Electronic Supporting Information

Dissolution of metal oxides in task-specific ionic liquid

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PXRD of the reagents ThO$_2$ and [Hbet][NTf$_2$]

**Fig. S1** Measured diffractogram of the reagent ThO$_2$ (black) compared to the ThO$_2$ pattern calculated from single-crystal data (green) in the range $5^\circ \leq 2\theta \leq 90^\circ$.

**Fig. S2** Experimental diffractogram of the synthesised [Hbet][NTf$_2$] compared to the reflection patterns of [Hbet][NTf$_2$] (middle) and [(Hbet)$_3$(bet)][NTf$_2$]$_3$ (bottom) simulated from single crystal data$^1$ in the range $5^\circ \leq 2\theta \leq 50^\circ$. 

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$^1$ Reference for single crystal data:

[1] Reference Number for Single Crystal Data
Fig S3 Rietveld refinement plot of the reagent [Hbet][NTf$_2$]. Peak positions of [Hbet][NTf$_2$] are marked in orange and of [(Hbet)$_3$(bet)][NTf$_2$]$_3$ in brown vertical bars. Ca. 66% of [Hbet][NTf$_2$] and 34% of [(Hbet)$_3$(bet)][NTf$_2$]$_3$ are present in the sample. $R_p = 3.8102$, $R_{wp} = 5.3084$, $R_{exp} = 7.7653$, GOF = 0.68.

Reaction mixtures in pure [Hbet][NTf$_2$]

Table S1 Product appearance and phases identified by PXRD of the reaction mixtures of a metal oxide and [Hbet][NTf$_2$]. A molar ratio of $n_{ox} : n_{IL} = 1 : 4$ and heating to 175 °C for 24 h was applied. Pastelike products crystallised when brought on a PXRD sample holder.

| Oxide   | Product appearance            | PXRD phases                                                                 |
|---------|--------------------------------|------------------------------------------------------------------------------|
| Al$_2$O$_3$ | White powder in colourless liquid | [Hbet][NTf$_2$]                                                              |
| BaO     | White paste                    | Many unidentified reflections                                                 |
| Bi$_2$O$_3$ | White powder in colourless liquid | Many unidentified reflections                                                 |
| CaO     | Clear, colourless solution     |                                                                              |
| Co$_3$O$_4$ | Black powder in slightly violet liquid | Co$_3$O$_4$                                                                |
| Cr$_2$O$_3$ | Green powder in colourless liquid | Cr$_2$O$_3$                                                                |
| Cu$_3$O$_4$ | Blue and white crystals         | Cu$_3$O$_4$, [Hbet][NTf$_2$], [(Cu$_3$(bet)$_4$(NTf$_2$)$_2$)][NTf$_2$]$_2$    |
| CuO     | Blue and white irregular crystals | [Cu$_3$(bet)$_4$(NTf$_2$)$_2$][NTf$_2$]$_2$, unidentified reflections        |
| Fe$_2$O$_3$ | Red powder in colourless liquid | Fe$_2$O$_3$                                                                |
| Ga$_2$O$_3$ | White powder in colourless liquid | Ga$_2$O$_3$, [Hbet][NTf$_2$]                                                  |
| GeO$_2$ | White powder in colourless liquid | GeO$_2$, [Hbet][NTf$_2$]                                                      |
| In$_2$O$_3$ | White powder in colourless liquid | In$_2$O$_3$, [Hbet][NTf$_2$]                                                  |
| MgO     | Clear, colourless solution     |                                                                              |
| MnO     | Pale orange, clear paste       | Many unidentified reflections                                                 |
| MnO$_2$ | Black powder in colourless liquid | MnO$_2$                                                                     |
| MoO$_3$ | White powder in colourless liquid | MoO$_3$, [Hbet][NTf$_2$]                                                      |
| Nb$_2$O$_5$ | White powder in colourless liquid | Nb$_2$O$_3$, [Hbet][NTf$_2$]                                                  |
| NiO     | Green powder in colourless liquid | NiO, [(Hbet)$_3$(bet)][NTf$_2$]$_3$                                           |
| PbO     | Clear, colourless solution     |                                                                              |
| PbO$_2$ | Clear, colourless solution     |                                                                              |
| ReO$_3$ | Red crystals in colourless liquid | ReO$_3$                                                                     |
| Sb$_2$O$_3$ | White powder in colourless liquid | Sb$_2$O$_3$, [(Hbet)$_3$(bet)][NTf$_2$]$_3$                                   |
| SnO     | White powder in brown liquid   | SnO, [Hbet][NTf$_2$]                                                        |
| Compound | Description          | Reflections                        |
|----------|----------------------|-----------------------------------|
| SrO      | Pale orange, opaque paste | Many unidentified reflections      |
| ThO₂     | Black powder in colourless liquid | ThO₂, few unidentified reflections (present in reagent) |
| TiO₂     | White powder in colourless liquid | TiO₂, [Hbet][NTf₂] |
| V₂O₃     | Small blue-green crystals in colourless liquid | Several unidentified reflections |
| V₂O₅     | Yellow powder in brown liquid | V₂O₅, many unidentified reflections |
| WO₃      | Yellow powder in colourless liquid | WO₃ |
| ZnO      | First colourless solution gels to white paste | Many unidentified reflections      |
Fig. S4 Experimental diffractograms of the samples Al₂O₃, BaO, Bi₂O₃, Co₃O₄, Cr₂O₃, Cu₂O, CuO, Fe₂O₃, Ga₂O₃, GeO₂, In₂O₃, MnO and MnO₂ + [Hbet][NTf₂] (black) in the range 5° ≤ 2θ ≤ 90° compared to the reflection patterns of the respective metal oxide if present (green) and (BiO)₂CO₃ (violet) simulated from single crystal data as well as the experimental reagent pattern of [Hbet][NTf₂] (grey). Unidentified reflections in predominantly or completely unidentified patterns (BaO, Cu₂O, CuO, MnO) are not marked as such.
Fig. S5 Experimental diffractograms of the samples MoO$_3$, Nb$_2$O$_5$, NiO, ReO$_3$, Sb$_2$O$_5$, SnO, SrO, ThO$_2$, TiO$_2$, V$_2$O$_3$, V$_3$O$_8$, WO$_3$ and ZnO + [Hbet][NTf$_2$] (black) in the range $5^\circ \leq 2\theta \leq 90^\circ$ compared to the reflection patterns of the respective metal oxide if present simulated from single crystal data (green) as well as the experimental reagent pattern of [Hbet][NTf$_2$] (dark grey) and the pattern of [(Hbet)$_3$(bet)][NTf$_2$]$_3$ (light gray) simulated from single crystal data. Unidentified reflections in completely unidentified patterns (SrO, V$_2$O$_3$, ZnO) are not marked as such.
Fig. S6 Experimental diffractograms of the samples Bi$_2$O$_3$ + [Hbet][NTf$_2$] reacted in argon flow (top) and on air before washing with acetone (bottom) compared to the experimental pattern of the reagent Bi$_2$O$_3$ (green) and the (BiO)$_2$CO$_3$ pattern calculated from single crystal data (violet) in the range 5° ≤ 2θ ≤ 90°.
Lattice energies and $U/x$ values

**Table S2** Data for the calculation of the lattice energy $U$ by the Born-Haber cycle and of the $U/x$ value. Furthermore, the binding energy of $O_2 B = 498.34$ kJ/mol and the electron affinities of $O$ $EA_1 = 141$ kJ/mol and $EA_2 = -844$ kJ/mol were used. $\Delta H_f$ values were obtained from *Thermochemical Data of Pure Substances*, $^2 \Delta H_m$, $\Delta H_r$ and $B$ from *Lange’s Handbook of Chemistry*, $^3$ and $I_e$ and $EA_i$ values from the NIST online database. $^4$

| Oxide | $x$ | $\Delta H_f$ [kJ/mol] | $\Delta H_m$ [kJ/mol] | $\Delta H_r$ [kJ/mol] | $\sum I_i$ [kJ/mol] | $U$ [kJ/mol] | $U/x$ [kJ/mol] |
|-------|-----|-----------------------|-----------------------|-----------------------|---------------------|--------------|---------------|
| Al$_2$O$_3$ | 2 | −1676 | 326 | − | − | 2394 | 15464 | 7732 |
| BaO | 1 | −554 | 7.12 | 140.3 | 1468 | 3121 | 3121 |
| Bi$_2$O$_3$ | 2 | −574 | 11.30 | 151 | 4781 | 13318 | 6659 |
| CaO | 1 | −635 | 8.45 | 154.7 | 1735 | 3486 | 3486 |
| Co$_2$O$_4$ | 3 | −910 | 424 | − | − | 4025 | 18067 | 6022 |
| Cr$_2$O$_3$ | 2 | −1140 | 397 | − | − | 5231 | 15252 | 7626 |
| Cu$_2$O | 2 | −171 | 337.7 | − | − | 745 | 3290 | 1645 |
| CuO | 1 | −156 | 337.7 | − | − | 2703 | 4150 | 4150 |
| Fe$_2$O$_3$ | 2 | −824 | 415.5 | − | − | 5283 | 15078 | 7539 |
| Ga$_2$O$_3$ | 2 | −1089 | 5.59 | 254 | 5523 | 15511 | 7756 |
| GeO$_2$ | 1 | −580 | 36.94 | 334 | 9997 | 12852 | 12852 |
| In$_2$O$_3$ | 2 | −926 | 243.1 | − | − | 5085 | 14439 | 7220 |
| MgO | 1 | −601 | 147 | − | − | 2188 | 3889 | 3889 |
| MnO | 1 | −385 | 12.9 | 221 | 2226 | 3798 | 3798 |
| MnO$_2$ | 1 | −520 | 12.9 | 221 | 10416 | 13075 | 13075 |
| MoO$_3$ | 1 | −745 | 664 | − | − | 20643 | 24909 | 24909 |
| Nb$_2$O$_5$ | 2 | −1900 | 726 | − | − | 12958 | 34030 | 17015 |
| NiO | 1 | −240 | 17.48 | 377.5 | 2490 | 4077 | 4077 |
| PbO | 1 | −218 | 195.2 | − | − | 2166 | 3532 | 3532 |
| PbO$_2$ | 1 | −274 | 195.2 | − | − | 9332 | 11706 | 11706 |
| ReO$_3$ | 1 | −589 | 779 | − | − | 20207 | 24433 | 24433 |
| Sb$_2$O$_3$ | 2 | −720 | 19.87 | 193.43 | 4878 | 13760 | 6880 |
| SnO | 1 | −286 | 7.03 | 296.1 | 2120 | 3662 | 3662 |
| SrO | 1 | −592 | 164.0 | − | − | 1614 | 3322 | 3322 |
| ThO$_2$ | 1 | −1226 | 13.81 | 514 | 6308 | 9967 | 9967 |
| TiO$_2$ | 1 | −945 | 469 | − | − | 8796 | 12114 | 12114 |
| V$_2$O$_3$ | 2 | −1219 | 516 | − | − | 4891 | 14890 | 7445 |
| V$_2$O$_5$ | 2 | −1551 | 516 | − | − | 15696 | 38738 | 19369 |
| WO$_3$ | 1 | −843 | 851 | − | − | 19761 | 24312 | 24312 |
| ZnO | 1 | −350 | 7.32 | 123.6 | 2640 | 4074 | 4074 |
The compound \([\text{Cu}_2(\text{bet})_4(\text{NTf}_2)_2][\text{NTf}_2]_2\]

**Fig. S7** Crystal structure of \([\text{Cu}_2(\text{bet})_4(\text{NTf}_2)_2][\text{NTf}_2]_2\). Coordinative interactions are marked as dotted lines. The ellipsoids enclose 70% of the probability density of the atoms at 100 K. H atoms are omitted for clarity.

**Fig. S8** Experimental diffractogram of \([\text{Cu}_2(\text{bet})_4(\text{NTf}_2)_2][\text{NTf}_2]_2\) after washing with acetone (black) compared to the pattern simulated from single crystal data of \([\text{Cu}_2(\text{bet})_4(\text{NTf}_2)_2][\text{NTf}_2]_2\) (blue) in the range \(5° \leq 2\theta \leq 90°\).
Assignment of IR bands of [Hbet][NTf₂]

Table S3 Positions and proposed assignment of the bands observed in the FTIR spectrum of [Hbet][NTf₂] in the range 500 cm⁻¹ ≤ \( \tilde{\nu} \) ≤ 4000 cm⁻¹. The symbols have their usual meaning: \( \nu \) stretching, \( \delta \) bending, \( \gamma \) out of plane bending or wagging, \( s \) symmetric, \( as \) asymmetric. Assignment with the aid of references 5–8.

| IR vibration of [Hbet][NTf₂] [cm⁻¹] | Proposed assignment |
|-------------------------------------|---------------------|
| 3301 \( \nu_{as} \) OH              |                     |
| 3053 \( \nu_s \) CH (CH₃)           |                     |
| 2999 \( \nu_{as} \) CH (CH₃)        |                     |
| 2966 \( \nu \) CH (CH₃)             |                     |
| 1770 \( \nu_{as} \) COO             |                     |
| 1496 \( \nu_{as} \) HCH (CH₃)       |                     |
| 1479 \( \delta_{as} \) CH₃          |                     |
| 1424 \( \delta_s \) HCH (CH₃-N)     |                     |
| 1350 \( \nu_{as} \) SO₂             |                     |
| 1331 \( \delta \) NCH               |                     |
| 1180 \( \nu \) CF₃                  |                     |
| 1142 \( \nu_s \) SO₂                |                     |
| 1050 \( \nu_{as} \) SN              |                     |
| 994 \( \nu_{as} \) C₃N              |                     |
| 955 \( \delta \) CCN                |                     |
| 931 \( \delta \) CNC                |                     |
| 883 \( \nu \) CC                    |                     |
| 795 \( \nu_s \) SN                  |                     |
| 766 \( \nu \) CS                    |                     |
| 743 \( \delta_s \) CF₃              |                     |
| 676 \( \nu \) CN                    |                     |
| 610 \( \delta \) CSN                |                     |
| 572 \( \gamma \) CH                 |                     |
| 518 \( \gamma \) CH                 |                     |
Fig S9 1H NMR spectra of [Hbet][NTf₂], the heated mixture of [Hbet][NTf₂] and [Hbet]Cl as well as several samples of metal oxide mixtures in the range 1 ppm ≤ δ ≤ 6 ppm, where all signals occur. Highlighted in green are the signals of CH₃ (3.1 ppm) and CH₂ (4.1 ppm), orange shading indicates the...
signal originating from the solvent DMSO-d$_6$. No signal is observed for the carboxyl proton of betainium, which is attributed to its low intensity and broadness due to fast exchange processes.\(^9\)

**Reaction mixtures in \([\text{Hbet}]\text{[NTf}_2\text{]}\)-\([\text{Hbet}]\text{Cl}\)**

**Table S4** Product appearance and phases identified by pXRD of the reaction mixtures of a metal oxide, \([\text{Hbet}]\text{[NTf}_2\text{]}\) and \([\text{Hbet}]\text{Cl}\). If not stated otherwise, a molar ratio of \(n_M : n_{[\text{Hbet}]\text{[NTf}_2\text{]}} : n_{[\text{Hbet}]\text{Cl}} = 1 : 2 : 2\) and heating to 175 °C for 24 h was applied.

| Oxide  | Product appearance          | PXRD phases                  | Varied reaction conditions | Product appearance                        |
|--------|-----------------------------|------------------------------|---------------------------|-------------------------------------------|
| Al$_2$O$_3$ | White powder in brown liquid | No reflections               |                           |                                           |
| BaO    | White powder in brown paste | BaCl$_2$, unidentified reflections | \(n_{\text{Ba}} : n_{[\text{Hbet}]\text{[NTf}_2\text{]} } : n_{[\text{Hbet}]\text{Cl}} = 3 : 18 : 1\) | Colourless liquid and white solid, identified as BaCl$_2$ by pXRD after washing |
| Bi$_2$O$_3$ | White powder in brown liquid | BiOCl, unidentified reflections |                           |                                           |
| CaO    | Paste of brown, orange and colourless crystals | Unidentified reflections | \(n_{\text{Ca}} : n_{[\text{Hbet}]\text{[NTf}_2\text{]} } : n_{[\text{Hbet}]\text{Cl}} = 3 : 18 : 1\) | Clear, colourless solution |
| Co$_3$O$_4$ | Blue crystals in colourless liquid | Unidentified reflections |                           |                                           |
| Cu$_2$O | White powder in yellow liquid | CuCl                         |                           |                                           |
| CuO    | Brown solid in brown liquid | Many unidentified reflections | 4 h                       | Green liquid, precipitation of blue, needle-shaped crystals overnight |
| Fe$_2$O$_3$ | Red powder in brown liquid | Fe$_2$O$_3$, unidentified reflections | \(n_{\text{Fe}} : n_{[\text{Hbet}]\text{[NTf}_2\text{]} } : n_{[\text{Hbet}]\text{Cl}} = 1 : 4 : 1\) | Red powder in slightly yellow liquid |
| Ga$_2$O$_3$ | White powder in brown paste | Ga$_2$O$_3$, unidentified reflections | \(n_{\text{Ga}} : n_{[\text{Hbet}]\text{[NTf}_2\text{]} } : n_{[\text{Hbet}]\text{Cl}} = 1 : 6 : 1\) | White powder in colourless liquid, only Ga$_2$O$_3$ identified by pXRD |
| GeO$_2$ | White powder in brown liquid | GeO$_2$                      |                           |                                           |
| In$_2$O$_3$ | Pale orange paste | In$_2$O$_3$, \([\text{Hbet}]_3\text{(bet)}\text{[NTf}_2\text{]}\), unidentified reflections | \(n_{\text{In}} : n_{[\text{Hbet}]\text{[NTf}_2\text{]} } : n_{[\text{Hbet}]\text{Cl}} = 1 : 6 : 1\) | Fine, yellow powder in colourless liquid, only In$_2$O$_3$ identified by pXRD |
| MgO    | Slightly brown solid        | Many unidentified reflections |                           | Clear, colourless solution                |
| MnO    | Light brown paste           | Many unidentified reflections |                           | Clear, light orange solution              |
| MnO$_2$ | Colourless crystals in brown liquid | Unidentified reflections |                           |                                           |
| MoO$_3$ | Brown, hard resin-like substance | MoO$_3$, unidentified reflections |                           |                                           |
| Nb$_2$O$_5$ | White powder in brown liquid | Nb$_2$O$_5$, unidentified reflections | \(n_{\text{Nb}} : n_{[\text{Hbet}]\text{[NTf}_2\text{]} } : n_{[\text{Hbet}]\text{Cl}} = 1 : 6 : 1\) | White powder in colourless liquid, Nb$_2$O$_5$ identified by |
| Compound | Appearance | pXRD |
|----------|------------|------|
| NiO      | Green solid (washing with acetone yields green liquid and hygroscopic yellow powder transforming to green liquid on air) | NiO, unidentified reflections |
| PbO      | White powder in light brown liquid | Unidentified pattern \( n_{\text{Pb}} : n_{[\text{Hbet}][\text{NTf}_2]} : n_{[\text{Hbet}]\text{Cl}} = 1 : 4 : 1 \) | White powder in orange solution |
| PbO₂     | White powder in brown liquid | Unidentified pattern |
| ReO₃     | Red crystals in brown liquid | ReO₃ |
| Sb₂O₃    | White powder in brown liquid | \([\text{Hbet}]_3(\text{bet})[[\text{NTf}_2]]_3\), unidentified reflections |
| SnO      | Brown paste | No reflections |
| SrO      | Clear, brown liquid | - |
| ThO₂     | White powder in brown solution | ThO₂ \( n_{\text{Th}} : n_{[\text{Hbet}][\text{NTf}_2]} : n_{[\text{Hbet}]\text{Cl}} = 1 : 12 : 2 \) | White powder and a few black particles in yellow liquid |
| TiO₂     | White powder in brown liquid | TiO₂, \([\text{Hbet}]_3(\text{bet})[[\text{NTf}_2]]_3\) |
| V₂O₃     | Fine, black powder in brown paste | V₂O₃ \( n_{\text{V}} : n_{[\text{Hbet}][\text{NTf}_2]} : n_{[\text{Hbet}]\text{Cl}} = 1 : 6 : 1 \) | Few black particles in grey liquid, no pXRD signals |
| V₂O₅     | Black powder in dark green paste | No reflections |
| WO₃      | Yellow powder in brown liquid | WO₃ |
| ZnO      | Clear, brown liquid | - |
**Fig. S10** Experimental diffractograms of the samples Al₂O₃, BaO, Bi₂O₃, CaO, Co₃O₄, Cr₂O₃, CuO, Cu₂O, Fe₂O₃, Ga₂O₃, GeO₂ and In₂O₃ + [Hbet][NTf₂] + [Hbet]Cl (black) in the range 5° ≤ 2θ ≤ 90° compared to the reflection patterns of the respective metal oxide (green) or metal chloride/oxide chloride (blue) if present simulated from single crystal data as well as the experimental reagent pattern of [Hbet][NTf₂] (dark grey) and the pattern of [(Hbet)(bet)][NTf₂]₃ simulated from single crystal data.¹ Unidentified reflections in completely unidentified patterns (CaO, Co₃O₄, CuO, MgO) are not marked as such.
Fig. S11 Experimental diffractograms of the samples MnO, MnO₂, MoO₃, Nb₂O₅, NiO, PbO, PbO₂, ReO₃, Sb₂O₅, SnO, ThO₂, TiO₂, V₂O₅, V₂O₃ and WO₃ + [Hbet][NTf₂] + [Hbet]Cl (black) in the range 5° ≤ 2θ ≤ 90° compared to the reflection patterns of the respective metal oxide if present simulated from single crystal data (green) as well as the pattern of [(Hbet)(bet)][NTf₂], simulated from single crystal data.¹ Unidentified reflections in predominantly or completely unidentified patterns (MnO, MnO₂, NiO, PbO, PbO₂) are not marked as such.
EDX of the sample ThO$_2$ + [Hbet][NTf$_2$] + [Hbet]Cl

Fig S12 SEM image of the white powder of the sample ThO$_2$ + [Hbet][NTf$_2$] + [Hbet]Cl ($n_{\text{Th}} : n_{[\text{Hbet}][\text{NTf}_2]} : n_{[\text{Hbet}]\text{Cl}} = 1 : 12 : 2$) with EDX measuring points indicated.

Table S5 Overview of the results of the EDX measurement. Besides C, O and Th, also La and Ta were detected. However, as their amounts were below the detection level, no assumption of the presence of small quantities of these elements can be made.

| Element | Pos. 1 | Pos. 2 | Pos. 3 | Pos. 4 | Average |
|---------|--------|--------|--------|--------|---------|
| C       | 52 %   | 50 %   | 56 %   | 50 %   | 52 %    |
| O       | 35 %   | 39 %   | 36 %   | 36 %   | 36 %    |
| Th      | 13 %   | 11 %   | 9 %    | 13 %   | 11 %    |

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