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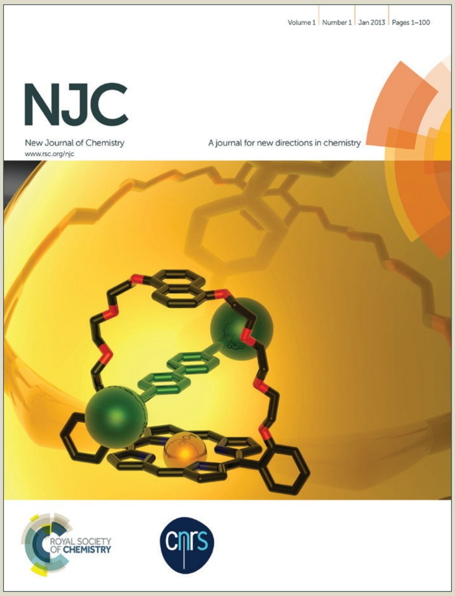

Journal Name

ARTICLE

Thermally stable bis(trifluoromethylsulfonyl)imide salts and their mixtures

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We show that both tetraphenylphosphonium bis(trifluoromethylsulfony)imide ($[PPh_4][NTf_2]$) and $Cs[NTf_2]$ are low melting salts of exceptionally high and also very similar thermal stability. This similarity indicates that the thermal stability is dominated by the anion. Moreover, eutectic mixtures of $[PPh_4][NTf_2]$ and $Cs[NTf_2]$ with melting points below 100 °C are presented. Surface analysis of the latter in the liquid state reveals a surprising depletion of $[PPh_4]^+$ ions from the surface.

Introduction

Due to their unique structural properties, ionic liquids (ILs) have established in the recent years as highly promising class of solvents, materials and performance chemicals.[1] However, for many prospective applications in which the extremely low vapor pressure of ILs would be of great advantage, e.g. as heat transfer media,[2] in high temperature catalysis[3] or in separation processes,[4] their limited long-term operational stability at temperatures above 250 °C has been found a serious limitation.[5]

The upper operational temperature limit of IL utilization is defined by both IL thermal decomposition and IL evaporation processes. Concerning IL decomposition, different mechanisms are discussed in the literature depending on the type of IL under investigation: For protic ionic liquids, thermal decomposition occurs through the protonation equilibrium between the salt form and the corresponding acid/base pair. The higher the pK_a difference between acid and base the higher is the thermal stability of the protic salt.[6] For non-protic ionic liquids, elimination of alkyl groups by breaking a carbon-hetero atom bond is the first major decomposition process during heating-up. In this process, the IL stability is a function of the counter-ion nucleophilicity with stronger nucleophilic anions leading to lower decomposition temperatures.[7] For very stable and weakly nucleophilic anions, such as e.g. the $[NTf_2]^-$ ion, pyrolysis and cracking reactions of the organic cation have been claimed to constitute the thermal stability limit.[5] Therefore, some research efforts have been directed towards low melting alkali $[NTf_2]^-$ salts to overcome this issue by using non-decomposable alkali ions in combination with one of the most stable IL anions.[8]

Note that the determination of thermal decomposition limits of ILs is not trivial. Apart from the very strong dependence of all stability data on the IL quality[9] and some reported dependency on the sample pans used,[5] there is a strong influence on the heating ramp in thermogravimetric analysis (TGA) experiments as both, decomposition and evaporation, are kinetic processes that proceed to a different degree with time. For example, MacFarlane and coworkers have shown, that the temperature at which 1% thermal degradation of $[EMIM][NTf_2]$ occurs is 307°C if the ionic liquid is exposed to thermal stress for 1h while it is only 251°C if the ionic liquid is exposed for 10h.[10]

In addition to thermal decomposition, mass loss by IL evaporation in form of neutral ion pairs also occurs at elevated temperatures and reduced pressures.[11] This process has been found to be of high practical relevance, e.g. for the controlled deposition of ultrathin IL films.[12,13] It may, however, also limit technical operation with ionic liquids in open systems at high temperatures. Recently, it has been shown that special TG experiments allow discriminating between thermal decomposition and evaporation by applying a combination of non-isothermal ambient pressure measurements with an overflow of inert gas with isothermal experiments conducted at high vacuum using a magnetic suspension balance.[14]

In this contribution we present a comparison of the long-term thermal behavior of the two $[NTf_2]^-$ salts, $Cs[NTf_2]$ and $[PPh_4][NTf_2]$. Both salts are in principal known from the literature: The solid state structure of $Cs[NTf_2]$ has been

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characterized in detail by Xue et al.,[15] the melting point of Cs[NTf$_2$] as well as its binary[8] and even ternary mixtures[16] with other alkali [NTf$_2$]$^-$ salts have also been studied. As the lowest melting point of such ternary eutectics, a mixture of Cs[NTf$_2$], Li[NTf$_2$], Na[NTf$_2$] in the molar ratio of 0.9:0.05:0.05 has been identified. The latter melts at 115 °C, as compared to 122 °C for pure Cs[NTf$_2$], reported in the same study.[8] Hagiwara et al. also give the thermal decomposition temperature of Cs[NTf$_2$] as 472 °C, which has been found to be the highest among the alkali bis(trifluoromethylsulfonyl)imide salts.[8]

[PPh$_4$][NTf$_2$] has been reported by one of us in 2013 as particularly thermally stable organic [NTf$_2$]$^-$ salt together with a number of other new phosphonium imide salts:[17] The melting point of [PPh$_4$][NTf$_2$] was reported to be 135 °C, and the thermal stability was studied by an isothermal stability test at 350 °C for 96 h in new porcelain crucibles, with 2.3 % mass loss found over this period. Undoubtedly, this result already gave a strong hint to an extraordinary thermal robustness of [PPh$_4$][NTf$_2$].

For this work, we were interested in a direct comparison of the thermal stability of Cs[NTf$_2$] and [PPh$_4$][NTf$_2$] under strictly comparable experimental conditions. With this comparative study we aim to prove that some IL cations are thermally more stable than the [NTf$_2$]$^-$ anion, thus a shift in attention on the anion is required in the development of thermally more stable ionic liquids. Moreover, we present data on mutual solubility and eutectic behaviour of mixtures of Cs[NTf$_2$] and [PPh$_4$][NTf$_2$] with the intention to qualify such mixtures as suitable liquid materials for high temperature applications, e.g. as heat transfer fluids with very low vapour pressures.

Results and discussion

To start with, we determined viscosity and density data of the two pure salts at 200 °C (Table 1).

Table 1: Relevant physico-chemical properties of Cs[NTf$_2$] and [PPh$_4$][NTf$_2$] salts.

Property	[PPh$_4$][NTf$_2$]	Cs [NTf$_2$]
melting point (DSC) / °C	134 (135)^1	125 (122)^2
density (200 °C) / g cm^{-3}	1.2	2.2
viscosity (200 °C) / mPa s	6	14

^{1} value in brackets is from reference[17]; ^{2} value from reference[8].

Furthermore, non-isothermal TG-experiments at different heating rates (0.5, 2, 10 K min^{-1}) were conducted. In order to discriminate between thermal decomposition and evaporation during these experiments, the latter were carried out in helium and nitrogen flow (100 ml min^{-1} NTP). This method and the subsequent data evaluation was already published by some of us recently.[14,18] The normalized rate of mass loss (derivation of mass signal m; DTG-signal; normalized to initial mass m$_0$) due to evaporation and/or thermal decomposition for a component i during such non-isothermal TG-experiments is expressed by:

$$\begin{aligned} -\frac{1}{m_{0,i}}\frac{dm_i}{dt}\bigg|_{total} &= -\frac{1}{m_{0,i}}\frac{dm_i}{dt}\bigg|_{vap} - \frac{1}{m_{0,i}}\frac{dm_i}{dt}\bigg|_{decomposition} \\ &= \frac{M_iA_C}{RT}\frac{Sh_dD_{i,g}}{d_Cm_{0,i}}p_{vap,i}+k_{decomposition,i}\frac{m_i}{m_{0,i}}. \end{aligned} \quad (1)$$

M stands for the molar mass of the sample; A$_C$ for the crucible's surface; R the molar gas constant; D$_{i,g}$ for the binary diffusion coefficient of the sample in the gas phase (N$_2$ and He; in this work the well-known correlation of Fuller, Schettler and Giddings was used with a maximum average error of about 15% [19]); d$_C$ for the diameter of the crucible and T the sample temperature. The Sherwood number Sh$_d$ for a crucible (h$_C$ crucible's height; h$_F$ crucible's actual filling height) in transversal gas flow is given by:

$$Sh_d = \left(\frac{h_C-h_F}{d_C}+\frac{1}{2.9+0.58\sqrt{Re_d}\sqrt[3]{Sc}}\right)^{-1} \quad (2)$$

with the Reynolds number

$$Re_d = \frac{ud_C}{\nu_g} \quad (3)$$

using the superficial velocity u and the kinematic viscosity ν$_g$ of the carrier gas g. The Schmidt number Sc is defined as the ratio of the kinematic viscosity ν$_g$ to the binary diffusion coefficient D$_{i,g}$. The vapor pressure p$_{vap}$ was calculated by a simplified Antoine equation assuming a constant (temperature independent) entropy term C$_{vap}$ and a constant enthalpy of vaporization Δ$_{vap}$H:

$$\frac{p_{vap}}{p_{ref}} = C_{vap}\cdot exp\left(-\frac{\Delta_{vap}H}{RT}\right) \text{ with } p_{ref}=1\,Pa. \quad (4)$$

The rate of the thermal decomposition was calculated assuming a first order reaction with the rate constant k$_{decomposition}$ and the formal kinetic parameters k$_0$ and E$_A$:

$$k_{decomposition} = k_0\cdot exp\left(-\frac{E_A}{RT}\right). \quad (5)$$

It should be emphasized that the formal kinetic estimates represent kinetic parameters for a global model in order to describe only the thermal decomposition at low conversion and not the complex chemical reactions in the course of decomposition. Eq. 1 was solved numerically using the software Berkeley Madonna (Robert Macey; University of California). To get a first impression on the thermal stability of both salts in direct comparison, Figure 1 shows TG experiments of Cs[NTf$_2$] and [PPh$_4$][NTf$_2$], along with the well-established ionic liquid [EMIM][NTf$_2$]. All three salts were first kept in the TG set-up at 120 °C for one hour to allow traces of humidity to be released. Then, the samples were heated with a defined heating ramp (2 K min^{-1}) under a constant nitrogen flow.

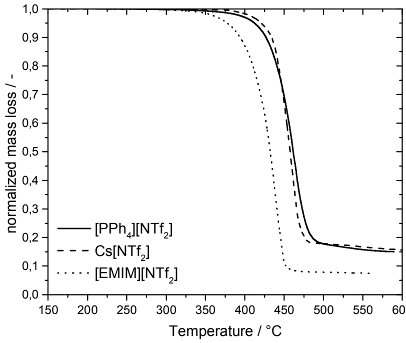

Figure 1: Comparative TG experiments of $[PPh_4][NTf_2]$, $Cs[NTf_2]$ and $[EMIM][NTf_2]$ in N_2 flow (100 mL min^{-1}), drying at 120 °C for 1 hour, heating rate 2 K min^{-1}.

Both, $Cs[NTf_2]$ and $[PPh_4][NTf_2]$, are thermally significantly more stable than $[EMIM][NTf_2]$. Moreover, $Cs[NTf_2]$ and $[PPh_4][NTf_2]$ show the same on-set of strong mass loss around 420 °C indicating that the decomposition mechanism must be very similar for both salts. We draw from this result the important conclusion that it is not the phosphonium cation of $[PPh_4][NTf_2]$ that limits thermal stability but the imide anion. The results of our more detailed kinetic evaluation of $Cs[NTf_2]$ and $[PPh_4][NTf_2]$ decomposition are given in Table 2. The agreement of the results of $[PPh_4][NTf_2]$ ($T_{max,2\% \text{ in } 96h}$ = 348 °C) with the isothermal measurements from the literature[17] is excellent. The vapor pressure of these two salts is by a factor of 4 and 18, respectively, lower than the imidazolium based IL $[EMIM][NTf_2]$ (p_{vap}(350 °C) ≈ 30 Pa). Nevertheless, during TG-experiments at low heating rates the evaporation is the major mass loss.

Table 2: Parameters of the vapor pressure (eqn. (1)), the kinetics of thermal decomposition (eqn. (2)) and the corresponding temperature range for $[PPh_4][NTf_2]$ and $Cs[NTf_2]$.

	$[PPh_4][NTf_2]$	$CsNTf_2]$	$[EMIM][NTf_2]$
k_0 / s^{-1}	$1.2 \cdot 10^{20}$	$8.6 \cdot 10^{19}$	$1.2 \cdot 10^{20}$
E_A / kJ mol^{-1}	325	325	317
C_{vap} / -	$3.2 \cdot 10^{11}$	$2.2 \cdot 10^{11}$	$3.5 \cdot 10^{11}$
$\Delta_{vap}H$ / kJ mol^{-1}	135	125	120
p_{vap} (T=350°C) / Pa	1.6	7.2	30.5
$T_{max, 1\%/a}$ / °C [1]	301	304	286

[1] 1% mass loss due to thermal decomposition per year

Next, we studied the melting points of $Cs[NTf_2]$-$[PPh_4][NTf_2]$ mixtures with the intention to combine extremely high thermal stability with lower melting points. Figure 2 shows the obtained phase diagram. From these experiments we conclude that $Cs[NTf_2]$ and $[PPh_4][NTf_2]$ form homogeneous liquid mixtures above the melting point of each compound. Moreover, the mixture is characterized by an eutectic composition $[PPh_4][NTf_2]$: $Cs[NTf_2]$ = 1:2.13 (32 mol-% $[PPh_4][NTf_2]$), with a melting point of 98.6 °C. The viscosity of this mixture at 200 °C has been determined to be 9 mPa s.

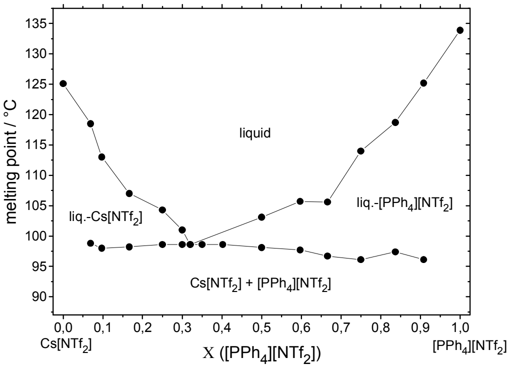

Figure 2: Phase diagram of $[PPh_4][NTf_2]$ and $Cs[NTf_2]$.

The behaviour of this eutectic mixture under thermal stress has been determined by the same TGA-method already used for the pure salts. Figure 3 shows the measured rate of mass loss (normalized to initial mass; see refs.[14,18]) and the calculated contributions of evaporation and thermal decomposition. Interestingly, the obtained overall rate of mass loss can be calculated over a wide range (until 60% mass loss) applying Raoult's law to an ideal mixture composed of independent ILs; i.e. the normalized mass loss (eq.(1)) and the effective available surface area AC in eq. (1) was calculated iteratively for each IL after each time step separately. Figure 3 shows the results of the simulations. It can be seen that the thermal stability of the mixture is determined by the thermal stability of $[PPh_4][NTf_2]$, and the overall mass loss at the beginning is dominated by the evaporation of $Cs[NTf_2]$.

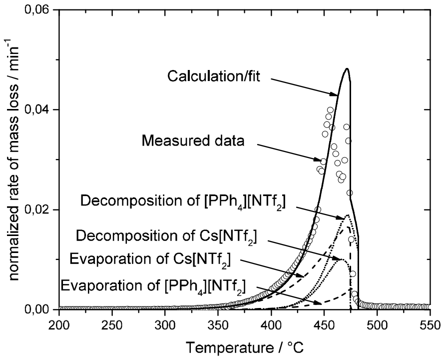

Figure 3: TG-experiments (N_2; 6 l h^{-1}; heating ramp = 2 K min^{-1}) with the eutectic mixture of the ionic liquids $Cs[NTf_2]$ and $[PPh_4][NTf_2]$ under ambient pressure - solid line; dashed and dotted lines are the corresponding contributions of evaporation and thermal decomposition of the individual components.

In the context of applications where a thin salt film coats a high surface-area support (e.g. SILP catalysis), the outermost surface is the dominating interface for substrates entering the reaction medium and for products leaving the reaction system.

In order to elucidate the surface composition of our salt mixtures, we performed angle-resolved X-ray photoelectron spectroscopy (ARXPS) under ultra-high vacuum conditions, similar to earlier measurements for acetate salt mixtures.[20] Figure 4 shows measurements with 25 mol% $[PPh_4][NTf_2]$ bulk content (according to XPS) at 130 °C, that is, in the liquid phase. The quantitative analysis of the bulk sensitive 0° spectra shows no contaminations within the XPS probing depth. The comparison of the spectra in the Cs 3d and C 1s regions at 0° and 80° allows for investigation of selective enrichment/ depletion effects.

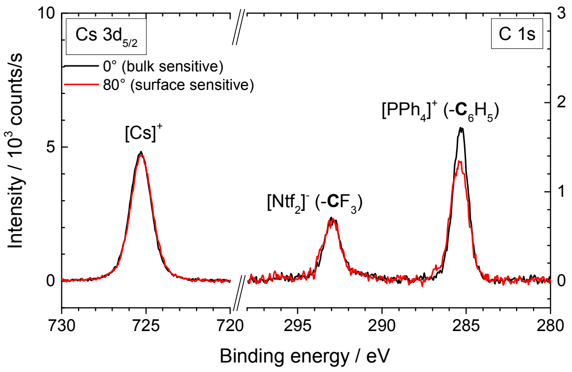

Figure 4: ARXP Cs 3d and C 1s spectra of a 25 : 75 mol% mixture of $[PPh_4][NTf_2]$: $Cs[NTf_2]$ at 130 °C.

A pronounced surface depletion of the phosphonium cation is deduced from the 80° spectra, where more than ~80% of the detected signal originates solely from the topmost layer: Whereas the Cs cation signal and the anion's CF_3 signal at 293 eV do not exhibit any changes with emission angle, the phosphonium C 1s signal at 285 eV decreases at 80°, corresponding to a $[PPh_4][NTf_2]$ surface content of only 20 mol% at 130 °C. This surface depletion of the bulky organic cation is surprising: in alkali-acetate mixtures, the larger cations were found to be surface enriched.[20]

Conclusions

In conclusion, we could demonstrate that the thermal stability of $[PPh_4][NTf_2]$ is not limited by its cation but by the imide anion. This finding confirms the exceptional thermal stability of the $[PPh_4]^+$ ion and may guide the way to the synthesis of even thermally more stable organic salts. In addition, it has been found that the relatively high melting points of both $Cs[NTf_2]$ and $[PPh_4][NTf_2]$ can – at least partly – be circumvented by applying binary mixtures of these two compounds. The fact that inorganic and bulky organic imide salts show excellent miscibility and eutectic behaviour is surprising and may open new routes to salt mixtures of new properties. In the special case of binary $Cs[NTf_2]$-$[PPh_4][NTf_2]$ mixtures this approach lowers the melting point of $[PPh_4][NTf_2]$ by around 40 °C and brings the melting point below 100 °C. Interestingly, the surface of the eutectic mixture in the liquid state favour the presence of Cs^+ ions on expense of the bulky $[PPh_4]^+$ ions as shown by ARXPS.

Experimental

Characterisation. The purity and identity of the compounds were determined by NMR, elemental analysis and DART-MS (Direct Analysis in Real Time Mass Spectrometry). The ^1H and ^{13}C NMR spectra were recorded on a Jeol ECX-400. The chemical shifts are in ppm relative to aceton-d_6 (^1H: 2.05 ppm; ^{13}C: 29.84 ppm, 206.26 ppm). The determination of the carbon, hydrogen, nitrogen and sulfur content was performed on a Carlo Erba EA 1106, 1107 and 1108 instrument at the Analytical Laboratories of the Chair of Inorganic and General Chemistry of the Friedrich-Alexander Universität Erlangen-Nürnberg (Erlangen, Germany). The DART-MS analysis was performed on a JMS-T100LP AccuTOF LC-plus 4G from Jeol with a He plasma ionization from ionSense, operating in both positive and negative-ion mode. The m/z values refer to the most abundant isotope.

Synthesis. All starting materials were used as received, without further treatment. The $[PPh_4][NTf_2]$ salt was synthesized by an ion exchange of 10.17 g (35.41 mmol) $Li[NTf_2]$ (Iolitec) and 13.27 g (35.41 mmol) $[PPh_4]Cl$ (Sigma Aldrich) in water. The precipitated product was filtrated and washed thoroughly with water to remove chloride impurities, the filtrate was tested with $AgNO_3$. The salt was dried in vacuum. ^1H NMR (δ, 293 K, aceton-d_6): 7.78 ppm (16 H, m), 7.95 ppm (4H, t) ^{13}C NMR (δ, 293 K, aceton-d_6): 117.81 ppm (1 C), 118.70 ppm (1 C), 130.50 ppm (8 C, d), 134.91 ppm (8 C, d), 135.54 ppm (4 C, d); Elemental Analysis: calculated: %C: 50.41; %H: 3.25; %N: 2.26; %S: 10.35; found: %C: 50.67; %H: 3.00; %N: 2.23; %S: 10,26; DART-MS (ESI^+): m/z = 339.09 for $[PPh_4]^+$; (ESI^-): m/z = 278.92 for $[NTf_2]^-$.

For the synthesis of $Cs[NTf_2]$ the acid $H[NTf_2]$ was obtained by sublimation from a reaction mixture of 10.23 g (35.63 mmol) $Li[NTf_2]$ and 10 equivalents of 98 % H_2SO_4 (Sigma Aldrich) at 80 °C and reduced pressure (0.5 mbar). Subsequently, $H[NTf_2]$ was reacted with 5.79 g (17.82 mmol) Cs_2CO_3 (Sigma Aldrich) in 10 mL methanol (Sigma Aldrich) at 50 °C. The solvent was removed at a rotary evaporator and the raw material was recrystallized from acetonitrile (Sigma Aldrich) and dried in vacuum. Elemental Analysis: calculated: %C: 5.82; %H: 0.00; %N: 3.39; %S: 15.52; found: %C: 5.77; %H: 0.00; %N: 3.50; %S: 15.63. DART-MS (ESI^+): m/z = 132.89 for Cs^+, m/z = 545.67 for $Cs_2[NTf_2]^+$; (ESI^-): m/z = 148.01 for $[NTf]^-$, m/z = 279.93 for $[NTf_2]^-$; m/z = 692.70 for $Cs[NTf_2]_2^-$.

The binary mixtures of the salts were obtained by mixing the right amounts and melting.

Viscosity measurements. The viscosity measurements were carried out with a rotary viscosimeter DV-II+ Pro Extra (Brookfield) with a home-made heating device using standard spindles in a temperature range from 120 to 250 °C.

Density measurements. The density was obtained by applying the Archimedean method measuring the reduced mass of a cylindrical glass-probe immersed into the molten salt. The balance was a Practum 124-1S from Satorius, the heating was home-made. The temperature range was 130 -250 °C.

Melting point determination. For the phase diagram melting point measurements were carried out using a dynamic differential scanning calorimetry setup from Phoenix DSC 204 F1 (Netzsch). 10 mg of the sample was weighted in aluminum crucibles. The heating and cooling rates were 2 K min^{-1}. The transition temperatures were determined from the heating process to avoid the uncertainty of supercooling.

TG-experiments. The thermo-gravimetric analysis at different heating rates (0.5, 2, 10 K min^{-1}) were conducted in a horizontal thermobalance EXSTAR 6300 TG/DTA from Hitachi High-Tech using quartz glass crucibles. The TG-experiments were conducted with N_2 (99.999 % purity) or He (99.996 % purity) as carrier gas with a gas flow rate of 6 l h^{-1} NTP. The temperature uncertainty in the TG-experiments was ± 0.1 K. The standard uncertainty of the kinetic parameters was about ± 15 %.

ARXPS investigations. The surface studies were performed using our new and unique laboratory electron spectrometer DASSA ("Dual Analyser System for Surface Analysis"), dedicated for investigations of liquid samples.[21] It comprises an ultrahigh vacuum chamber equipped with two electron analysers (ARGUS, Scienta-Omicron), for simultaneous measurements at 0° and 80°, relative to the surface normal of a horizontally mounted liquid sample; measurements at 0° are considered as bulk sensitive (information depth 7-9 nm), and measurements at 80° as surface sensitive (information depth 1-1.5 nm). By employing monochromatic Al Kα radiation (1486.6 eV), a combined energy resolution of 0.4 eV is achieved. The sample temperature is controlled within ± 1°C, which allows for following changes in bulk and surface composition as a function of temperature.

Acknowledgements

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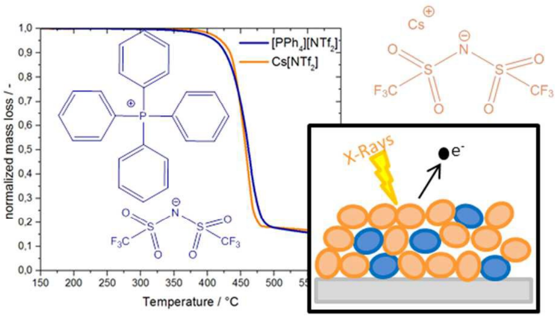

The investigated salts form an eutectic mixture which melts below 100 °C and surface analysis show a depletion of phosphonium cations.