

Electronic Supplementary Information

Ionic liquids with polychloride anions as effective oxidants for the dissolution of UO_2

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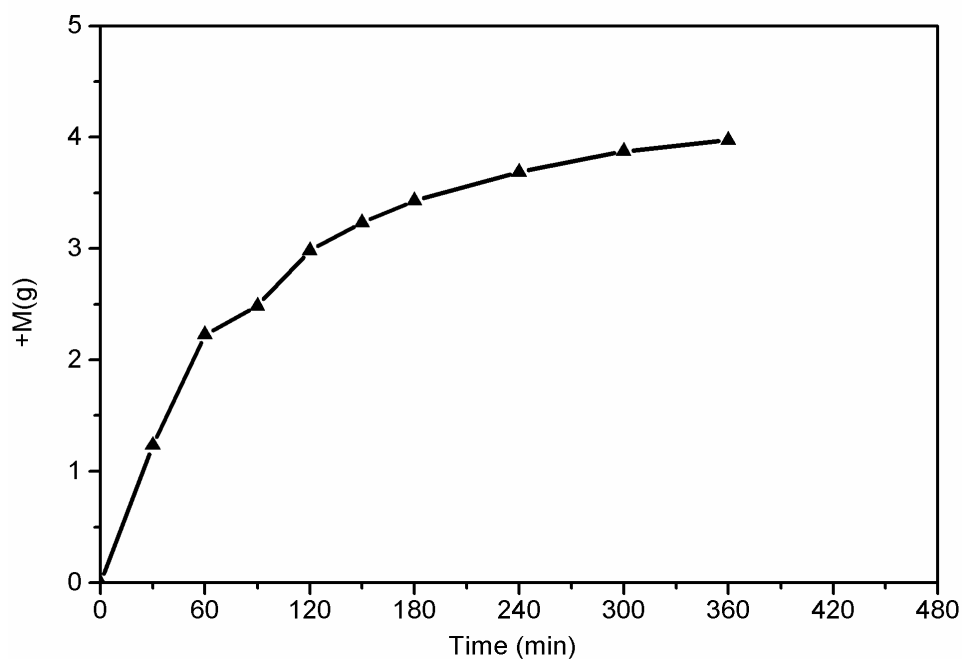


Fig. S1 Mass gain of [Pmim]Cl IL with the addition of chlorine gas as a function of time.

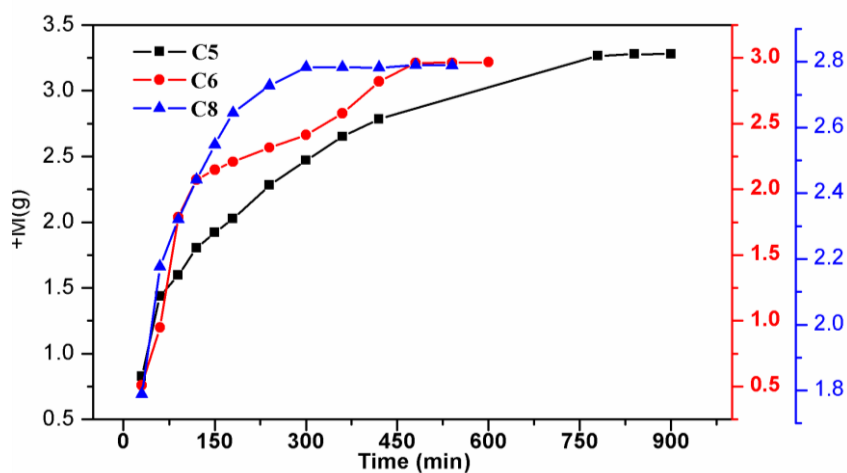


Fig. S2 Mass gain of [Pnmim]Cl, [Hmim]Cl and [Omim]Cl IL with the addition of chlorine gas as a function of time (■ [Pnmim]Cl, ● [Hmim]Cl and ▲ [Omim]Cl).

Table S1 The amount of Cl₂ uptake (mmol) after reaching equilibrium in the mixed ILs with different molar ratios of [Bmim]Cl versus [Bmim][Tf₂N].

molar ratio ([Bmim]Cl vs. [Bmim][Tf ₂ N])	1 : 0	1 : 1	1 : 2	1 : 4	0 : 1
[Bmim]Cl (mmol)	17.17	5.05	2.96	1.62	0
[Bmim][Tf ₂ N] (mmol)	0	5.05	5.92	6.48	7.15
Cl ₂ uptake (mmol)	31.05	7.54	4.92	3.35	1.14
Cl ₂ solubility in [Bmim][Tf ₂ N] (mmol)	—	0.81	0.94	1.03	1.14
molar ratio of [Cl] _{Cl} /[Bmim]Cl	4.62	3.67	3.68	3.85	0
molar ratio of [Cl] _T /[Bmim]Cl	4.62	3.99	4.32	5.13	—

[Cl]_T means, the mole amount of Cl resulting from all the amount of chlorine gas absorbed by the IL mixture and [Bmim]Cl. [Cl]_{Cl} means, the mole amount of Cl resulting from Cl₂ soluble in [Bmim]Cl (all the amount of chlorine gas absorbed by the IL mixture, subtracts, that from a part of Cl₂ soluble in [Bmim][Tf₂N]) and [Bmim]Cl.

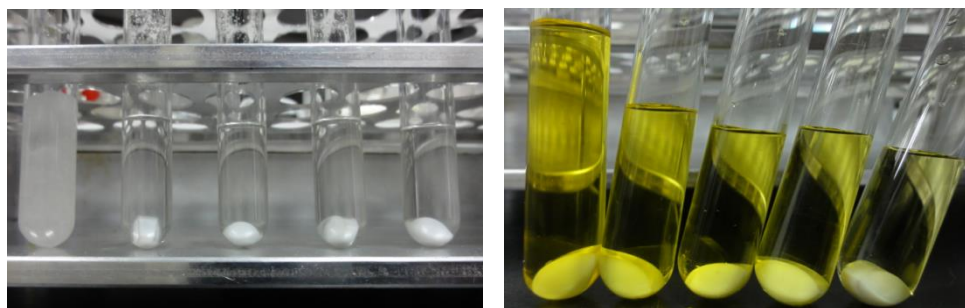


Fig. S3 Different molar ratio mixed ILs of [Bmim]Cl and [Bmim][Tf₂N] (1 : 0, 1 : 1, 1 : 2, 1 : 4 and 0 : 1 from left to right) before and after adding Cl₂.

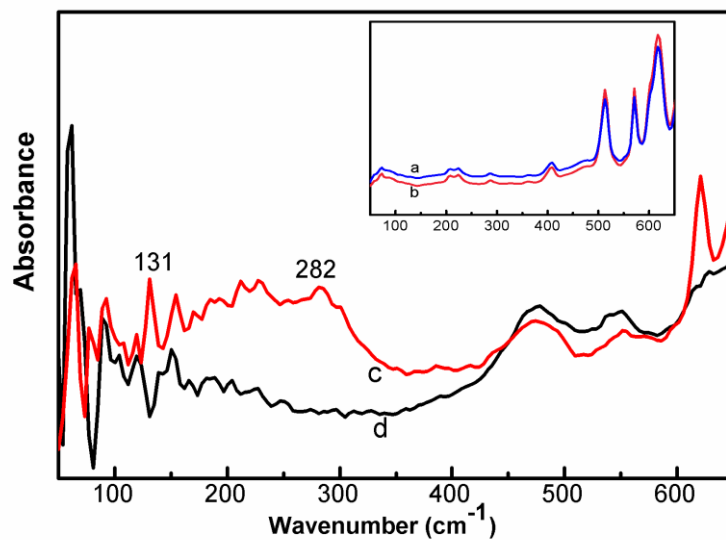


Fig. S4 IR spectra of (a) [Bmim][Tf₂N], (b) passing Cl₂ into [Bmim][Tf₂N] for one hour, (c) passing Cl₂ into [Bmim]Cl for one hour, and (d) [Bmim]Cl.

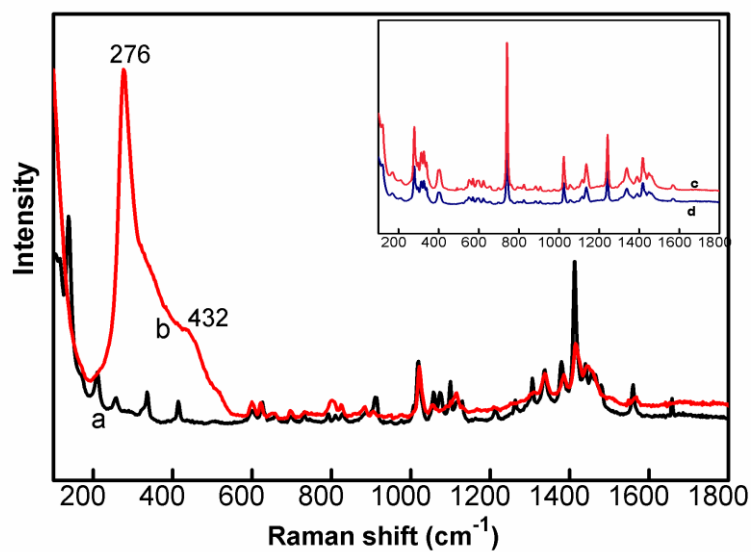


Fig. S5 Raman spectra of (a) [Bmim]Cl, (b) passing Cl₂ into [Bmim]Cl for one hour, (c) [Bmim][Tf₂N] and (d) passing Cl₂ into [Bmim][Tf₂N] for one hour.

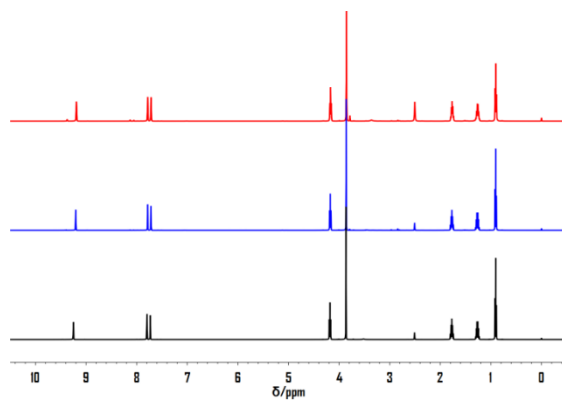


Fig. S6 ^1H NMR spectra of: the crystal obtained, the UO_2 reaction solution and the pure unreacted ionic liquid mixtures (from top to bottom).

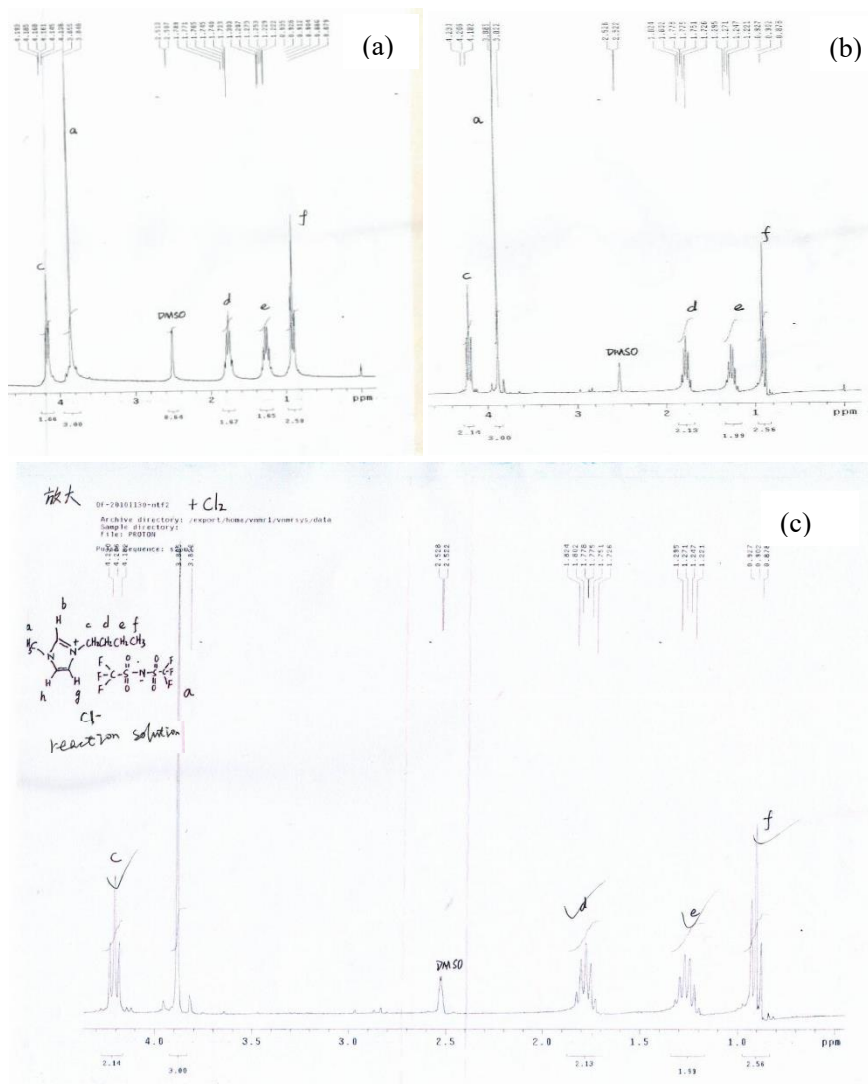


Fig. S7 ^1H NMR spectra of: (a) the unreacted ionic liquid mixtures, (b) the UO_2 reaction solution after bubbling chlorine gas, and (c) the expanded NMR spectra of (b).

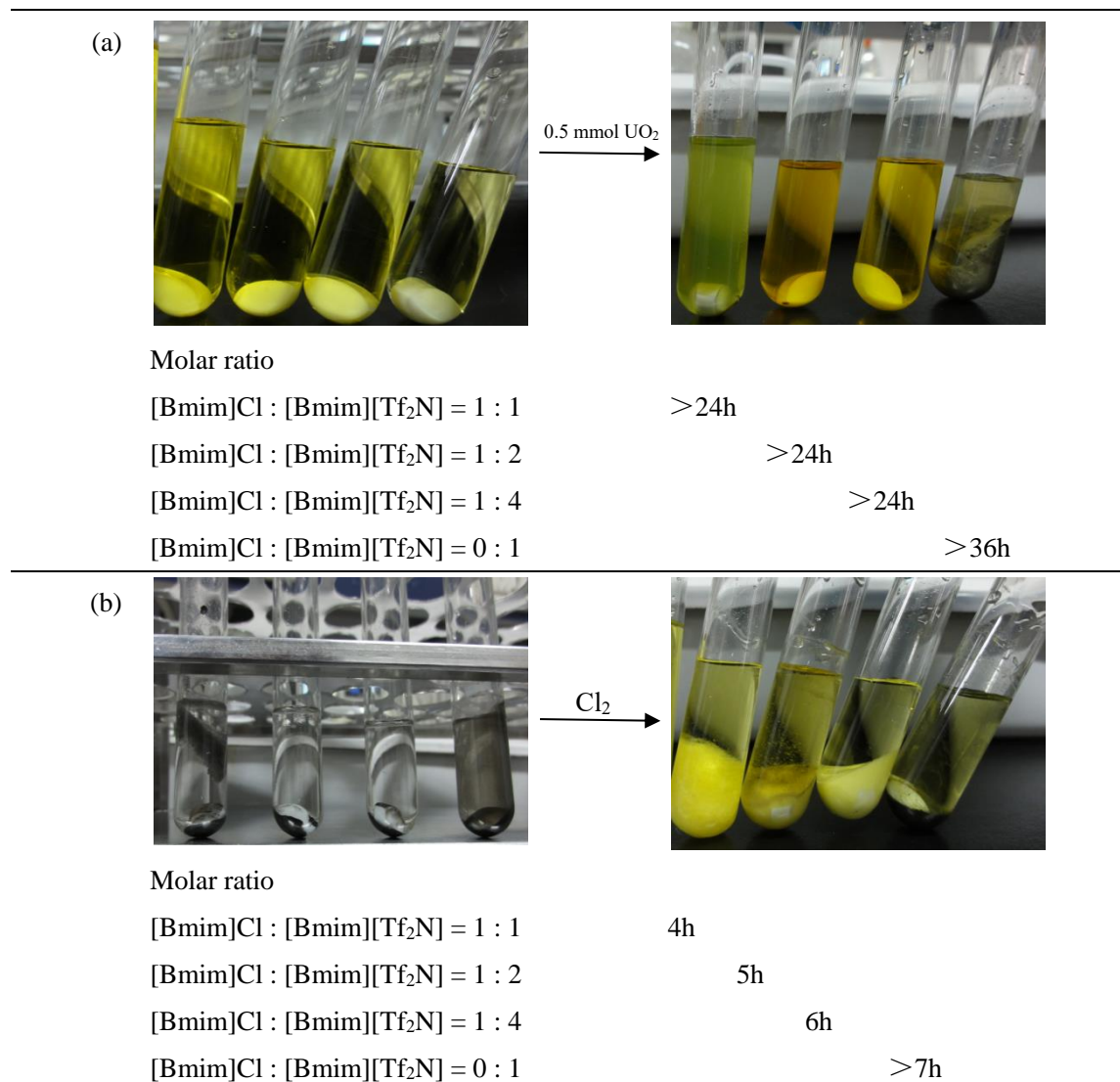


Fig. S8 Photograph of the 0.5 mmol of UO_2 dissolution in the mixed ILs using two different methods at a certain time (a, adding UO_2 into the synthesized polychloride ILs, and b, adding Cl_2 into the UO_2 reaction mixture filled with $[\text{Bmim}]\text{Cl}$ and $[\text{Bmim}][\text{Tf}_2\text{N}]$).

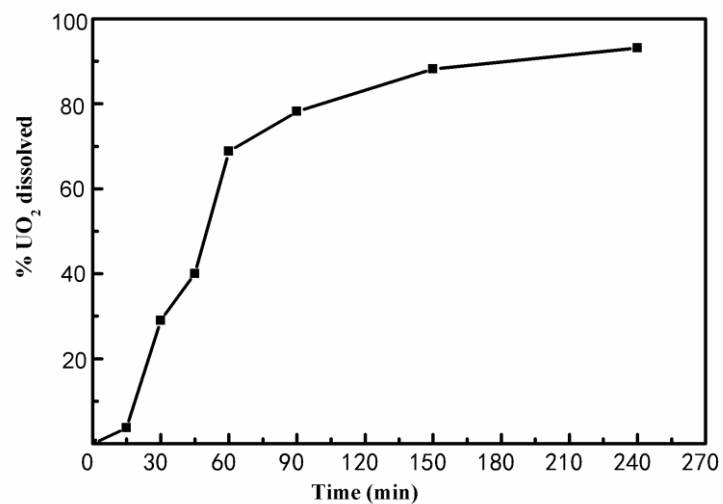


Fig. S9 % UO₂ dissolved in the mixed IL of [Bmim]Cl and [Bmim][Tf₂N] at room temperature as a function of duration Cl₂ time (0.3 mmol UO₂, 1.28 mmol [Bmim]Cl and 3.5 mmol [Bmim][Tf₂N]).

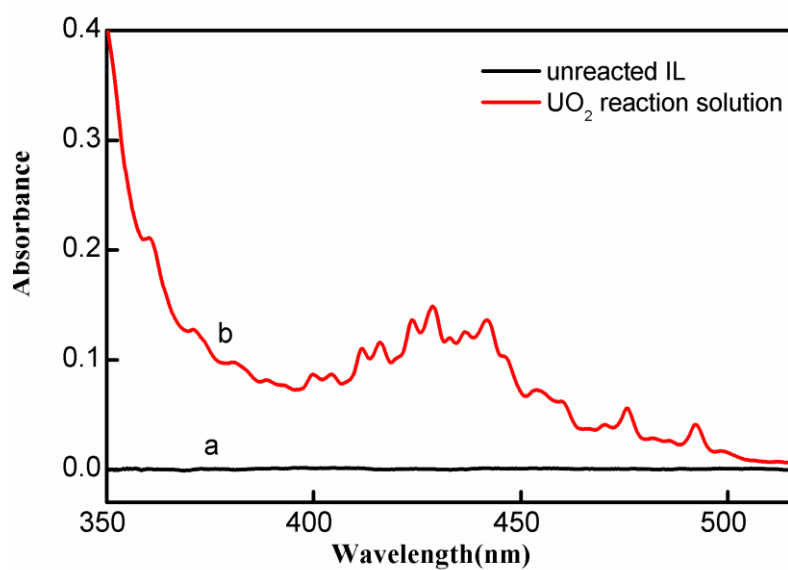


Fig. S10 UV-visible absorption spectra for (a) the unreacted IL mixture, and (b) UO₂ reaction solution in the mixed IL.

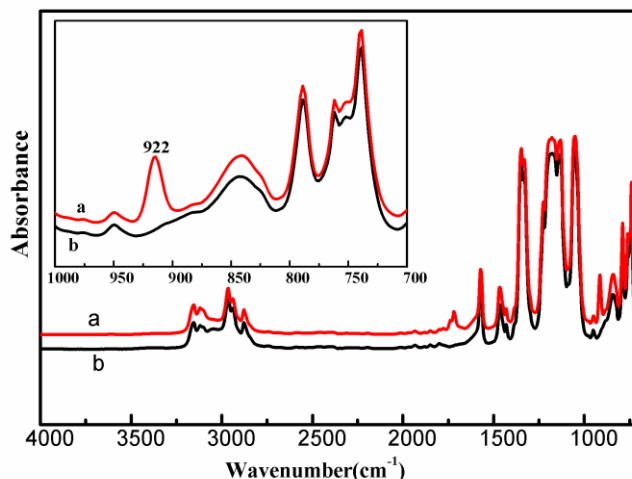


Fig. S11 ATR-IR spectra for (a) UO_2 reaction solution in the mixed IL, and (b) the unreacted IL mixture.

The water effect for the dissolution of Gd_2O_3 in the mixture of $[\text{Bmim}]\text{Cl}$ and $[\text{Bmim}][\text{Tf}_2\text{N}]$

Gadolinium(III) oxide (0.395 g) was separately added to the system from A to C (Table S2) at room temperature for two hours by bubbling dry chlorine gas into the reaction system, and H_2O in Table S2 means the artificial additional ultrapure water. Before the experiments, all the ILs were kept in a vacuum drying oven at $70\text{ }^\circ\text{C}$ for 24 h. The solution was centrifuged (5500 rpm, 5 min), the liquid was decanted, and 0.3 mL of the liquid was taken out and analyzed for its metal content by ICP-AES.

Table S2 The dissolution of Gd_2O_3 in the system of $[\text{Bmim}]\text{Cl}$ and $[\text{Bmim}][\text{Tf}_2\text{N}]$ (3 g, molar ratio:1/2).

System ID	Component	dissolved $\text{Gd}_2\text{O}_3/\text{mg}$
A	0.517g $[\text{Bmim}]\text{Cl}$, 2.48 g $[\text{Bmim}][\text{Tf}_2\text{N}]$	0.78
B	A + 0.022g H_2O	29.8
C	A + 0.171g H_2O	121.5

It could be found that almost 0.78 mg Gd_2O_3 dissolved in the system A, and the water amounted to 1670 ppm after the dissolution experiment. The dissolution amount of Gd_2O_3 increased with the artificial water addition into the reaction system, 29.8 mg in system B and 121.5 mg in system C. It suggested that water made the chlorine gas into HCl and HClO acid, thus producing reactive protons and leading to the

dissolution of Gd₂O₃. It has been reported that the availability of reactive protons is essential for the dissolution of metal oxides in ionic liquids.¹⁻⁴

Table S3 Crystallographic data for [Bmim]₂[UO₂Cl₄].

Compound	[Bmim] ₂ [UO ₂ Cl ₄]
Chemical formula	C ₁₆ H ₃₀ Cl ₄ N ₄ O ₂ U
<i>T</i> (K)	293(2)
Formula weight	690.27
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	8.5021(2)
<i>b</i> , Å	17.4789(3)
<i>c</i> , Å	10.3866(2)
<i>β</i> , deg	125.2340(10)
<i>V</i> , Å ³	1260.75(4)
<i>Z</i>	2
<i>D_c</i> , g/cm ³	1.818
<i>μ</i> (Mo Kα), mm ⁻¹	6.878
<i>F</i> (000)	660
Crystal size, mm ³	0.20 × 0.18 × 0.05
<i>T</i> _{min} , <i>T</i> _{max}	0.316, 0.721
<i>θ</i> _{min} , <i>θ</i> _{max} , deg	3.42, 27.50
no. total reflns.	18214
no. uniq. reflns. (<i>R</i> _{int})	2895 (0.0473)
no. obs. [<i>I</i> ≥ 2σ(<i>I</i>)]	1967
no. params	124
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0247, 0.0577
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (all data)	0.0474, 0.0623
GOF	0.988
Δρ, e/Å ^{3c}	0.420, -0.826
max. and mean Δ/σ ^d	0.000, 0.000

^a*R*₁ = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^b*wR*₂ = [Σ*w*(*F*_o² - *F*_c²)²]/Σ*w*(*F*_o²)²]^{1/2}. ^cMaximum and minimum residual electron density. ^dMaximum and mean shift/sigma.

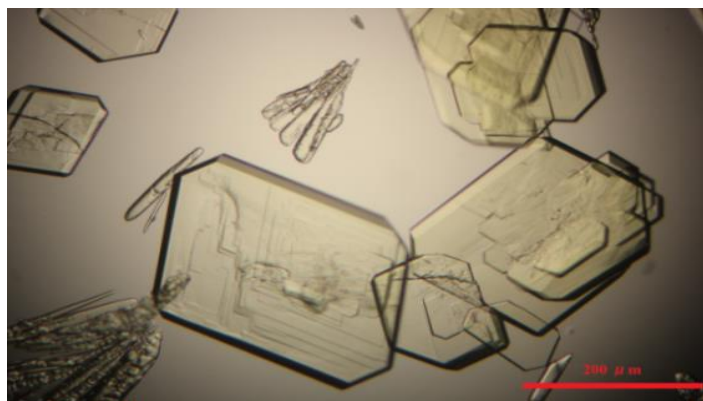


Fig. S12 The polarizing optical microscopy photos of [Bmim]₂[UO₂Cl₄].

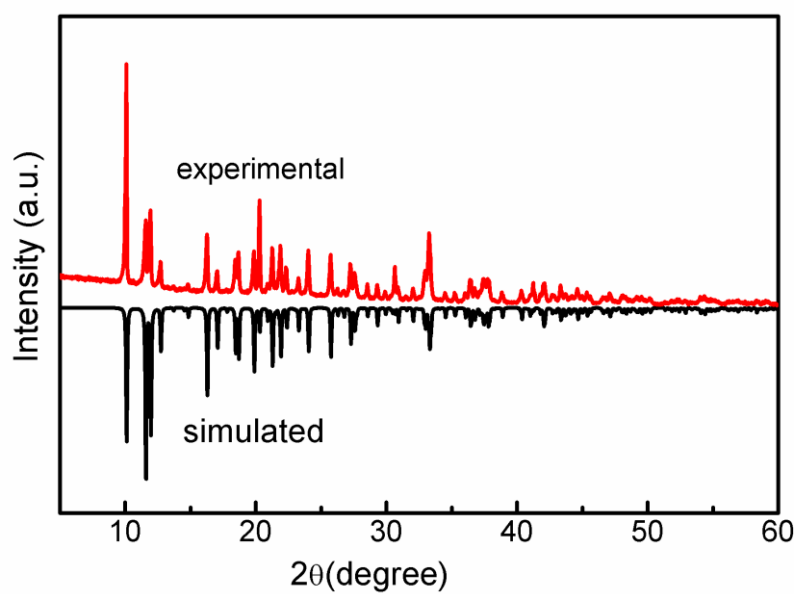


Fig. S13 Experimental (red) and simulated (black) PXRD patterns of [Bmim]₂[UO₂Cl₄].

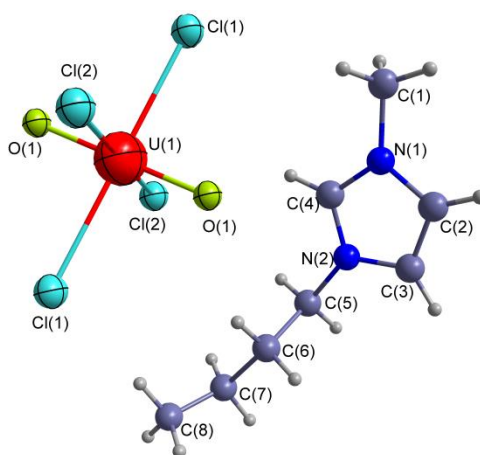


Fig. S14 ORTEP drawing of the [Bmim]⁺ cation and the [UO₂Cl₄]²⁻ anion. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

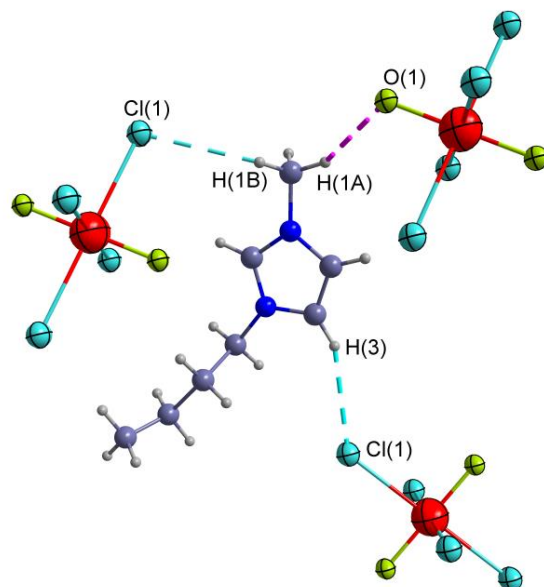


Fig. S15 Representation of C-H...O and C-H...Cl interactions in the solid compound
[Bmim]₂[UO₂Cl₄].

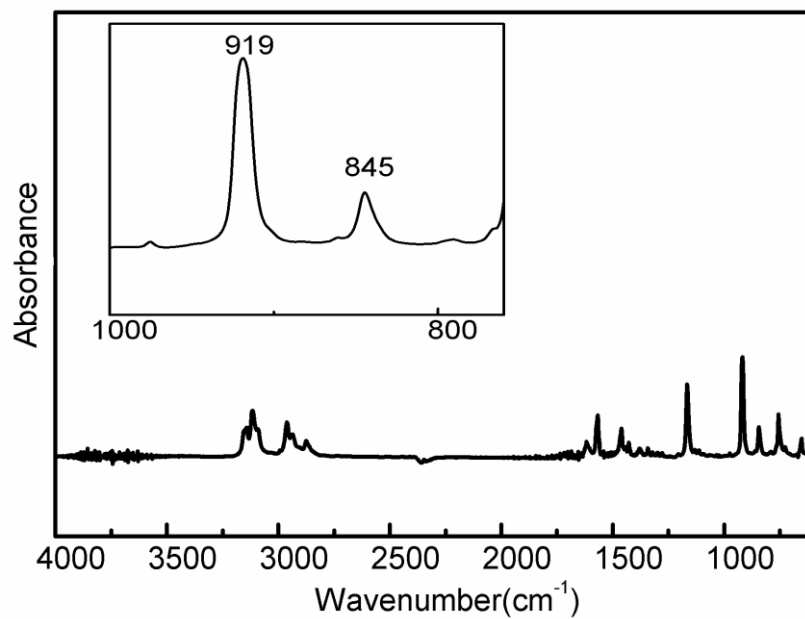


Fig. S16 IR spectra of the U-crystal obtained from the dissolved IL mixture at room temperature.

Reference:

- [1] I. Billard, C. Gaillard and C. Hennig, *Dalton Trans.*, 2007, 4214-4221.

- [2] P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978-20992.
- [3] P. Nockemann, R. Van Deun, B. Thijs, D. Huys, E. Vanecht, K. Van Hecke, L. Van Meervelt and K. Binnemans, *Inorg. Chem.*, 2010, **49**, 3351-3360.
- [4] S. Wellens, T. Vander Hoogerstraete, C. Möller, B. Thijs, J. Luyten and K. Binnemans, *Hydrometallurgy*, 2014, **114**, 27-33.