

ELECTRONIC SUPPORTING INFORMATION

Highly selective extraction of the uranyl ion with hydrophobic amidoxime-functionalized ionic liquids via η^2 coordination

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Experimental:

Reagents were used as obtained from commercial sources (Sigma-Aldrich, Milwaukee, WI) unless otherwise noted. All solvents were 'solvent grade' and used as received without additional purification. The cyano-derivatized imidazolium halides (**a** and **b**) were synthesized by a previously reported procedure.¹ The ¹H and ¹³C NMR spectra were recorded using Bruker AV-360 and AV-500 (Karlsruhe, Germany) spectrometers operating at 500 or 360 MHz and 125 MHz, respectively. Infrared (IR) analyses were obtained by direct measurement of the neat samples by utilizing a Bruker Alpha FT-IR instrument, Bruker Optics Inc. (Billerica, MA) featuring an attenuated total reflection (ATR) sampler, and spectra were obtained in the range of $\nu_{\text{max}} = 400\text{--}4000\text{ cm}^{-1}$. Thermogravimetric analyses (TGA) were performed using a TGA 2950, TA Instruments, Inc. (New Castle, DE). These experiments were conducted under air atmosphere and measured in a dynamic heating regime. Samples between 5–10 mg were heated from 30–800 °C under constant heating ramp of 5 °C min⁻¹ with a 60 min isotherm at 75 °C.

Synthesis of ILs:

Caution! Chloroacetonitrile is a hazardous irritant/lachrymator potentially tumorigenic/teratogenic/mutagenic. Protective clothing/gloves and a properly ventilated workspace should be utilized when handling this material. Please refer to Material Safety Data Sheet (MSDS) for further details (CAS # 107-14-2). Hydroxylamine can become explosive if concentrated above 50 wt%. Please refer to Material Safety Data Sheet (MSDS) for further details (CAS # 7803-49-8).

1-(Cyanomethyl)-3-methyl-1H-imidazol-3-ium chloride (a): 10.0 g (1 eq, 121 mmol, 9.7 mL) methyl imidazole and 11.0 g (1.2 eq, 146 mmol, 9.25 mL) chloroacetonitrile were stirred in air at room temperature for 8 h. A solid product was formed and was washed with ethyl acetate (3 x 100 mL) to remove unreacted reagents. The solid was filtered and dried in air to give 18.40 g of a grey/brown material. Yield = 96.5% ¹H NMR (360 MHz, DMSO-d₆) δ 9.48 (s, 1H), 7.98 (t, *J* = 1.8 Hz, 1H), 7.86 (t, *J* = 1.8 Hz, 1H), 5.76 (s, 2H), 3.92 (s, 3H).

1-(3-Cyanopropyl)-3-methyl-1H-imidazol-3-ium chloride (b): 10.00 g (1 eq, 121 mmol, 9.70 mL) methyl imidazole and 11.00 g (1.2 eq, 146 mmol, 9.25 mL) 4-chlorobutanenitrile were stirred in air at 50 °C for 8 h. An oily product was formed and was washed with ethyl acetate (3 x 100 mL) to remove unreacted reagents. The residual ethyl acetate was removed under vacuum to give 18.15 g of a grey/brown material. Yield = 80.8% ¹H NMR (360 MHz, DMSO-d₆) δ 9.34 (s, 1H), 7.88 (t, *J* = 1.8 Hz, 1H), 7.80 (t, *J* = 1.8 Hz, 1H), 4.30 (t, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.16 (quin, *J* = 7.2 Hz, 2H).

1-(2-Amino-2-(hydroxyimino)ethyl)-3-methyl-1H-imidazol-3-ium

bis(trifluoromethylsulfonyl)amide ([AO1mim][NTf₂]): 1.00 g (6.35 mmol) 3-(cyanomethyl)-1-methyl-1H-imidazol-3-ium chloride (b) and 0.625 mL (0.671 g, 10.2 mmol, 1.6 eq) 50% aqueous NH₂OH solution were dissolved in 10 mL H₂O and heated overnight at 80 °C. The solution was cooled and 2.20 g (7.8 mmol, 1.2 eq) lithium bis(trifluoromethylsulfonyl)amide was added. The product phase separated from the aqueous layer after overnight stirring. The separated product was further purified by dissolution in acetone, drying over MgSO₄, and decolorizing with carbon black. The trace water was removed under high vacuum to give 1.10 g of a slightly yellow liquid. Yield = 39.6% ¹H NMR (360 MHz, DMSO-d₆) 9.51 (s, 1H), 9.12 (bs, 1H), 7.71 (m, 2H), 5.86 (bs, 2H), 4.80 (s, 2H), 3.88 (s, 3H) ¹³C NMR (360 MHz, DMSO-d₆) 147.81, 137.69, 123.72, 123.52, 118.68, 49.11, 36.20; FT-IR (ν_{max} in cm⁻¹) 3480 (w), 3379 (w), 3159 (w), 1672 (m), 1578 (m), 1345 (s), 1178 (s), 1130 (s), 1050 (s), 904 (w), 841 (w), 790 (m), 740 (m), 610 (s), 569 (s), 507 (s).

1-(4-amino-4-(hydroxyimino)butyl)-3-methyl-1H-imidazol-3-ium

bis(trifluoromethylsulfonyl)amide ([AO2mim][NTf₂]): 1.00 g (4.34 mmol) 3-(cyanopropyl)-1-

methyl-1H-imidazol-3-ium bromide (**b**) and 0.625 mL (0.671 g, 10.2 mmol, 2.3 eq) 50% NH₂OH solution were dissolved in 10 mL H₂O and heated overnight at 80 °C. The solution was cooled and 2.20 g (7.8 mmol, 1.8 eq) lithium bis(trifluoromethylsulfonyl)amide was added. The product separated from the aqueous layer after stirring overnight. The separated product was further purified by dissolution in acetone, drying over MgSO₄, and decolorizing with carbon black. The trace water was removed under high vacuum to give 1.65 g of a clear liquid. Yield = 82.0% ¹H NMR (500 MHz, DMSO-d₆) 9.08 (s, 1H), 8.83 (bs, 1H), 7.74 (s, 1H), 7.69 (s, 1H), 5.42 (bs, 2H), 4.16 (t, *J* = 6 Hz, 2H), 3.85 (s, 3H), 2.01 (m, 2H), 2.00 (m, 2H) ¹³C NMR (125 MHz, d₆-DMSO) 151.96, 137.14, 124.01, 122.77, 118.68, 48.84, 40.489, 36.18, 27.90, 26.87; FT-IR (*v*_{max} in cm⁻¹) 3492 (w), 3383 (w), 3157 (w), 1660 (m), 1575 (m), 1346 (s), 1178 (s), 1130 (s), 1050 (s), 931 (w), 838 (w), 789 (m), 740 (m), 611 (s), 569 (s), 508 (s).

Metal Complex Synthesis:

A spot test for reactivity of uranyl towards the ionic liquids was conducted by mixing 1-2 mL of ~0.005 M UO₂(NO₃)₂ • 6H₂O dissolved in methanol with about 50 mg of either ionic liquid. For both ionic liquids, the color of the methanol solution immediately changed from yellow to red-orange upon mixing the uranyl solution and the ionic liquid. X-ray quality single crystals were obtained from the mixture of UO₂(NO₃)₂•6H₂O and [AO2mim][NTf₂] after several days of slow evaporation under ambient conditions.

Extractions:

Caution! ²³⁸U and ²³²Th are radioactive and weak alpha emitters. Handle with gloves and avoid raising dust. ²³³U and ^{152,154}Eu are highly radioactive alpha and gamma emitters. Minimize handling time and activity used to reduce exposure. Consult and comply with all local regulations regarding storage and disposal of radioactive materials.

The activities (counts per minute, cpm) of the solutions were measured using a Packard Cobra-II gamma counter (Meriden, CT). The counting windows for each isotope were as follows: 15-200 keV for ²³³U, 15-1600 keV for ^{152,154}Eu, and 15-500 keV for ²³²Th.

Prior to extraction the IL was equilibrated with water by mixing 0.64–0.79 g IL and 0.7 mL deionized water followed by vortexing (2 min) and centrifugation (2000 g, 2 min) to separate the phases. Either Eu³⁺ or UO₂²⁺ tracers (²³³UO₂Cl₂, *ca.* 0.005 μCi, ¹⁵²EuCl₃, *ca.* 0.01 μCi) were

then added to the aqueous phase followed by vortexing (2 min) and centrifugation (2000 g, 2 min). After separating the phases, 150 μL of each phase was dispensed into plastic tubes and the gamma activity was measured. The distributions ratios were calculated as the activity (counts per minute, cpm) in the IL (lower) phase divided by the activity in the aqueous (upper) phase. Each experiment was done in duplicate and the results agreed within 5%.

Due to the lower activity of ^{232}Th , a more concentrated solution, 0.027 M ThCl_4 , was prepared for use. After the water and IL phases were equilibrated, as mentioned above, the water phase was removed and 0.700 mL of 0.027 M ThCl_4 ($^{232}\text{ThCl}_4$, *ca.* 0.001 μCi) was added followed by vortexing (2 min) and centrifugation (2000 g, min). After separating the phases, 150 μL of each phase was dispensed into plastic tubes and the gamma activity was measured using a Packard Cobra-II gamma counter. The distributions ratios were calculated as the activity in the IL (lower) phase divided by the activity in the aqueous (upper) phase. The experiment was done in duplicate and the results agreed within 5%.

Metal ion extractions with a $^{233}\text{UO}_2\text{Cl}_2$ radiotracer were carried out in varying concentrations of HNO_3 (0.001 – 10 M) and NaNO_3 (0.001 – 4 M). These solutions were prepared as follows: stock solutions of 10 M HNO_3 or 4 M NaNO_3 were prepared by weighing the appropriate amount of either reagent into volumetric glassware and dissolving in or diluting with deionized water. These solutions were further diluted with deionized water to prepare the aqueous phases for the extraction experiments. The extractions were then conducted using the same procedure as above, and the distribution ratios plotted as a function of concentrations.

Millimolar extractions were performed using the same procedure as above for analysis by ^1H and ^{19}F NMR. 76 mg (0.015 mmol) $\text{UO}_2\text{NO}_3\cdot 6\text{H}_2\text{O}$ was dissolved in 5 mL distilled water. The pH of the solution was ~ 5 . 750 mg (1.6 mmol) $[\text{AO}2\text{mim}][\text{NTf}_2]$ was added and the two solutions were vortexed. The pH of the resulting aqueous phase remained at ~ 5 . Aliquots were taken from each phase and analyzed by NMR.

Phase diagrams:

Equal portions of IL and water were mixed (~ 3 g) and stirred at 80 $^\circ\text{C}$ until a single phase was formed. Each mixture was then dispensed into test tubes and maintained at the appropriate temperature (-2, 10, 23, and 50 $^\circ\text{C}$). After 24 h, an aliquot of each phase from each sample was removed and dissolved in DMSO-d_6 . ^1H -NMR spectra were recorded, the integrals of the methyl

proton and the H₂O proton peaks were compared, and the mole fraction of water and IL in each phase was calculated. The values were then plotted as a function of temperature.

X-ray Crystallographic Characterization:

Data were collected on a Bruker diffractometer with an Apex II CCD area detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection was performed at -100 °C. Data were measured using a strategy of omega scans of 0.5° per frame and an acquisition time of 10 s per frame. Data were integrated with Bruker SAINT, and an absorption correction was performed using Bruker AXScale.² The structure was solved by direct methods and refined by least square methods on F² using the SHELXTL³ program package. All non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms on all positions, except the amine and the free water, were added geometrically and their parameters constrained to ride on the parent atom. The amine hydrogen atoms were refined freely. Attempts to locate hydrogen atoms on the uncoordinated water molecule were unsuccessful. Although difference map peaks at the appropriate distance for a hydrogen atom bonded to water do appear, any attempt to include them resulted in an unstable refinement. However, the formula is presumed correct on the basis of charge balance and the water molecule is appropriately positioned to donate two hydrogen bonds to hydrogen bond acceptors (the imidazolium ring and the oximate oxygen atom). Intermolecular contacts and packing diagrams were made using SHELXTL or Mercury.⁴ The X-ray crystallographic information file can be obtained free of charge from the CSD at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: data_request@ccdc.cam.ac.uk). CCDC 890413 contains the supplementary crystallographic data for the complex described in this paper.

Packing Figures:

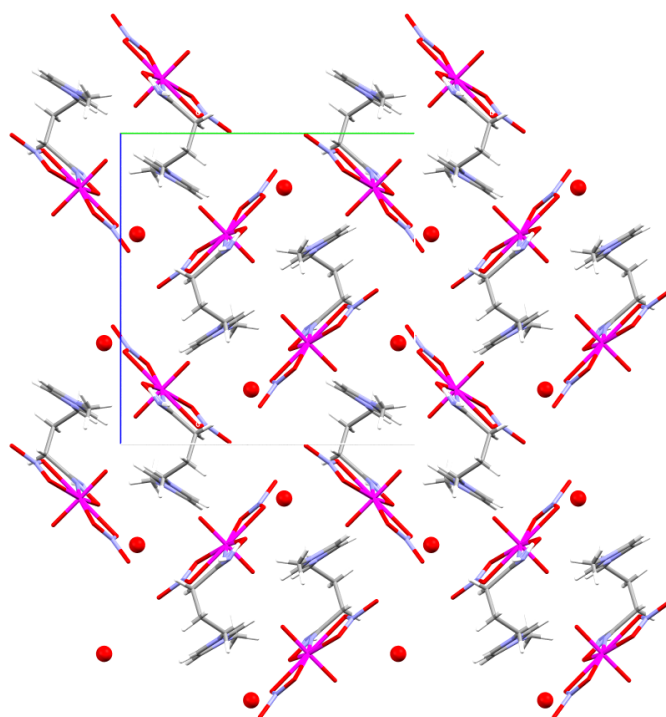


Fig. S1 Packing diagram viewed along the *a*-axis showing perpendicular dimers along the *bc* diagonals. Axes are color coded: red = *a*, green = *b*, blue = *c*.

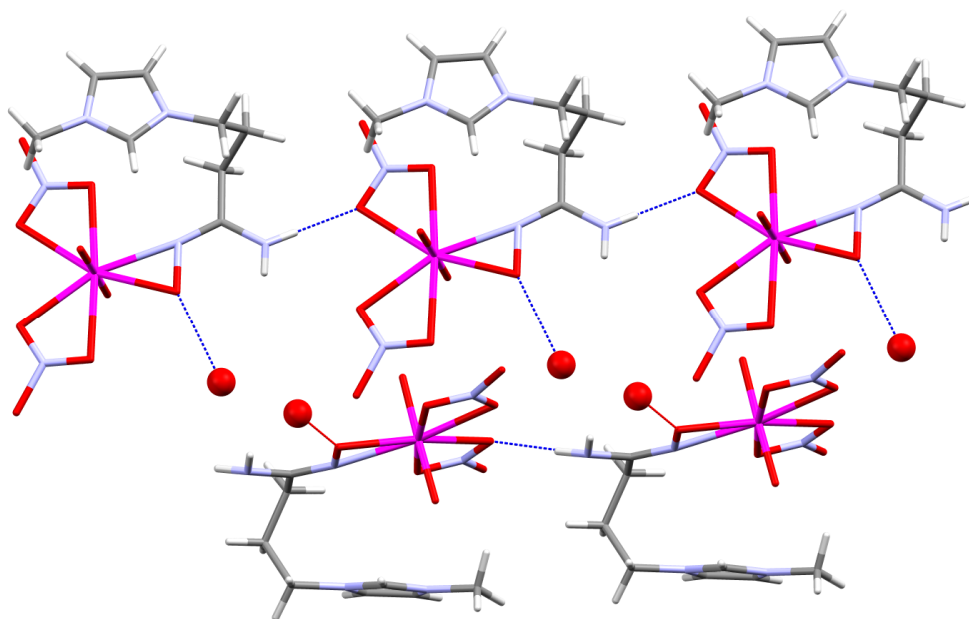


Fig. S2 Packing diagram showing chains of hydrogen bonding interactions (blue dashed) along the *a*-axis.

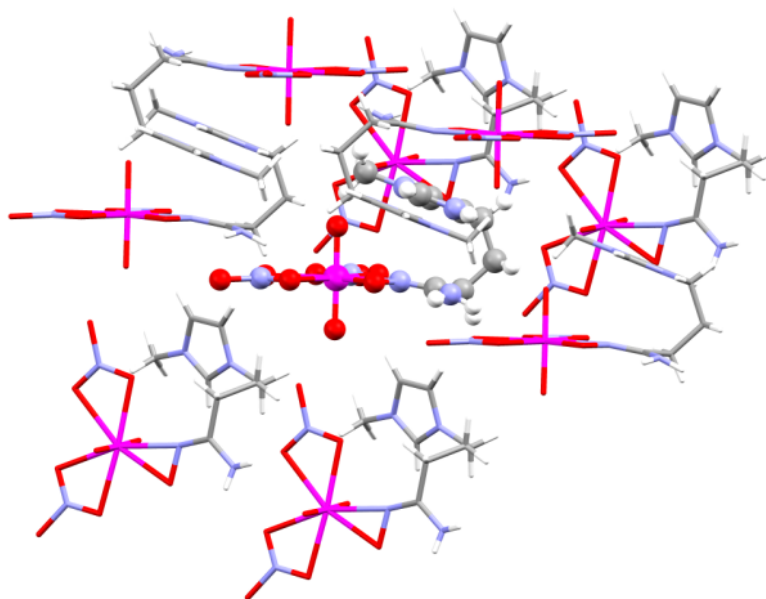


Fig. S3: (*top*) Position and orientation of the neighboring molecules (capped sticks) for a given molecule in the crystal structure (ball and stick).

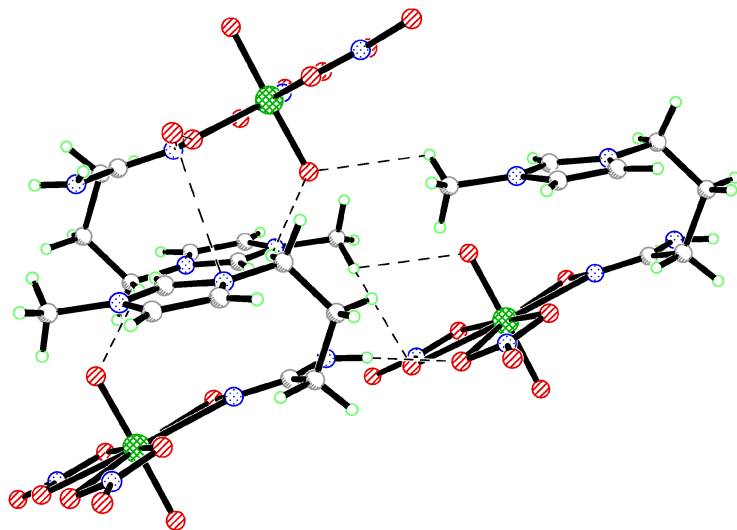


Fig. S4 Intermolecular hydrogen bonding interactions.

Infrared Spectroscopy:

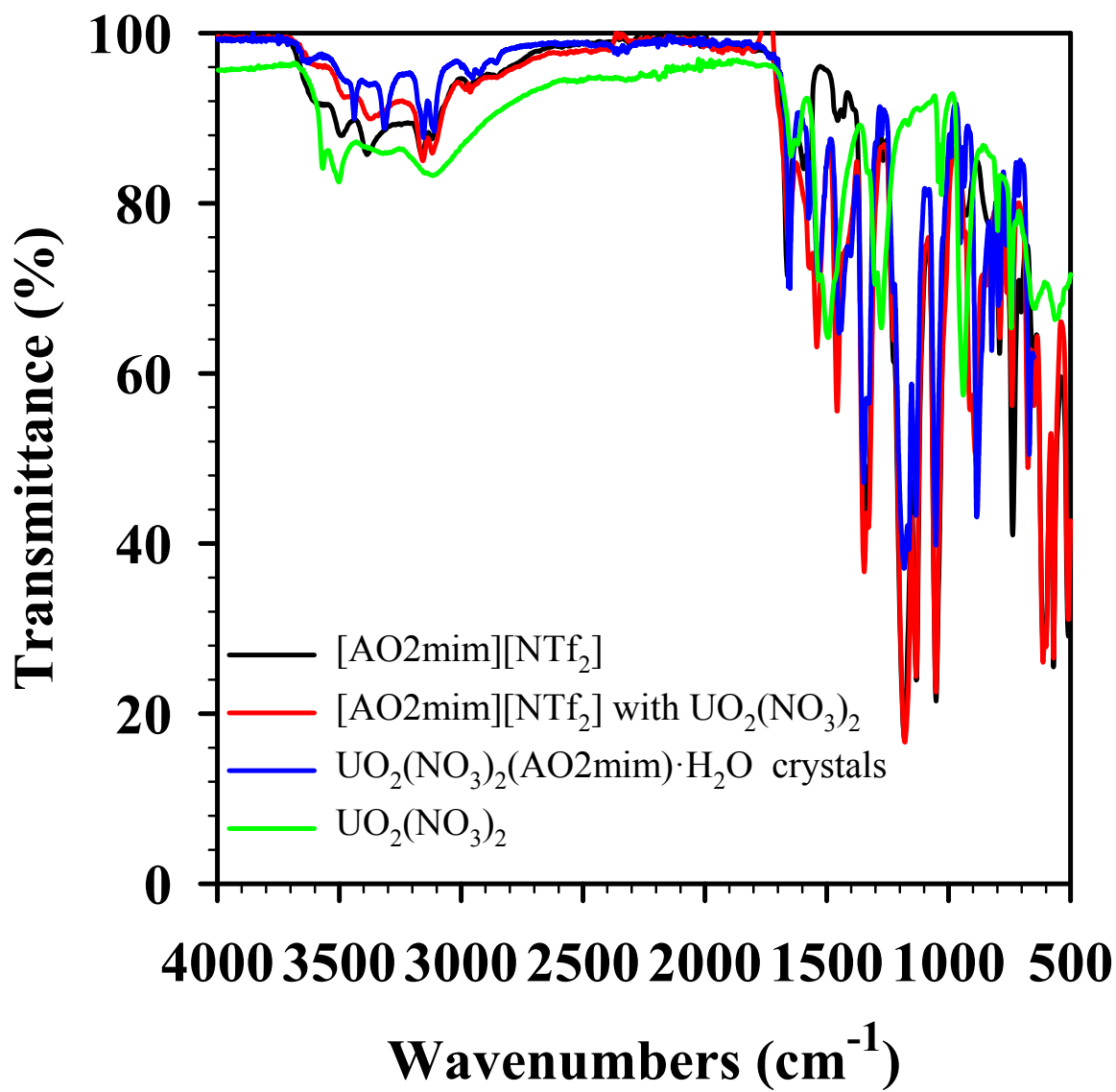


Fig. S5 Infrared spectroscopy comparing [AO2mim][NTf₂], (black), [AO2mim][NTf₂], with UO₂(NO₃)₂ (red), UO₂(NO₃)₂ (green), and crystals of [UO₂(NO₃)₂([AO2mim])·H₂O] (blue).

Thermogravimetric Analysis:

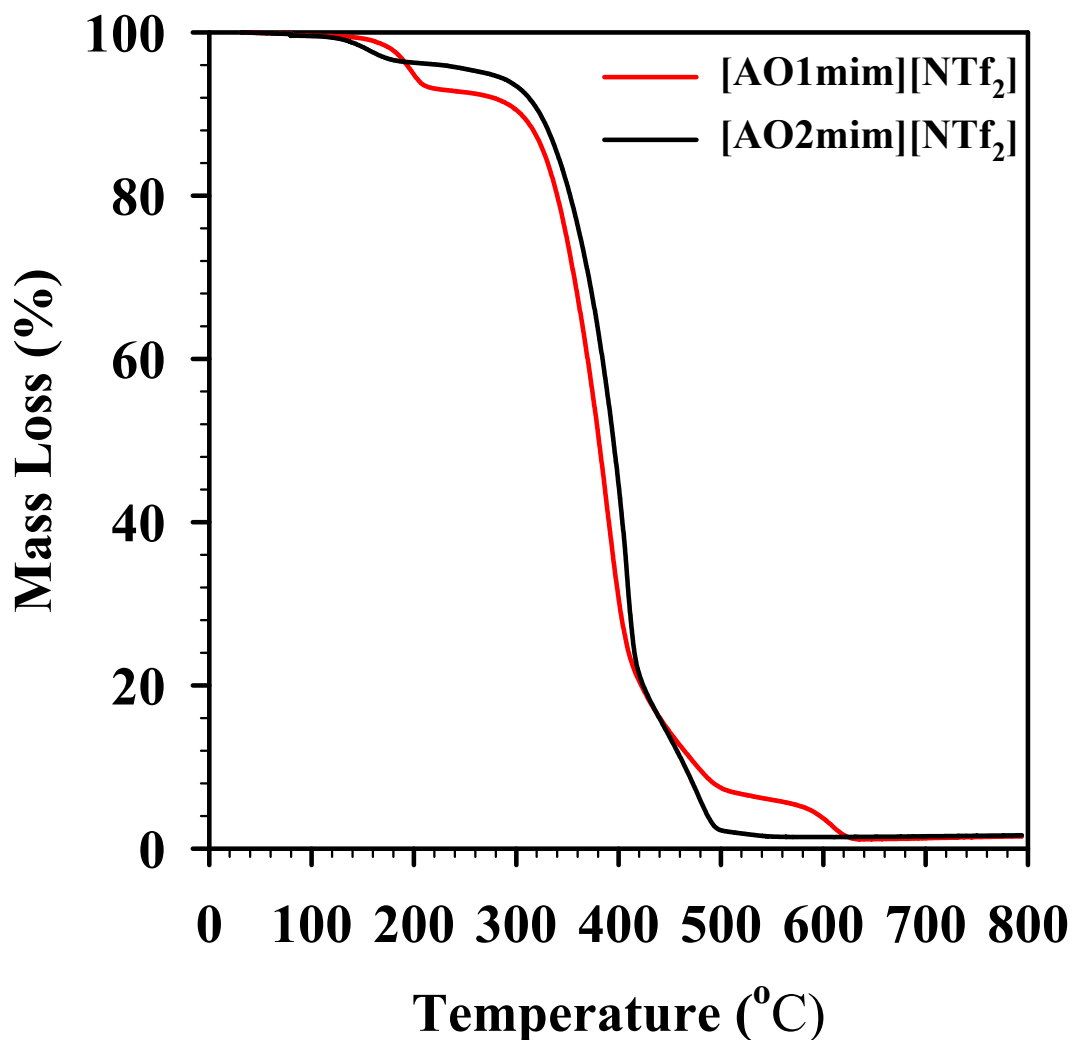


Fig. S6 Thermogravimetric analysis of [AO1mim][NTf₂] (red) and [AO2mim][NTf₂] (black).

References:

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- ⁴ C. F. Macrae, J. I. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.* 2008, **41**, 466.