

Supplementary materials:

### Experimental

[OMim]NTf<sub>2</sub> was synthesized according to literature.<sup>20</sup>

#### *Synthesis of the Deuterated ionic liquid D23-[OMim]NTf<sub>2</sub>*

a) preparation of [D17]-1-octylimidazole:

To a stirred suspension of sodium hydride (1.84 – 27 mmol) (60% in mineral oil – previously washed with pentane) in dry THF (20 mL) cooled to 0°C, was added dropwise a solution imidazole (1.84 g - 27 mmol) in dry THF (10 mL). The mixture was stirred for 30 minutes and allowed to warm to room temperature. A solution of bromooctane – d17 (5,00 g – 25,9 mmol) in dry THF (20 mL) was then added and the mixture was stirred overnight at 40°C.

After cooling to room temperature, the mixture was filtered. The salts were washed with pentane. The combined organic phase were evaporate to dryness, dissolved in pentane and wished twice with water, dried over sodium sulfate and concentrated under vacuum affording [D17]-1-octylimidazole as colorless liquid (4.66 g - > 99%)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.52 (s, 1H); 7.05 (s, 1H); 6.89 (s, 1H)

<sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ(ppm): 137.1; 129.1; 119.0; 46.6 (m); 30.2 (m); 27.9 (m); 25.4 (m); 21.5 (m)

b) preparation of [D17]-1-octyl-[D3]-3-methylimidazolium iodide:

To a trouble solution of [D17]-1-octylimidazole (4,66 g – 23,68 mmol) in acetonitrile (15 mL) was added a solution of iodomethane-d3 (1,7 mL – 26,4 mmol) in acetonitrile (5 mL). The solution became clear and was stirred overnight at room temperature. The yellow mixture was then concentrated to dryness. The residue was then triturated with diethylether and dried under vaccum affording [D17]-1-octyl-[D3]-3-methylimidazolium iodide as a yellow oil (8.14 g – quant).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 10.10 (s, 1H); 7.50 (s, 1H); 7.34 (s, 1H)

<sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): δ(ppm): 137.3; 123.8; 122.1; 49.8 (m); 36.6 (m); 29.2 (m), 27.8 (m); 25.2 (m); 21.4 (m); 13.0 (m).

c)[D17]-1-octyl-[D3]-3-methyl-[D3]-imidazolium bis(trifluoromethylsulfonyl)imide:

To a stirred solution of [D17]-1-octyl-[D3]-3-methylimidazolium iodide (8.14 g – 23.8 mmol) in D<sub>2</sub>O (10 mL) was added potassium hydroxide (0.2 g – 4,7 mmol). The mixture was then heated at 60°C over night. After cooling to room temperature, a solution of lithium bis(trifluorosulfone)imide (7,49 g – 26 mmol) in D<sub>2</sub>O (15 mL) was added and the solution was stirred for 3 hours.

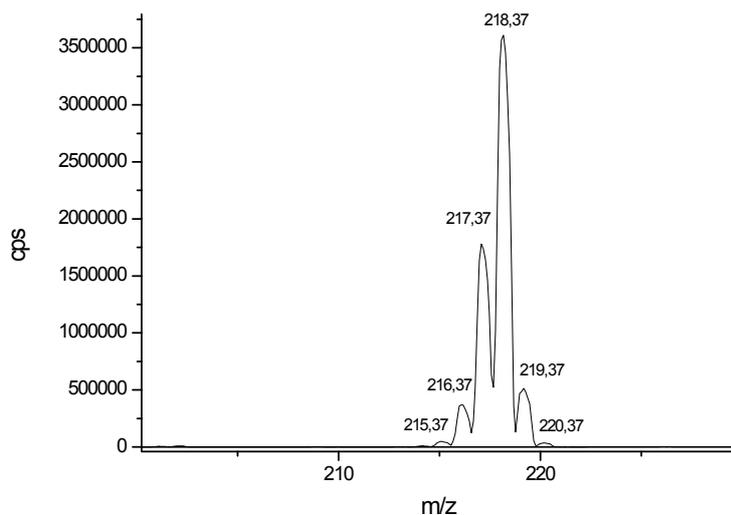
Aqueous was phase then removed and the ionic liquid was washed with D<sub>2</sub>O until pH reaches neutrality and the silver nitrate test becomes negative (4 x 30 mL). The organic phase was then dried under vacuum at 60°C for 3 h affording the [D23]-octylmethylimidazolium bis(trifluorosulfone)imide as slightly viscous yellow oil (11,3 g – 96%)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ(ppm): -79.0

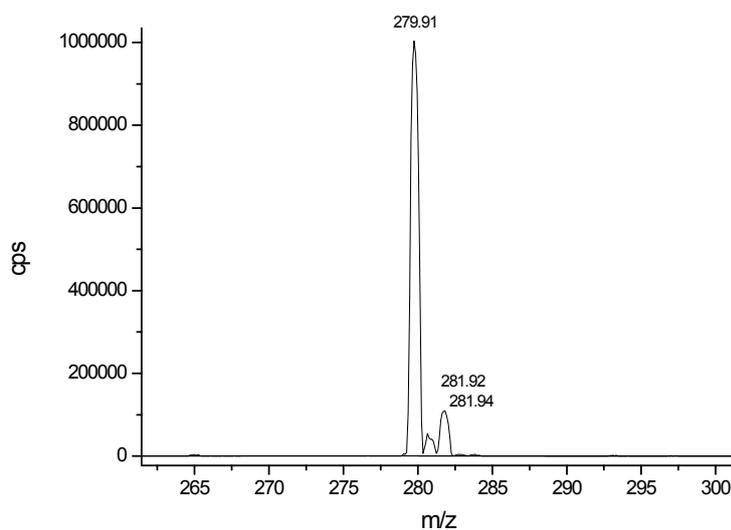
$^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm): 135.9 (t,  $J = 33.0$  Hz); 123.5 (t,  $J = 30.0$  Hz); 122.1 (t,  $J = 30.0$  Hz); 124.8-121.6-118.4-115.2 (q,  $J = 321$  Hz,  $\text{CF}_3$ ); 49.7 (m); 35.9 (m); 29.0 (m), 27.8 (m); 25.0 (m); 21.4 (m); 13.0 (m).

MS (ESI+)  $m/z$ : 215.37 (1.3 %); 216.37 (9.5 %); 217.37 (47.8 %); 218.37 (100.0 %); 219.37 (14.2 %); 220.37 (0.9 %).

MS (ESI-)  $m/z$ : 279.94 (100 %); 280.91 (4.1 %); 281.92 (10.9 %)



ESI MS (+) of [D23]-[OMIM] NTf2



ESI MS (-) of [D23]-[OMIM] NTf2

Extraction analysis:

Uranium and iron extractions were analysed by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES, Spectro Arcos). Water extraction was characterized by Karl Fisher titration of the organic phases using a Metrohm 831 KF Coulometer, while phosphoric acid extraction was determined on back extracted aqueous phases by phosphorous analysis using ICP-AES.

The distribution coefficients of the metals and the selectivity were computed from the ICP-AES results:

$$D_M = \frac{[M]_{initial} - [M]_{aq}}{[M]_{aq}} \quad \text{and} \quad \alpha_{U/Fe} = \frac{D_U}{D_{Fe}}$$

$D_M$  - distribution coefficient of the metals (uranium or iron)

$[M]_{initial}$  – initial concentration of metal in the aqueous phase before the contact

$[M]_{aq}$  – remaining metal concentration in the aqueous phase after the contact, measured by the ICP-AES

Extraction properties of pure [OMim]NTf<sub>2</sub> compared to synergistic ratio of HDEHP/TOPO in IL:

	$D_U$	$\alpha_{u/Fe}$	H <sub>2</sub> O (mmol/L)	H <sub>3</sub> PO <sub>4</sub> (mmol/L)
Pure [OMim]NTf <sub>2</sub>	0.076	5.6	610	0.25
40% of TOPO in HDEHP/TOPO mixture in IL	2.1	47	748	39

**Table 1** Extraction properties of pure [OMim]NTf<sub>2</sub> compared to synergistic ratio of HDEHP/TOPO in IL

#### Small angle X-ray scattering

SAXS experiments were carried out on a bench built by Xenocs and using Mo radiation ( $\lambda = 0.71 \text{ \AA}$ ). A large on-line scanner detector (MAR Research 345) located at 750 mm from the sample stage was used to record the scattered beam. Thanks to off-centre detection, a large scattering vector  $q$  range was covered ( $2 \times 10^{-1} \text{ nm}^{-1} < q < 30 \text{ nm}^{-1}$ ). Collimation was applied using a 12:∞ multilayer Xenocs mirror (for Mo radiation) coupled to two sets of Forvis scatterless slits providing a 0.8 mm × 0.8 mm X-ray beam at the sample position. The experimental resolution is  $\Delta q/q = 0.05$ . The detector count is normalized to differential cross section per volume (in  $\text{cm}^{-1}$ ) with either a 2.36-mm-thick high-density polyethylene sample (from Goodfellow®) ( $I_{\text{max}} = XX \text{ cm}^{-1}$ ) and 3 mm water for which the level of scattering at low  $q$  is known ( $1.64 \times 10^{-2} \text{ cm}^{-1}$ )[39]. Data preanalysis was performed using FIT2D software, taking into account the electronic background of the detector (the flat field response being homogeneous), transmission measurements (using a photodiode that can be inserted upstream the sample) and empty cell subtraction. The scattering intensities were thus expressed versus the magnitude of the scattering vector.

#### Small angle neutron scattering

SANS experiments were performed at the French neutron facility Laboratoire Léon Brillouin/Orphée (LLB/Orphée) on PACE and PAXY spectrometers. Two configurations were used on the PAXE spectrometer with one sample to detector distance of 1145 mm, two values of wavelength  $\lambda$  respectively equal to 7.8 Å and 4 Å ( $\Delta\lambda/\lambda \approx 10\%$ ) and a standard two diaphragms collimation geometry (7 mm/20 mm, collimation distance of 2500 mm). By shifting the position of the detector relative to the neutron beam center, we can both increase the accessible  $Q_{\max}$  and the overlap between the two configurations which permit to cover a total  $q$ -range from 0.01 to 0.6 Å<sup>-1</sup>. All measurements were done under atmospheric pressure and room temperature. Measurements were performed in quartz Hellma cells of optical path of 2 mm. Pasinet software (ref Pasinet: <http://didier.lairez.fr/dokuwiki/doku.php?id=pasinet>) was used for data reduction, standard corrections (for sample volume, neutron beam transmission, empty cell signal subtraction, inelastic scattering, and detector efficiency) and normalization procedure (from the incident neutron beam).

Guinier determination of the aggregates radii:

