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# Uranium tetrafluoride *via* direct conversion of uranium dioxide using silver bifluoride in an ionic liquid medium

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Conventional methods to prepare crystalline uranium tetrafluoride (UF<sub>4</sub>) involve the fluorination of uranium fluoride (UO<sub>2</sub>) with corrosive chemicals (*i.e.*, HF<sub>(g)</sub>) at elevated temperatures. Here, a novel method for producing UF<sub>4</sub> in a room temperature ionic liquid (RTIL) medium is presented. This method involves the fluorination of UO<sub>2</sub> in 1-methyl-1-butyl piperidinium bis(trifluoromethylsulfonyl)imide using silver bifluoride (SBF). The effect of RTIL volume, temperature, and water content on reaction yields and products is discussed. The volume of RTIL and reaction temperature are critical parameters in the formation of crystalline UF<sub>4</sub>. The reaction of UO<sub>2</sub> with SBF at 200 °C with an RTIL volume of 0.5 mL gives crystalline UF<sub>4</sub> with the highest yield (94%). The presence of water in the RTIL led to the formation of hydrated UF<sub>4</sub>, while the reaction performed at 150 °C resulted in amorphous UF<sub>4</sub>.

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## Introduction

Uranium tetrafluoride is a key material in the nuclear industry,<sup>1–5</sup> it occurs in the UF<sub>6</sub> enrichment/deconversion cycle,<sup>4–8</sup> it is used as a precursor for uranium metal production<sup>9</sup> and plays an important role in molten salt reactors.<sup>10–13</sup> Most of the reported methods for the preparation of UF<sub>4</sub> involve the use of hazardous corrosive fluorinating agents, *i.e.*, HF<sub>(aq)</sub> or HF<sub>(g)</sub>,<sup>14</sup> and F<sub>2(g)</sub><sup>5,6,15</sup> at high temperatures (~550 °C). Research has explored alternative fluorination methods that involve mild fluorinating agents such as NF<sub>3(g)</sub><sup>6,16–18</sup> and bifluoride salts (AHF<sub>2</sub>; A = NH<sub>4</sub>, Ag).<sup>3</sup> Recent works have also used room temperature ionic liquids (RTIL) alone or in combination with HPF<sub>6</sub> for UF<sub>4</sub> synthesis.<sup>19,20</sup> The use of RTILs has attracted significant attention in actinide separation, electrochemical recovery, synthesis, and catalysis. Their appeal arises from distinctive physicochemical properties, including high thermal stability, low vapor pressure, wide electrochemical window, low hydrophobicity, non-flammability, and strong ability to dissolve a variety of metal complexes.<sup>21–25</sup> The fluorination of alkaline earth (Sr), transition (Fe, Co, Zn, and Ir), and lanthanide (La, Ce, Pr, Nd, Sm, Eu, Er, and Y) metal species using BF<sub>4</sub><sup>–</sup> and PF<sub>6</sub><sup>–</sup> containing RTIL has been documented.<sup>26–28</sup> For the actinides, UF<sub>4</sub> was successfully prepared from the fluorination of UO<sub>2</sub> or uranium

oxalate in 1-butyl-3-methylimidazolium hexafluorophosphate (C<sub>4</sub>mim-PF<sub>6</sub>) in the temperature range 180–150 °C.<sup>19,20</sup> In both studies, PF<sub>6</sub><sup>–</sup> acts as the fluorinating agent, and the possible degradation of the RTIL occurred during the reaction. While HPF<sub>6</sub> is a promising fluorinating agent,<sup>19</sup> it decomposes to HF and PF<sub>5</sub> upon drying. The commercially available HPF<sub>6</sub> is an aqueous solution (60–65%) consisting of ~21 wt% H<sub>2</sub>O, 6% HF, and 8% of the phosphoric acids (*i.e.*, HPO<sub>2</sub>F<sub>2</sub>, H<sub>2</sub>PO<sub>3</sub>F, and H<sub>3</sub>PO<sub>4</sub>).<sup>29</sup>

To prepare anhydrous UF<sub>4</sub> while preventing the RTIL degradation, the fluorination of UO<sub>2</sub> in a stable RTIL using mild fluorination agents is proposed. One class of stable RTIL that could be employed is those containing the bistriflimide (TFSI) anion. Previous studies have shown that RTILs containing the TFSI anion are stable towards hydrolysis and do not decompose with water or acids.<sup>22,30</sup> Concerning fluorination, it has been shown that silver bifluoride (AgHF<sub>2</sub>, SBF) can effectively fluorinate uranium oxides.<sup>3,31</sup> Silver bifluoride exhibits several advantages over ammonium bifluoride, such as decomposition temperature (160 °C *vs.* 240 °C) and absence of byproducts (*i.e.*, NH<sub>4</sub>F, NH<sub>3</sub>, and NO<sub>x</sub>) that could interfere during the reaction.<sup>32</sup> The fluorination of UO<sub>2</sub> with SBF in air gives mixed UF<sub>4</sub> products (UF<sub>4</sub>, UF<sub>4</sub>·xH<sub>2</sub>O (*x* = 1.5–2)), and a N<sub>2</sub> atmosphere is required for the formation of anhydrous UF<sub>4</sub>.<sup>3,31</sup> The fluorination of UO<sub>2</sub> with SBF in RTIL would present several advantages. The RTIL, as a medium, would provide homogeneous HF concentration for fluorination; it can also help in the formation of different UF<sub>4</sub> morphologies by tuning the reaction conditions. The addition of RTIL to the UO<sub>2</sub> powder minimizes handling and prevents health hazards.

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Here, a novel method for the preparation of anhydrous  $\text{UF}_4$  was developed. This method involved the fluorination of  $\text{UO}_2$  with SBF in 1-methyl-1-butyl piperidinium bis(trifluoromethylsulfonyl)imide (MBPi-TFSI). The effect of reaction parameters (RTIL volume, temperature, water content) on reaction yield and reaction products was investigated. The synthesis conditions enable control over the reaction pathway, allowing tuning of the  $\text{UF}_4$  phase and hydration state through adjustment of reaction conditions.

## Results and discussion

The experimental setup is similar to the one previously used to prepare uranium fluoride microstructures<sup>3,31</sup> and consists of an autoclave and a box furnace. Before performing the fluorination experiment with uranium, the stability of the RTIL in the absence and presence of SBF was evaluated (*vide infra*). In a typical fluorination experiment, uranium dioxide was suspended in the RTIL, and the fluorinating agent (SBF) was introduced in the autoclave but outside of the RTIL, and heated at the desired temperature for 24 hours. A scheme of the setup is shown in Fig. 1, and the detailed procedure is presented in the Experimental section. Following fluorination, the uranium products were collected, washed, and analysed by powder X-ray diffraction (PXRD).

### Evaluation of the RTIL for $\text{UF}_4$ synthesis

To evaluate MBPi-TFSI as the medium for the reaction, its stability was studied by TGA and FTIR spectroscopy in the presence and absence of SBF as a function of temperature. The relevant conditions are listed in Table 1.

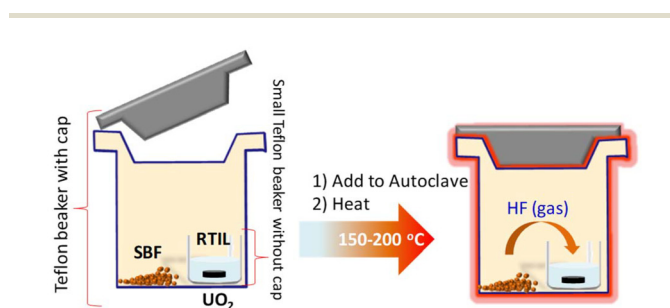


Fig. 1 Experimental setup used for the fluorination of  $\text{UO}_2$  in RTIL.

**Table 1** The experimental conditions ( $T$  and SBF mass) used to evaluate the stability of the RTIL and the observation/product after 24 hours of reaction with 2 mL of RTIL

$T$ ( $^{\circ}\text{C}$ )	SBF (mg)	Observation
200	0	Color change <sup>a</sup>
150	0	No color change
200	312.0 mg (inside RTIL)	Ag metal
200	318.6 mg (outside RTIL)	Color change <sup>a</sup>

<sup>a</sup> Color change from clear to brown.

Previous TGA studies showed TFSI-based RTILs to be stable up to 350  $^{\circ}\text{C}$ .<sup>32,33</sup> Initial experiments (Fig. S1, SI) have shown that the thermal treatment of SBF in RTIL produces Ag metal (Fig. S2 and S3). Silver metal will likely be congruently recovered with the uranium product, affecting both product yield and purity. Control experiment with *in situ* SBF in the absence of  $\text{UO}_2$  powder also resulted in Ag metal, suggesting no involvement of  $\text{UO}_2$  in Ag metal formation (Fig. S4). Consequently, the fluorination of  $\text{UO}_2$  will be performed *ex situ*, with SBF outside the RTIL (see Fig. 1).

Previous TGA studies have shown the RTIL to be thermally stable.<sup>32,33</sup> Here, a noticeable color change from clear to brown was observed after treatment of MBPi-TFSI at 200  $^{\circ}\text{C}$  (Fig. S5). Similar color changes were reported for  $\text{C}_4\text{mimPF}_6$  at 180  $^{\circ}\text{C}$ <sup>20</sup> and for butyl-methylpyrrolidinium-TFSI and butyl methyl-imidazolium-TFSI at  $<250$   $^{\circ}\text{C}$ .<sup>34</sup> Here, the color changes suggest possible thermal degradation or chemical modification of the RTIL under the ionothermal conditions. Typically, TGA studies show the temperature of degradation of the bulk RTIL, whereas the color change may have started before bulk degradation.<sup>34</sup> The FTIR of the colored MBPi-TFSI does not show any difference with neat MBPi-TFSI (Fig. S6), suggesting the extent of degradation to be minor, but leads to the formation of chromophoric impurities.<sup>35</sup> Ionothermal studies indicate no color change at 150  $^{\circ}\text{C}$  (Fig. S7).

### Fluorination of $\text{UO}_2$ in RTIL

The initial study shows MBPi-TFSI to be stable in the temperature range 150–200  $^{\circ}\text{C}$ . Based on initial results, the effect of SBF, RTIL volume, water content, and temperature of the reaction products and yields is examined. The experimental conditions and reaction products are presented in Table 2. An excess of SBF with respect to  $\text{UO}_2$  (molar ratio SBF:  $\text{UO}_2 > 15$ ) was used in all the reactions.

The role of the SBF as a fluorinating agent was confirmed by reacting  $\text{UO}_2$  in MBPi-TFSI without SBF. The product obtained from the control reaction matches well with the starting  $\text{UO}_2$  powder (Fig. S3).<sup>36</sup> This eliminates the possibility of the TFSI anion as the fluorinating agent.

### Effect of RTIL volume

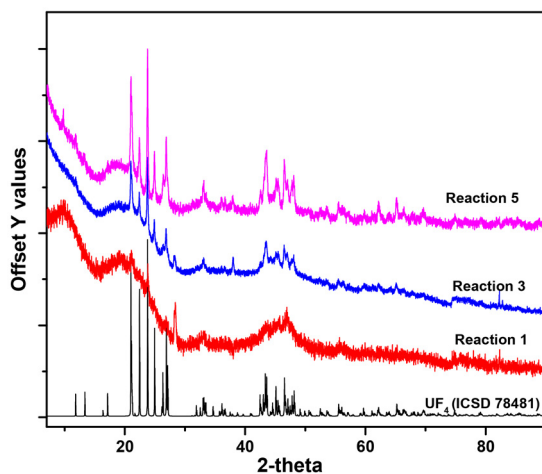
At constant temperature, U/SBF ratio, and water content, a decrease of the RTIL volume should lead to an increase of HF concentration in the RTIL and consequently an increase of the fluorination rate. In this context, several reactions were performed at constant temperature, U/SBF ratio, and various volumes of RTIL (2, 1, and 0.5 mL). For reaction 1 (2 mL of MBPi-TFSI), a powder (Fig. S8) with a green color characteristic of  $\text{UF}_4$  and a very weak diffraction pattern was obtained (Fig. 2). The green powder was further analysed by FTIR and TGA. The TGA shows a major mass loss near the melting point of  $\text{UF}_4$  (1036  $^{\circ}\text{C}$ ) (Fig. S9).<sup>4</sup> A small mass loss near 400  $^{\circ}\text{C}$  may be due to the presence of residual MBPi-TFSI in the solid after the isopropyl alcohol (IPA) washing. The FTIR spectrum of the product was recorded after several IPA washings.



**Table 2** The experimental condition (*T*, UO<sub>2</sub> mass, SBF mass, RTIL volume) and the major product obtained after 24 hours of reaction

Reaction	<i>T</i> (°C)	RTIL (mL)	UO <sub>2</sub> (mg)	Pre-conditioning	SBF (mg)	Major U product (mg) (% yield)
1	200	2	39.6	No	374.0	UF <sub>4</sub> amorphous (42.1) (91.4%)
2	200	2	35.1	Yes	321.5	UF <sub>4</sub> amorphous (35.6) (87.3%)
3	200	1	39.9	No	370.2	UF <sub>4</sub> crystalline (40.1) (87.1%)
4	200	1	37.0	Yes	421.0	UF <sub>4</sub> crystalline (36.1) (83.9%)
5	200	0.5	39.5	No	374.1	UF <sub>4</sub> crystalline (43.5) (94.8%)
6 <sup>a</sup>	200	0.5	38.8	No	384.5	UF <sub>4</sub> amorphous (39.4) (87.4%)
7	150	0.5	33.8	No	357.1	UF <sub>4</sub> amorphous (35.4)(90.1%)

Pre-conditioning: treated under vacuum for 24 hours at 50 °C. <sup>a</sup> RTIL saturated with water prior the reaction.

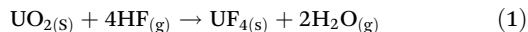


**Fig. 2** PXRD of the product obtained from reactions 1, 3, and 5 and PXRD of UF<sub>4</sub> from the ICSD database (ICSD 78481).<sup>37</sup>

The decrease in the peak intensity >1000 cm<sup>-1</sup> in the FTIR spectrum after the IPA washings suggested the presence of residual MBPi-TFSI in the solid used for the TGA studies (Fig. S10). Those results are consistent with the formation of amorphous UF<sub>4</sub>.

Reaction 3 (1 mL) also resulted in a green solid but with higher crystallinity than reaction 1 (Fig. 2). The TGA of the solid recovered after reaction 3 shows only ~4% mass loss up to 600 °C, likely due to water, residual IPA, or RTIL (Fig. S11).

The primary source of water in the reaction is due to the conversion of UO<sub>2</sub> to UF<sub>4</sub> (eqn (1)).



Though the reaction is performed at 200 °C, a small amount of water may be present in MBPi-TFSI, resulting in the water coordination to the precipitated UF<sub>4</sub>. The PXRD of the recovered sample of reaction 3 after TGA shows the predominant presence of crystalline UF<sub>4</sub> (Fig. S12).

Reaction 5 (0.5 mL) led to an increase in UF<sub>4</sub> crystallinity (Fig. 2), with 94.8% yield. The TGA of the reaction 5 product shows <2.5% mass loss up to 600 °C, with prominent transitions at 45 °C, 175 °C, and 415 °C (Fig. S13). This transition may be arising from residual IPA/H<sub>2</sub>O (45 °C and 175 °C) and RTIL (415 °C) in the anhydrous UF<sub>4</sub> product. The FTIR of the

reaction 5 product was also recorded. Small but distinct peaks (Fig. S13) suggest the presence of residual IPA/H<sub>2</sub>O and RTIL and corroborate well with the TGA data.

To better understand the effect of RTIL volume on reaction products, the concentration of HF in the RTIL (2 mL, 1 mL, and 0.5 mL) after reaction was determined. The HF concentration increases almost 2-fold with the reduction of RTIL volume from 2 mL (0.45 (±0.022) M) to 1 mL (0.92 (±0.025) M) and remains close to 1 M for the 1 mL (0.92 (±0.025) M) and 0.5 mL samples (0.99 (±0.031) M) (Fig. S14). This suggests HF saturation in the RTIL (~1 M) with 1 mL or lower volumes. The increase in the concentration of HF at a lower volume may be the factor driving the formation of crystalline material.

### Effect of water

The RTILs absorb water even at room temperature, and the amount of water depends mainly on the nature of the anion of the RTIL, relative humidity, and temperature.<sup>38–42</sup> To understand the effect of the water content on the reaction product, a pre-conditioning drying step was introduced. In this pre-conditioning step, UO<sub>2</sub>, MBPi-TFSI, and SBF were vacuum dried at 50 °C for 24 hours.

This process was used to dehydrate RTIL<sup>43</sup> and to remove absorbed moisture from solid surfaces. The reaction 2 product is very similar to the reaction 1 product from PXRD and TGA studies (Fig. S15 and S16). This suggests removal of water does not add to any major changes in the UF<sub>4</sub> product at 2 mL volume. No significant change in the PXRD of the product with and without pre-conditioning was observed even for 1 mL RTIL volume (Fig. S17), and hence, the pre-conditioning step was omitted in the further studies.

To further understand the role of water, an additional reaction with water-saturated RTIL was examined (reaction 7). A reaction performed using 2 mL of water-saturated MBPi-TFSI ([H<sub>2</sub>O] ~11 000 ppm) at 200 °C with 0.5 mL RTIL resulted largely in amorphous UF<sub>4</sub> product, but with some peaks in the PXRD, suggesting formation of hydrated UF<sub>4</sub> (Fig. 3). This implies that excess water drives the reaction to the formation of amorphous and hydrated UF<sub>4</sub>.

### Effect of temperature

The studies using a control blank of MBPi-TFSI indicate no color change at 150 °C (Table 1 and Fig. S6). The UF<sub>4</sub> synthesis



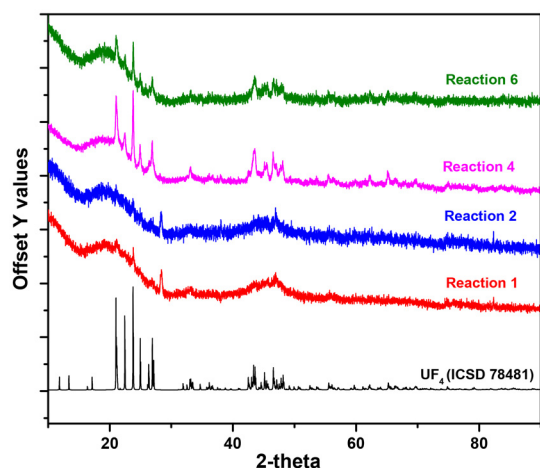


Fig. 3 PXRD of the product obtained from reactions 1, 2, 4, and 6 and PXRD of  $\text{UF}_4$  from the ICSD database (ICSD 78481).<sup>37</sup>

at 150 °C with 0.5 mL of MBPI-TFSI results in an amorphous green product with PXRD peaks corresponding to  $\text{UF}_4$ . Under similar chemical conditions, reaction at 200 °C gives a more crystalline product, suggesting that a lowering in the temperature led to the formation of an amorphous product (Fig. 4).

The use of PXRD to analyse the solid crystalline material is well established, as is its ability to estimate or identify amorphous compounds as impurities. To confirm the product specification, SEM-EDS studies were performed for reaction 5 (Fig. S18 and S19). It is important to mention that the elemental mapping by EDS suffers from poor detection of lower  $Z$  elements such as fluorine. The EDS mapping of the reaction 5 product gave an atomic ratio of 3.57 for F/U (Table S1), which is lower than the expected stoichiometric value due to analytical uncertainties associated with the quantification of fluorine and uranium. In combination with the PXRD results, these data support the assessment of the compound as  $\text{UF}_4$ . The

SEM-EDS studies also indicate the absence of other secondary amorphous phases.

## Conclusions

In summary, a novel method for the preparation of anhydrous  $\text{UF}_4$  in high yield has been developed. The method involves the fluorination of  $\text{UO}_2$  in RTIL using SBF as a fluorinating agent. The volume of RTIL and temperature have an important role in the formation of crystalline  $\text{UF}_4$ . The reaction of  $\text{UO}_2$  with SBF at 200 °C with an RTIL volume of 0.5 to 1 mL gives crystalline  $\text{UF}_4$ . The highest yield (94.8%) was obtained for a volume of 0.5 mL, though a color change in the MBPI-TFSI after the ionothermal reaction was observed, the FTIR spectra of the MBPI-TFSI after the reaction do not show any degradation. The presence of water in the MBPI-TFSI led to the formation of hydrated  $\text{UF}_4$ . The reaction at a lower temperature (150 °C) reduces thermal degradation (*i.e.*, color change) but primarily results in amorphous  $\text{UF}_4$ . The formation of crystalline  $\text{UF}_4$  in MBPI-TFSI in high yield from the fluorination of  $\text{UO}_2$  is promising, and this method could be transposed to other actinides. For example,  $\text{PuF}_4$  could be prepared similarly using  $\text{PuO}_2$  or Pu-oxalates as precursors. Current work is in progress, and results will be reported in due course.

## Experimental

### Materials and methods

**Caution!** <sup>238</sup>Uranium is an  $\alpha$  emitter with  $E_{\text{max}} = 4.26$  MeV. All the manipulations were performed in a designed radiochemistry laboratory equipped with fume hoods and HEPA filters.

Silver bifluoride ( $\geq 99\%$ , Alfa Aesar), 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (iolitec, Germany), and  $\text{UO}_2$  powder were used from the laboratory stock. The PXRD of the  $\text{UO}_2$  powder confirms the phase purity (Fig. S20).

### Fluorination of uranium dioxide in RTIL

For the uranium dioxide fluorination reactions,  $\text{UO}_2$  powder and SBF were placed in autoclaves separated by a Teflon vial. Uranium dioxide (30–35 mg, 0.11–0.13 mmol) powder was mixed with different volumes of MBPI-TFSI (2 mL–0.5 mL), and placed in a 15 mL Teflon vial. The Teflon vial was then placed in the Teflon liner of an autoclave containing an excess of SBF (SBF: 300–350 mg; molar ratio  $[\text{SBF}]/[\text{UO}_2] > 15$ ) (Fig. 1).

A pre-conditioning step was introduced in some samples to dry the reactants before the fluorination reaction. During the pre-conditioning step, the reactants  $\text{UO}_2$ , MBPI-TFSI, and SBF were vacuum dried at 50 °C for 24 hours.

All the fluorination reactions were conducted under air in a Parr model 4749 autoclave using a previously reported procedure.<sup>44</sup> The entire assembly was sealed and added to the autoclave, where it was heated for 24 hours using Thermo Scientific Thermolyne Benchtop Muffle Furnace (model FB1315M) at the predefined temperature.

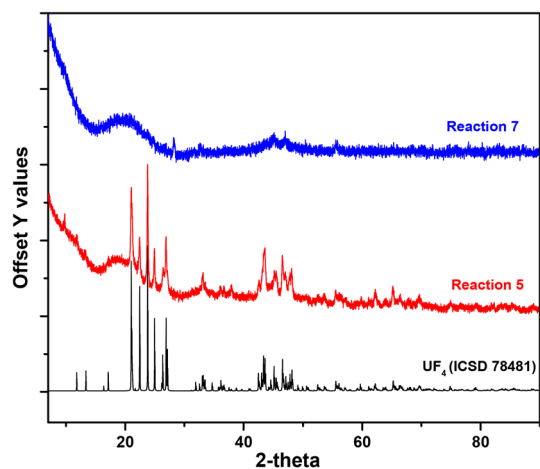


Fig. 4 PXRD of the product obtained from reactions 5 and 7 and PXRD of  $\text{UF}_4$  from the ICSD database (ICSD 78481).<sup>37</sup>



### Recovery of the solid UF<sub>4</sub>

After fluorination, the green product was separated from MBPI-TFSI by centrifugation at 6000 RPM for 15 minutes. The MBPI-TFSI was transferred using a pipette, and the solid product was washed 2–3 times with isopropyl alcohol (IPA, 2 mL) to remove any residual MBPI-TFSI. The removed solid was dried at room temperature and used for further characterization. The FTIR spectrum of the dried solid product was recorded to ascertain complete removal of the MBPI-TFSI and IPA.

### Solid product characterization

**FTIR.** The FTIR spectra were recorded using an Agilent 630 FTIR instrument. The solid was placed on the diamond crystal and pressed to avoid any air gap between the diamond crystal and the solid. One hundred scans were recorded and averaged for each FTIR measurement in the 650–4000 cm<sup>-1</sup> range with 4 cm<sup>-1</sup> resolution.

**Powder X-ray diffraction studies.** The powder X-ray diffraction (PXRD) measurements were performed on a XRDynamic 500 diffractometer (Anton Parr) with a fixed sample stage. The measurements were done with a Cu-K<sub>α</sub> radiation source ( $\lambda = 1.54 \text{ \AA}$ ) from 7° to 90° 2 $\theta$  in Bragg–Brentano geometry. The PXRD patterns were analysed using the PC-PDF database or the ICSD database.

**Scanning electron microscopy (SEM) measurements.** The SEM–EDS analyses for the prepared sample were conducted with a Tescan Clara (Field-Emission scanning electron microscope). The elemental quantification was done with an Oxford EDS detector with an accelerating voltage of 15 kV at a working distance of 15 mm. The samples were mounted on carbon tape without coating.

**TGA measurements.** The TGA–DSC measurements were performed with a TA Instruments SDT 650 Discovery series TGA–DSC from 25–1300 °C with a heating rate of 20 °C per minute. All the samples were measured in alumina cups with lids under a constant flow of argon gas (100 mL min<sup>-1</sup>) over the sample and balance.

**Karl-Fisher titration.** The water content in the MBPI-TFSI was measured using Karl Fisher titration. A known mass of the MBPI-TFSI was added to the anolyte and allowed to equilibrate for 10 seconds. The electrochemically generated I<sub>2</sub> was used for titration. The water saturation of the MBPI-TFSI was achieved by equilibrating an equal volume of the MBPI-TFSI with deionised water (resistivity 18.2 M $\Omega$ ) for 1 hour. The MBPI-TFSI phase was separated by centrifugation at 6000 RPM for 5 minutes, and small aliquots of the MBPI-TFSI were used for the titration.

**HF estimation.** The HF concentration in the MBPI-TFSI phase was determined by both pH measurements and acid–base titration using phenolphthalein as an indicator. A known volume of the MBPI-TFSI (200–300  $\mu$ L) was mixed with twice its volume of deionised water and vortexed. The two phases were separated by centrifugation at 5000 RPM for 10 minutes, and the acidity of the aqueous phase was determined. For pH

measurement, the aqueous phase was diluted 60 times, and the pH of the resulting solution was recorded using thermo-fisher pH meter. For acid–base titration, an aliquot of 25–50  $\mu$ L was added to deionised water and titrated with standard 0.1 M NaOH using phenolphthalein as an indicator.

### Author contributions

Parveen Kumar Verma: conceptualization; data curation, formal analysis, investigation, methodology and writing – original draft. Frederic Poineau: conceptualization, supervision, writing – review and editing. Jason Victor: investigation and laboratory assistance. Kenneth Czerwinski: funding acquisition; conceptualization; supervision; writing – review and editing.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. The supplementary information includes the experimental setup, photographs of the reaction products (RTIL color change and recovered solid product), XRD data of several reactions, TGA data, ATR-FTIR, and SEM-EDS. See DOI: <https://doi.org/10.1039/d5dt02703a>.

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