16 h and a temperature of 70 °C. For this purpose six equivalents of water were added to the DMF-phase after the reaction and the resulting suspension was extracted with 3 mL hexane three times. The solvent of the combined organic phases was removed by rotary evaporation and the residue dried in vacuum yielding pure methyl cinnamate in high isolated yield as confirmed by ^{1}H- and ^{13}C{1H}-NMR spectroscopy (see Supporting information; ^{1}H NMR (400 MHz, $CDCl_3$): δ[ppm] = 7.70 (d, $^3J_{HH} = 16.0$ Hz, 1H), 7.59–7.46 (m, 2H), 7.43–7.35 (m, 3H), 6.45 (d, $^3J_{HH} = 16.1$ Hz, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ[ppm] = 167.47, 144.93, 134.42, 130.36, 128.95, 128.14, 117.84, 51.76.). Turnover number (TON) for the reaction was calculated using Eq. (2).

$$TON = n_{(product)}/n_{(catalyst)} \qquad (2)$$

The cumulative TON is the summation of the individual TON per run after separation of the product phase and addition of new reagents. In further experiments leaching of the fluorous IL **1** was investigated by combining 1.00 g with 1.00 mL DMF without further reagents stirring at 70 °C for 30 min and cooling down to −18 °C. A sample of 0.500 mL was taken from the upper organic phase, the solvent removed in oil pump vacuum and the residue weighted. This process was repeated three times and the results averaged.

3. Results and discussion

3.1. Physical properties

The fluorous IL **1** is a thermal, air and water stable white solid if crystallized, forming a slightly yellow liquid above its melting point or in the presence of small amounts of organic solvents. In supercooled state the IL is observed as highly viscous, slightly yellow liquid. To investigate the effect of increasing fluorination in the cation on the physicochemical properties a comparison with the semi-fluorinated and non-fluorinated analogue was made. To investigate the influence of the anion choice the results were also compared to the widely used IL $[BMIM][NTf_2]$ which incorporated the same anion. DSC measurements were performed to investigate the phase transition behavior. Low scan speeds of ± 1 °C/min were chosen to ensure the suppression of supercooling through thermal quenching which can result in solely glass formation and thereby incomplete determination of the phase transition points [35]. Thermal stability was examined by means of dynamic TGA. As method for the empirical determination of solvent polarity the solvatochromic dye Nile Red [36] was applied which was also used for polarity determination for a range of other ionic liquids [37]. The more commonly used Reichardt's Dye [38] was found to be insoluble in the fluorous IL **1**. The empirical polarity determination is used to gain insight into the interactions on molecular level instead of using macroscopic parameters like relative permittivity, dipole moment or refractive index [39]. The polarities of ILs are of special interest as they allow conclusions about miscibility and phase behavior along with comparison to molecular solvents. The results of the transition and decomposition temperatures along with the E_{NR} for empirical polarity are summarized in Table 1. The DSC traces of the phosphonium ILs with different degree of fluorination are shown in Fig. 1. Upon cooling, the fluorous IL **1** exhibits only a glass transition T_g at -18 °C and no crystallization peak which is a commonly observed phenomenon in ILs [40]. In the heating cycle a cold crystallization T_{cc} is observed at 14 °C followed by a melting T_m at 69 °C. These results show that although the fluorous IL **1** is not a room-temperature ionic liquid (RTIL), it can be observed in the liquid state at ambient temperature. This is due to supercooling and suppressed crystallization which is an intrinsic property of most ILs [41], resulting from anti-crystal engineering [42]. A similar behavior is observed for the non-fluorinated sample $[P(oct)_3hex][NTf_2]$ and $[BMIM][NTf_2]$ [43] as example of a widely applied imidazolium IL. For these salts also T_g, T_{cc} and T_m were observed in the heating curve and only T_g in the cooling step. In contrast for the semi-fluorinated ionic liquid $[P(oct)_3R_{f4}][NTf_2]$ only T_g is observed for both heating and cooling.

Table 1

Glass transition T_g, cold crystallization T_{cc}, melting T_m and decomposition T_d temperatures along with the polarity values E_{NR} determined by the solvatochromic shift of Nile Red for the investigated ILs.

Property	IL **1** $[P(R_{f6})_3R_{f4}][NTf_2]$	$[P(oct)_3R_{f4}][NTf_2]$	$[P(oct)_3hex][NTf_2]$	$[BMIM][NTf_2]$
cation composition	highly fluorinated	semi-fluorinated	non-fluorinated	non-fluorinated, aromatic
T_g/°C	−18	−75	−89	−86 (−87)[a]
T_{cc}/°C	14	–	−40	−56
T_m/°C	69	–	−18	−2 (−3)[a]
T_d/°C	345	374	395	431 (427)[a]
λ_{max}/nm	546.6	548.2	548.6	548.8
E_{NR}/kJ mol^{-1}	218.8	218.2	218.1	218.0 (218.0)[b]

[a] Values taken from Ref. [44].

[b] Value taken from Ref. [37].

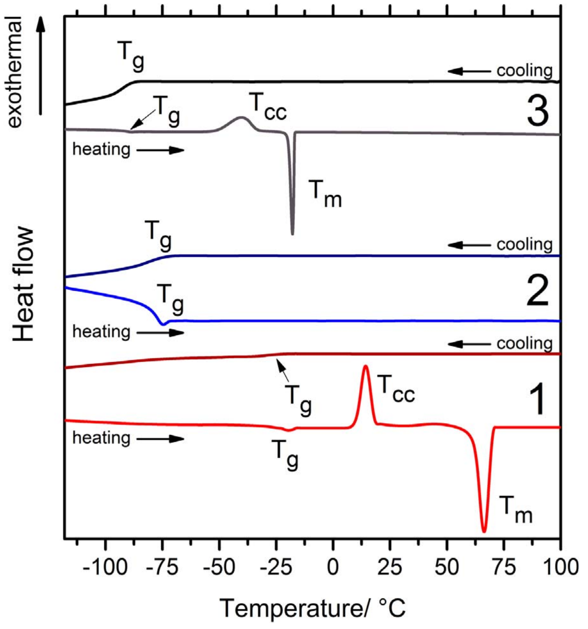


Fig. 1. DSC thermograms of the highly fluorinated IL **1** (1), the semi-fluorinated [P$(oct)_3R_{f4}$][NTf_2] (2) and the non-fluorinated [P$(oct)_3$hex][NTf_2] (3) with indicated transition temperatures. Exothermal transitions are plotted as positive peaks.

The absence of a melting point in the semi-fluorinated IL can be rationalized by symmetry-breaking effects [45] induced by the fluorinated chain leading to a destabilized crystalline structure due to packing effects. For IL **1** and the tetraalkylphosphonium IL a higher grade of symmetry is incorporated as these samples have four substituents of similar chemical composition. The thermal stability of the phosphonium ILs containing the NTf_2^--anion was found to be lower than for the imidazolium-cation with the same anion. The obtained TGA curves are shown in Fig. 2. It is well known that the decomposition temperature of ILs is mainly related to the anion-cation choice and functional groups incorporated. Elongation of attached chains of similar chemical structure is reported to have only minor effects on the thermal stability [46]. By comparing the thermal stability of ILs with the same anion it is ensured that the determined decomposition is mainly related to the thermal stability of the cation. The decomposition temperatures of the phosphonium compounds decreases upon increasing number of attached perfluoroalkyl-chains. However the observed decomposition temperatures are still comparatively high with the lowest value being 345 °C for IL **1**. For the fluorous IL [P$(R_{f8})_2R_{f6}CH_2CH(CH_3)CH_2C(CH_3)_3$][$NTf_2$] bearing three fluorinated chains, a T_d of 407 °C was reported [47]. Phosphonium ILs containing one fluorous tail and other anions like BF_4^- or OTf^- were furthermore found to have decomposition temperatures above 300 °C [48].

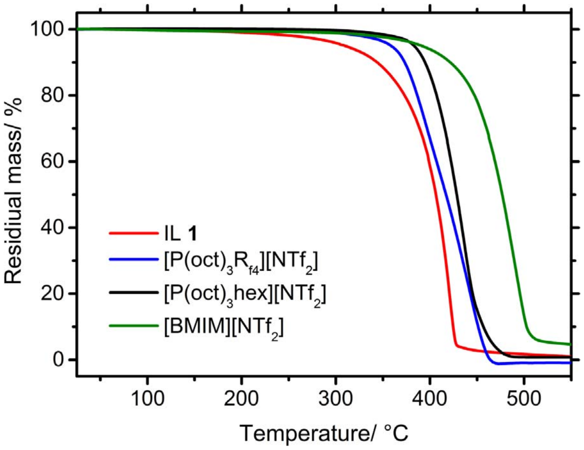


Fig. 2. TGA traces of the investigated ionic liquids at 10 °C/min heating rate.

The polarity values E_{NR} determined by the solvatochromic shift of Nile Red are increasing with the degree of fluorination but show only minor overall differences. Higher E_{NR}-values are related to lower solvent polarities. As the combination of other anions with the thoroughly investigated [BMIM] cation show similar ranges of deviations, the main contribution to the E_{NR}-values for the ILs investigated here seems to result from the NTf_2^--anion. This is in accordance with literature reports that the dominating contribution to the solvatochromic shift of Nile Red is the hydrogen-bond ability of the cation towards the dye [49]. Protons of significant acidity are intrinsically absent in quarternary phosphonium cations due to their molecular structure in contrast to dialkylimidazolium or protic ILs. The application of Reichardt's Dye to other phosphonium-based ILs revealed much larger differences in the empirical polarity towards imidazolium based samples [38]. Molecular solvents of similar E_{NR}-values than these ILs are ethanol (E_{NR} = 218.2 kJ/ mol^{-1}) or 1-butanol (E_{NR} = 218.5 kJ/ mol^{-1}). The E_{NR} value reported for a comparable IL [P$(hex)_3C_{14}H_{29}$][NTf_2] (E_{NR} = 218.7 kJ mol^{-1}) is quite similar to the values obtained [50]. A slightly lower polarity was found for an IL based on [BMIM] and a highly fluorinated borate anion (E_{NR} = 220.7 kJ mol^{-1}) [13].

3.2. *Crystal structure of the fluorous ionic liquid*

The crystalline structure of **1** was investigated by means of single crystal X-ray diffraction. Suitable single crystals could be obtained by slowly evaporating saturated solution IL **1** in benzotrifluoride. Crystal growth occurred in the form of colorless needles and plates. Although a lot of crystallization methods and solvents were investigated, benzotrifluoride was the only solvent applicable for crystal growth. Evaporation or slow cooling of a saturated solution of IL **1** in other solvents resulted in the formation of liquid biphasic systems. Owing to the nature of the substitution pattern, the shorter perfluoroalkyl-chain R_{f4} and one of the slightly longer chains R_{f6} occupied alternating positions leading to disordering. Furthermore the packing of the interactions between the perfluorinated molecular fragments driven by weak van der Waals forces lead to disordering in the periphery of the molecule. These effects overall lead to comparable high value for the final R-indices. Obtaining a suitable single crystal for XRD from ILs was found to be rather difficult even for symmetrical ions [51] as ILs are designed to contain destabilized crystalline structures. The highly fluorinated IL crystallizes in the triclinic, centrosymmetric P-1 space group showing two formula units per elemental cell. The unit cell and packing diagram are shown in Fig. 3. The NTf_2^--anions adopted a *trans*-configuration in the solid state as it is reported for the majority of measured IL samples in literature [52]. The fluorinated IL **1** showed structuring in domains of ionic moieties consisting of the phosphonium core and the anion on the one hand and the perfluoroalkyl-segments on the other. This organization into blocks of molecular segments of the same polarity driven by solvophobic interactions was also reported for imidazolium ionic liquids with perfluorinated anions [19]. Similar structural motifs and self-assembled nanostructures resulting from solvophobic interactions were reported for ILs with perfluoro-groups in bulk state leading to tricontinuous nanostructures of ionic, alkyl and fluorinated domains [25,53].

3.3. *Miscibility and phase behavior towards organic solvents*

In order to find an appropriate solvent for the fluorous biphasic catalysis and to demonstrate the fluorophilic characteristics of IL **1** the miscibility of the phosphonium ILs with a range of commonly applied solvents was investigated. The solvents investigated ranged from solvents of high polarity such as water to the highly nonpolar, fluorophilic perfluoroheptane. Mixing behavior and miscibility of the three

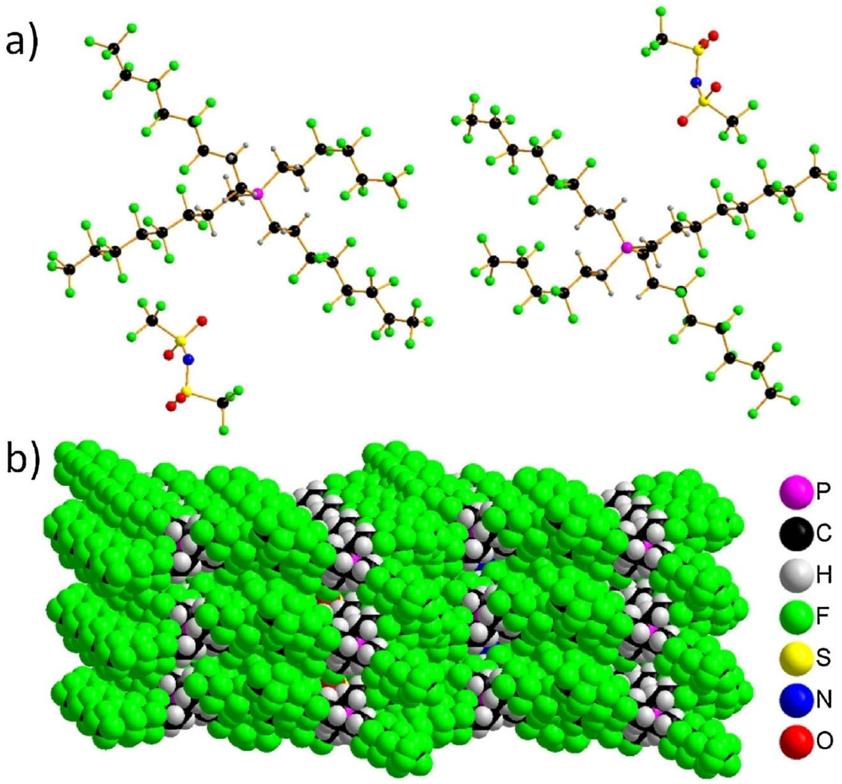


Fig. 3. Crystalline structure of the fluorous IL **1**. a) centrosymmetric elemental cell containing two formula units and b) packing diagram showing the composition of ionic and perfluorinated domains.

Table 2
Solubility of the investigated phosphonium ILs with common molecular solvents at 25 °C.

Solvent	IL **1**/g L^{-1}	$[P(oct)_3R_{f4}][NTf_2]$/g L^{-1}	$[P(oct)_3hex][NTf_2]$/g L^{-1}
perfluoroheptane	1.76	immiscible	immiscible
hexane	immiscible	13.76	12.30
toluene	1.6	miscible	miscible
Et_2O	8.3	miscible	miscible
THF	20.7	miscible	miscible
$CF_3C_5H_6$	4.7	miscible	miscible
CH_2Cl_2	0.65	miscible	miscible
acetone	274.5	miscible	miscible
DMF	15.6	miscible	miscible
methanol	76.6	miscible	miscible
H_2O	immiscible	immiscible	immiscible

phosphonium ILs with common solvents at 25 °C are listed in Table 2. The criteria to find an appropriate second solvent for fluorous biphasic catalysis are thermomorphic mixing behavior towards the fluorous solvent and minimal solubility at ambient temperature or the temperature at which the second solvent is extracted. The first criterion is crucial to ensure mixing of fluorous and organic phase and homogenous reaction kinetics. In general the FBC could also be performed if the catalyst with perfluorinated ligands shows a highly increased solubility in the organic phase at elevated temperatures so that a homogenous catalysis can be performed. The second criterion is demanded to avoid leaching of the fluorous phase accompanied with catalyst leaching. By this way an efficient catalyst retention and stable catalytic performance can be guaranteed. Furthermore it is in general preferable to apply high boiling solvents for both the fluorinated and organic phase as this minimizes losses through evaporation and allows higher critical mixing temperatures associated with lower miscibilities at moderate temperatures. All investigated ILs were found to be completely insoluble in water. This results from the combination of a hydrophobic anion with a hydrophobic cation. Although ILs with the NTf_2^--anion are well known to form a biphasic liquid system upon addition of water they display a slight water solubility when combined with a hydrophilic cation [54].

Upon combination with the highly hydrophobic cations which incorporate long hydrophobic alkyl or even fluorous chains, the solubility drops below the detection limit. The non-fluorinated and semi-fluorinated phosphonium ionic liquids show a similar phase behavior and were found to be completely miscible at ambient temperature with a wide range of organic solvents, ranging from polar methanol to nonpolar toluene. Only with the nonpolar aliphatic hydrocarbon hexane a limited solubility was found, being slightly higher for the semi-fluorinated $[P(oct)_3R_{f4}][NTf_2]$. Both ILs are immiscible with the fluorous solvent perfluoroheptane. The miscibility behavior towards organic solvents of a wide polarity range can be rationalized by the amphiphilic character of these ILs consisting of polar ionic and nonpolar alkyl motifs. These results show that a higher degree of fluorination is demanded to ensure a limited miscibility of ILs towards organic solvents at ambient temperature. For the highly fluorinated compound **1** the situation is indeed very different. The fluorous IL shows only limited solubility with the investigated organic solvents. The highest solubility was found for acetone reaching 274.5 g L^{-1}. Solubilities for the other molecular solvents were overall significantly lower but slightly higher for oxygen containing liquids like methanol, DMF, THF and Et_2O. Similar limited solubilities were obtained for the highly fluorinated IL described by van Koten and coworkers. where a solubility of 580 g/L of the fluorous IL in acetone was found [13]. For organic solvents without oxygen the solubility of IL **1** per liter was even lower. In the aliphatic hexane the fluorinated IL was found to be insoluble whereas it displayed a slight solubility in the fluorous solvent perfluoroheptane. In summary the IL **1** showed a miscibility behavior that is comparable to molecular fluorous solvents, showing limited solubilities with organic solvents at ambient temperature. However because of the additional ionic groups the solubility with the conventional fluorous liquids was also very limited. Following these results we investigated the thermomorphic mixing behavior of **1** with DMF in dependence on the volume fraction to determine the phase diagram. The thermoregulated mixing behavior and the obtained phase diagram are displayed in Fig. 4.

The aprotic DMF is a commonly applied solvent for the Heck cross

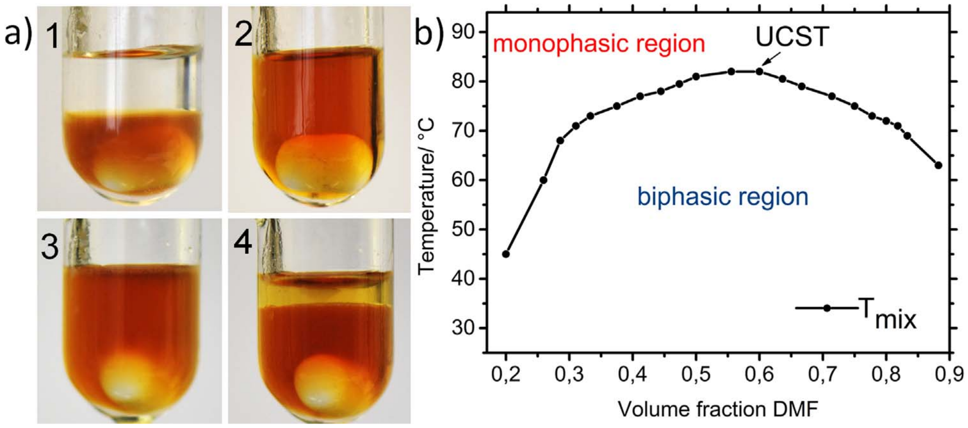
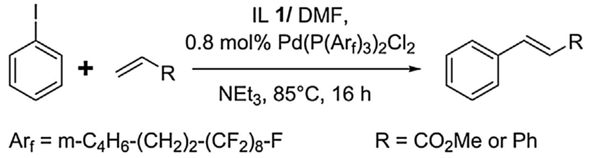


Fig. 4. a) Phase behavior of **1** (lower phase) with DMF (upper phase). Photographs: 1) formation of a biphasic mixture at room temperature; 2) heating above mixing temperature ($T > T_{mix}$); 3) cloud point upon cooling ($T < T_{mix}$); d) ongoing phase separation of fluorous and organic phase. b) Phase diagram: mixing temperatures T_{mix} in dependence of the volume fraction φ_{DMF}.

coupling reaction as it shows a comparatively high polarity capable to dissolve a wide range of educts and the base which is essential for the catalytic cycle in the reaction mechanism by base-induced reductive elimination [55]. It was found that IL **1** and DMF form a biphasic mixture at room temperature when the volume fraction of DMF (φ_{DMF}) exceeded 0.2 and had an upper critical solution temperature UCST of 82 °C at $\varphi_{DMF} = 0.57$. Above the respective mixing temperatures a homogenous monophasic system was found. The phase diagram showed the characteristic progression for liquid–liquid phase diagrams with upper critical solution temperature. As indicated in the phase diagram, slight amounts of DMF are miscible with **1** at room temperature resulting in a moderately viscous fluorine rich phase which remained liquid and homogeneous even at −18 °C.

3.4. Catalyst retention in Heck reactions

To investigate the performance of the fluorinated IL **1** as fluorous phase for the immobilization of a fluorous catalyst we investigated the Heck cross coupling as a model reaction for palladium catalysis. Homogenous palladium catalysis is a very important, widespread and versatile method utilized in chemical laboratories as well as on industrial scale [56]. One important drawback of conventional Pd-catalysis is the loss of the relative expensive catalyst that cannot or hardly be recovered [57]. Among other immobilization strategies the catalyst retention in a fluorous phase seems to be a promising way to overcome this drawback and to provide overall more sustainable processes [58]. Fluorophilic catalysts can be obtained by simply attaching perfluorinated alkyl-groups in the periphery of catalyst that are known to show high activity and stability [59]. By using highly fluorinated ionic liquids is should become possible to further eliminate the drawbacks of the volatile molecular perfluorinated solvents that were found to have a range of negative impacts on the environment. The Heck reaction allows the selective formation of C—C bonds between aryl halides and activated alkenes but an efficient catalyst recovery was found to be difficult [31]. This results from the usage of multiple reagents along with different obtained products or side products that disturb the catalytic cycle or lead to inactivation of the catalyst. The catalyst with highly fluorinated ligands [$Pd(P(m\text{-}C_6H_4\text{-}(CH_2)_2\text{-}(CF_2)_8F)_3)_2Cl_2$] [29] used for the cross coupling reactions was found to be insoluble in pure DMF and many other common organic solvents at ambient temperatures. However concentrations of at least 1.2×10^{-2} mol L^{-1} could be obtained in IL **1** saturated with DMF. We first investigated a thermoregulated biphasic system consisting of 1.00 g of IL **1** and 1.00 mL DMF at 85 °C as this temperature is above the upper critical solution temperature UCST. Scheme 2 shows the reactions and conditions applied for the first experiments coupling iodobenzene with either methyl acrylate or styrene. The results for the yield, TON and cumulative TON are given in Table 3.



Scheme 2. Reaction scheme of iodobenzene and methyl acrylate or styrene applying IL **1** under fluorous biphasic catalysic conditions.

Table 3
Catalyst recycling using the thermomorphic biphasic system applying IL **1** as fluorous phase[a].

	R = CO_2Me[b]			R = Ph[c]		
run	yield[d]/%	TON	cumulative TON	yield[d]/%	TON	cumulative TON
blank[e]	99	124	–	94	118	–
1	99	124	124	93	116	116
2	99	124	248	94	118	234
3	98	123	371	93	116	350
4	99	124	495	92	115	465
5	97	121	616	94	118	583
6	96	120	736	93	116	699
7	96	120	855	90	113	812
8	88	110	965	86	108	920
9	76	95	1060	75	94	1014
10	67	84	1144	61	76	1090
11[f]	92	115	1259	85	106	1196

[a] Conditions: 1.0 g **1**, 0.296 mmol iodobenzene (1.0 eq.), 0.355 mmol olefine (1.2 eq.) and 0.355 mmol NEt_3 (1.2 eq.) in 1.00 mL DMF, 8.0 mg catalyst (0.8 mol%), 16 h (unless stated otherwise).
[b] *Trans* only.
[c] *Trans/cis*.
[d] Determined by HPLC.
[e] No fluorinated IL added; catalyst not recovered.
[f] t = 32 h.

After each run the upper organic phase was carefully removed and the yield determined by means of HPLC. To proof the efficient catalyst retention fresh reagents were added and the catalytic process repeated. A blank run using only fluorous catalyst in DMF showed a similar thermoregulated mixing behavior and was able to efficiently catalyze the Heck reaction. However the recovery was not possible under these conditions. The catalyst recovery using the fluorous IL **1** was found to be efficient for seven runs without significant decrease in yield for both the coupling to methyl cinnamate and stilbene being 90% and more. The yields for methyl cinnamate were found to be slightly higher than those for stilbene which is also found for other multiphasic systems investigating the Heck reaction [60]. For the runs eight to ten a decrease in the catalytic activity was found. By doubling the reaction time for the eleventh run it was possible to increase the yield again whereby the obtained yields remained lower than for the initial runs.

These results already show the potential of the fluorous IL for the

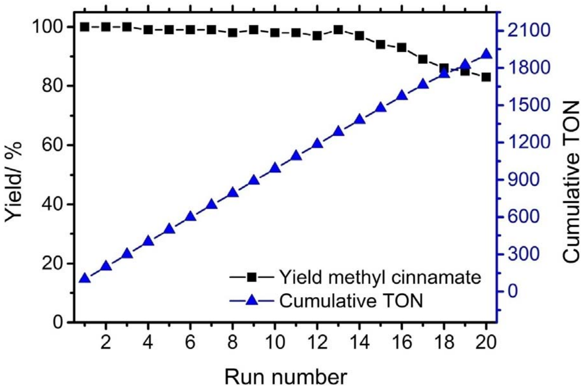


Fig. 5. Yield of methyl cinnamate per run and cumulative TON for the overall catalysis.

Table 4
Isolated mass of the pure methyl cinnamate and corresponding yield per run.

run	mass isolated methyl cinnamate/mg	yield/%
1	46.09	96
2	45.62	95
3	46.23	96
4	46.31	96
5	44.93	94
6	45.47	95

retention of the fluorous catalyst. We believe that the loss in catalytic activity results mainly from thermal degradation of the catalyst rather than leaching to the organic phase. This was indicated by a color change of the solutions of the blank run and the IL **1** in the thermomorphic catalysis to orange-red which was reported to result from the formation of nanoparticles in solution [61]. Inactivation of the same catalyst after prolonged exposure to higher temperatures was also reported before [62]. We therefore investigated the performance of the catalyst in the biphasic system at lower temperatures to reduce the extend of thermal catalyst degradation. Hence we performed the cross-coupling reactions at 70 °C, increased the catalyst concentration to 1 mol% and kept the same conditions for the coupling of iodobenzene and methyl acrylate to methyl cinnamate. The results for the TON and cumulative TON for this reaction conditions are plotted in Fig. 5.

By using these conditions the fluorous catalyst showed nearly quantitative yields for 14 runs and only a slight drop remaining 83% yield for run 20. Nearly quantitative yield of 96% could be restored for the 21. run by increasing the reaction time to 32 h. To demonstrate facile product isolation and removal of side product triethylammonium iodide from the reductive elimination an extraction process was performed for the first six runs in an additional experiment. For this purpose six equivalents of water were added to the carefully separated DMF phase after the reaction and the resulting suspension was extracted with 3 mL hexane three times. After solvent removal from the combined organic phases the residue was dried in oil-pump vacuum yielding pure methyl cinnamate in high isolated yield. Purity of the isolated methyl cinnamate was confirmed by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy. The yields of the isolated methyl cinnamate are stated in Table 4 and were 95% in average. In further experiments the leaching of the fluorous IL **1** was found to be as low as 1.2% per run which is rather low and demonstrates the high fluorophilic character of the IL. Overall these results proofed the utilization of a highly fluorinated IL for catalyst retention in the Pd-catalyzed Heck reaction under fluorous biphasic conditions with high yields, high number of performable runs and low leaching of the fluorous phase.

4. Conclusion

We successfully synthesized a novel highly fluorinated ionic liquids and showed the effect of fluorination on the physicochemical properties in comparison to the non-fluorinated and semi-fluorinated analogue. The fluorous IL was found to have a higher melting point, high thermal stability and a slightly lower polarity investigated by means of the solvatochromic dye Nile Red. Single crystal X-ray analysis showed the formation of fluorinated and ionic domains driven by solvophobic interactions. The fluorinated IL was found to have only limited solubility in a wide range of investigated organic liquids comparable to molecular perfluorinated solvents. The non- and semi-fluorinated analogues showed completely different behavior being completely miscible in polar as well nonpolar organic solvents. The thermoregulated mixing behavior towards DMF was investigated in detail. The fluorinated IL could be successfully applied as a substitute for volatile fluorocarbon compounds that pose environmental threats but are still commonly applied solvents in the fluorous biphasic catalysis. Thus the incorporation of perfluoroalkyl-groups adds fluorophilicity as possible modification to the widely tuneable properties of ILs. By investigating the Heck reaction as exemplary reaction for palladium catalyzed C—C bond formation we were able to proof the applicability of the fluorous ionic liquid to the very widely used Pd-catalyzed reactions. The highly fluorinated IL was found to efficiently immobilize a perfluoro-tagged catalyst which allowed repetitive usage for up to 14 runs with only minor loss in catalytic activity and up to 21 runs with yields still being 83% and higher. By this multiphasic catalysis reaction conditions the activity of the expensive Pd-catalyst can be preserved for multiple reaction runs thus leading to more economic and environmental friendly processes. In further studies we will investigate the expansion of the fluorous IL to other catalytic systems and reactions as well as the application of catalytic systems that show increased thermal stability.

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