

## Electronic Supporting Information

### **Ionic liquids tethered to a preorganised 1,2-diamide motif for extraction of lanthanides**

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## General materials and methods

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or TCI (UK) and used without further purifications.

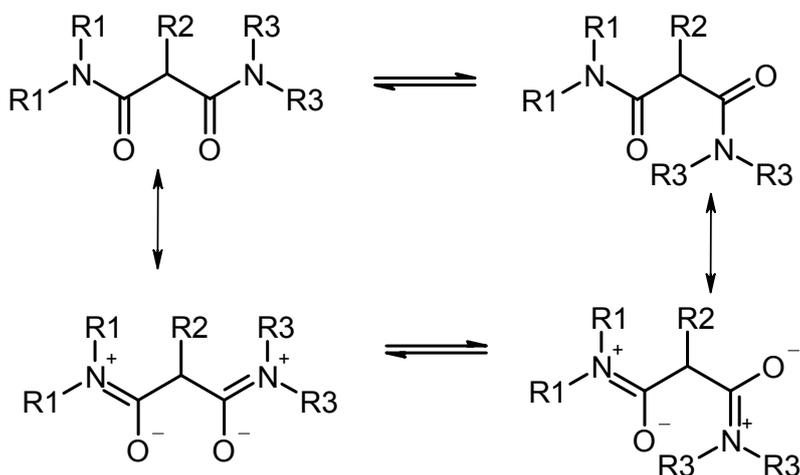
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz). ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an  $m/z$  range of 50 to 1500. Samples were injected as dilute solutions in dry acetonitrile. FTIR spectra were obtained at room temperature on a PerkinElmer Spectrum 100 (ATR-IR).

Metal analysis was performed using ICP on a Thermo Elemental IRIS Intrepid ICP-OES. The Limits of detection for  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$  on ICP-EOS are 0.001, 0.006, 0.001 and 0.001 ppm, respectively.

**TGA:** The temperature of decomposition was measured on a TA instrument TGA Q5000 with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under dinitrogen atmosphere. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature.

**DSC:** Thermal profiles of the ionic liquids were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS), equipped with an auto-sampler. A cooling and heating ramp of  $2\text{ }^\circ\text{C min}^{-1}$  was used, ranging between  $-100\text{ }^\circ\text{C}$  and  $120\text{ }^\circ\text{C}$ , depending on the ionic liquid system.

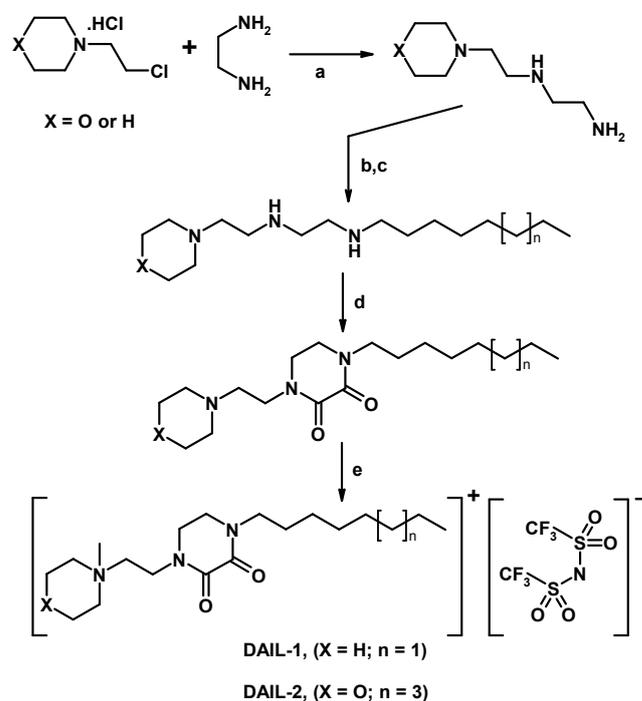
### Typical diamides (*bis*-malonamides) used in the literature for lanthanide extractions



**Scheme A:** Scheme showing the equilibria of typical malonamide conformers. The structures at the *top* depict standard forms and the at the bottom showing charged resonance forms where steric repulsions can be seen due lack of preorganization.

## Synthesis of DAIL ionic liquids and related substituted triamines

The ionic liquids, DAIL-1 and DAIL-2, were synthesised according to the reaction sequence shown in scheme 1.

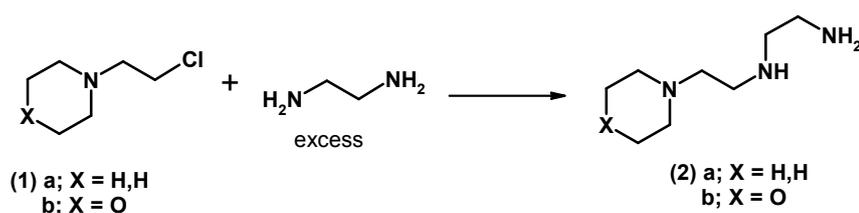


**Scheme 1.** Synthesis of ionic liquids **DAIL-1** and **DAIL-2**

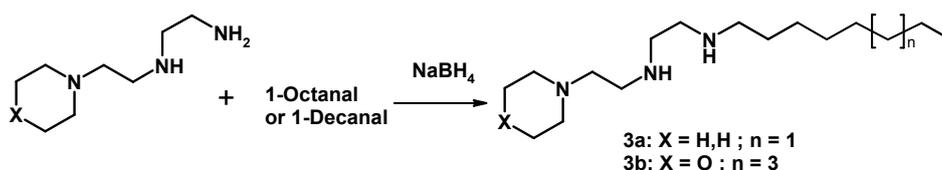
## Synthesis of substituted triamines

These compounds were prepared following a known method described by Gusev *et. al.*, as reported in *ACS catalysis*, 2016, **6**, 6967–6981.

## Synthesis of 2a and 2b



A solution of **1** (0.1 mol) in water 10 mL was added to a solution of ethylenediamine (30g, 0.5 mol) in water 35 mL. The reaction mixture was stirred and refluxed overnight. NaOH (ca. 10 g) was added until the solution was saturated. The resulting solution was extracted several times with ether. The combined organic layers were dried over  $\text{K}_2\text{CO}_3$  and evaporated. The obtained oil was distilled under high vacuum to give **2**. Yields of **2a** is 30%; **2b** 35%.

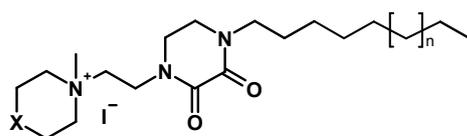


To a solution of **2** (10 mmol) in ethanol (10 mL) cooled at 0°C was added 1-alkanal (1-octanal or 1-decanal) (10 mmol). After 1.5 h at 0°C, NaBH<sub>4</sub> (1.4153g, 37 mmol) was added portion wise and the reaction mixture was stirred at 0 °C for 4h. The reaction was quenched by addition of water. Evaporate solvent and the aqueous phase was extract with Et<sub>2</sub>O several times. The ether layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. Compounds **3a** and **3b** were obtained as colorless liquids (**3a**, 66% and **3b**, 70%).

Compounds **5a** and **5b** were synthesised according to a procedure reported by S. Matsubara and co-workers (*Organic Letters*, 2010, **12**, 5204-5205), as follows:

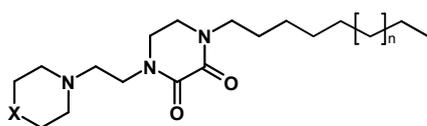
#### Preparation of (4)

**3** (1.8g, 6.642 mmol) and diethyl oxalate (1.0677g, 7.3 mmol) were added to a closed vessel. The reaction mixture was stirred at 100 °C for 12 h. After evaporating the excess diethyl oxalate and the product **4** was further dried *in vacuo* (80°C) for 24h. A brown viscous liquid was obtained (Yields: **4a**, 90%; **4b**, 97%).



#### Preparation of (5)

**4** (0.4528g, 1.4 mmol) and CH<sub>3</sub>I (0.568g, 4 mmol) were added to a screw-cap tube with CH<sub>2</sub>Cl<sub>2</sub> (5 ml). The reaction mixture was stirred at 50°C for 6 h. The contents of the vessel reaction was transferred to a 50 mL round-bottom flask, evaporated the excess CH<sub>3</sub>I and CH<sub>2</sub>Cl<sub>2</sub> on a Rotavap to produce a viscous liquid. The product **5** was further dried *in vacuo* (60°C) for 12h. A brown viscous liquid was obtained (Yields: **5a**, 97%; **5b**, 98%).



### Metathesis with lithium bis-trifamide

A solution of 5 (8.133g, 17.4 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was mixed with 10 mL deionised aqueous solution of LiNTf<sub>2</sub> (6.0g, 20.87 mmol). The mixture was stirred at room temperature for 1h, then separated the organic phase by using a separating funnel. The CH<sub>2</sub>Cl<sub>2</sub> layer was washed with deionised water several times to remove the LiCl salt from the organic phase. The organic solvent was then removed by rotary evaporation and the brown liquids thus obtained was kept under high vacuum, at 60 °C, overnight (yields: DAIL-1, 95%; DAIL-2, 96%).

### Analytical data for DAIL-1 and DAIL-2

**DAIL-1:** <sup>1</sup>H NMR (400 MHz, in CD<sub>3</sub>OD): δ 3.88-3.80(2H, m, **CH<sub>2</sub>**), 3.7-3.6(4H, m, **2xCH<sub>2</sub>**), 3.5-3.4(8H, m, **4xCH<sub>2</sub>**), 3.07(3H, s, **NCH<sub>3</sub>**), 1.61(2H, m, **CH<sub>2</sub>**), 1.44-1.21(16H, m, **5xCH<sub>2</sub>** & **2xCH<sub>3</sub>**), 0.9(3H, t, **CH<sub>3</sub>**).

<sup>13</sup>C NMR (100 MHz, in CD<sub>3</sub>OD): δ 159.9, 158.3, 121.2(q, NTF<sub>2</sub>), 58.3, 56.9, 48.0, 46.3, 45.4, 42.2, 32.9, 32.8, 30.4, 30.3, 28.0, 27.9, 23.7, 14.9, 8.0.

ESMS: For cation C<sub>19</sub>H<sub>38</sub>N<sub>3</sub>O<sub>2</sub> requires 340.2964; observed 340.2976

For anion C<sub>2</sub>S<sub>2</sub>NF<sub>6</sub>O<sub>4</sub> requires 279.9173; observed 279.9265

**DAIL-2:** <sup>1</sup>H NMR (400 MHz, in CDCl<sub>3</sub>): δ 4.06-3.85(6H, m, **3xCH<sub>2</sub>**), 3.8(2H, m, **CH<sub>2</sub>**), 3.72(2H, m, **CH<sub>2</sub>**), 3.67-4.48(6H, m, **3xCH<sub>2</sub>**), 3.39(2H, t, **CH<sub>2</sub>**), 3.3(3H, s, **N-CH<sub>3</sub>**), 1.55(2H, m, **CH<sub>2</sub>**), 1.34-1.19(14H, brm, **7xCH<sub>2</sub>**), 0.88(3H, t, **-CH<sub>3</sub>**).

<sup>13</sup>C NMR (100 MHz, in CDCl<sub>3</sub>): δ 158.8, 156.5, 119.8(q, NTF<sub>2</sub>), 61.2, 60.6, 60.5, 47.8, 47.0, 45.3, 44.4, 41.0, 32.0, 29.7, 29.6, 29.4, 27.2, 27.0, 22.8, 14.2

ESMS: For cation C<sub>19</sub>H<sub>38</sub>N<sub>3</sub>O<sub>2</sub> requires 382.5590; observed 382.5599

For anion C<sub>2</sub>S<sub>2</sub>NF<sub>6</sub>O<sub>4</sub> requires 279.9173; observed 279.9211

## Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of new products

Figure S1: NMR spectra of compound **4**.

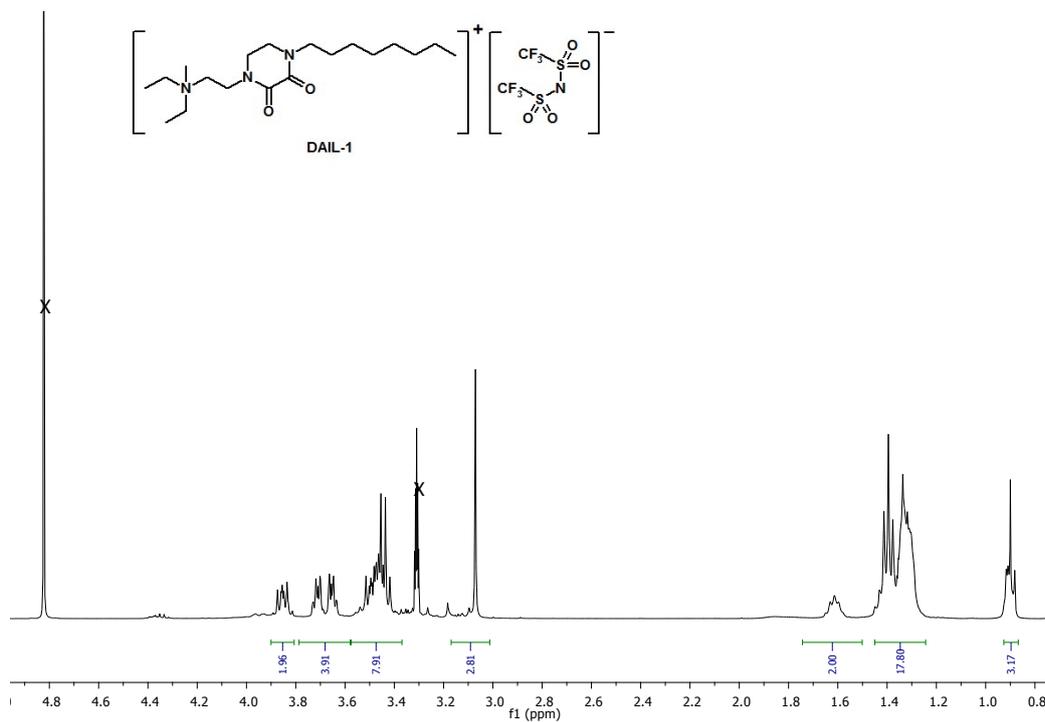


Figure-S1:  $^1\text{H}$  NMR spectrum of DAIL-1 in  $\text{CD}_3\text{OD}$

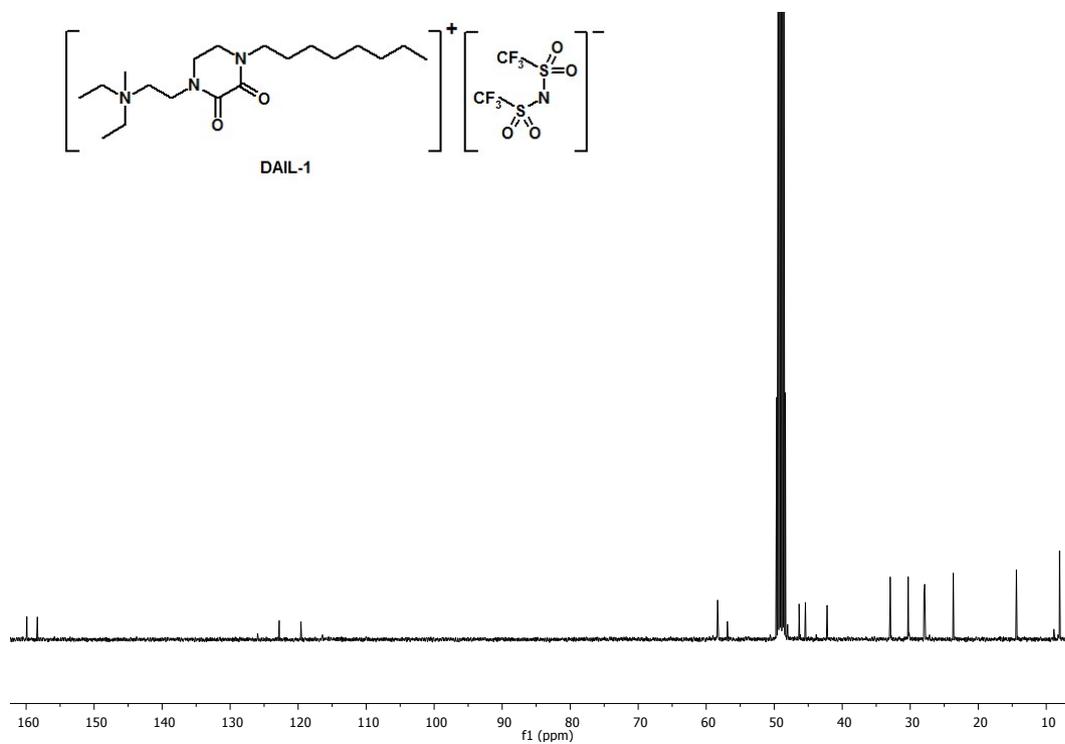


Figure-S2:  $^{13}\text{C}$  NMR spectrum of DAIL-1 in  $\text{CD}_3\text{OD}$

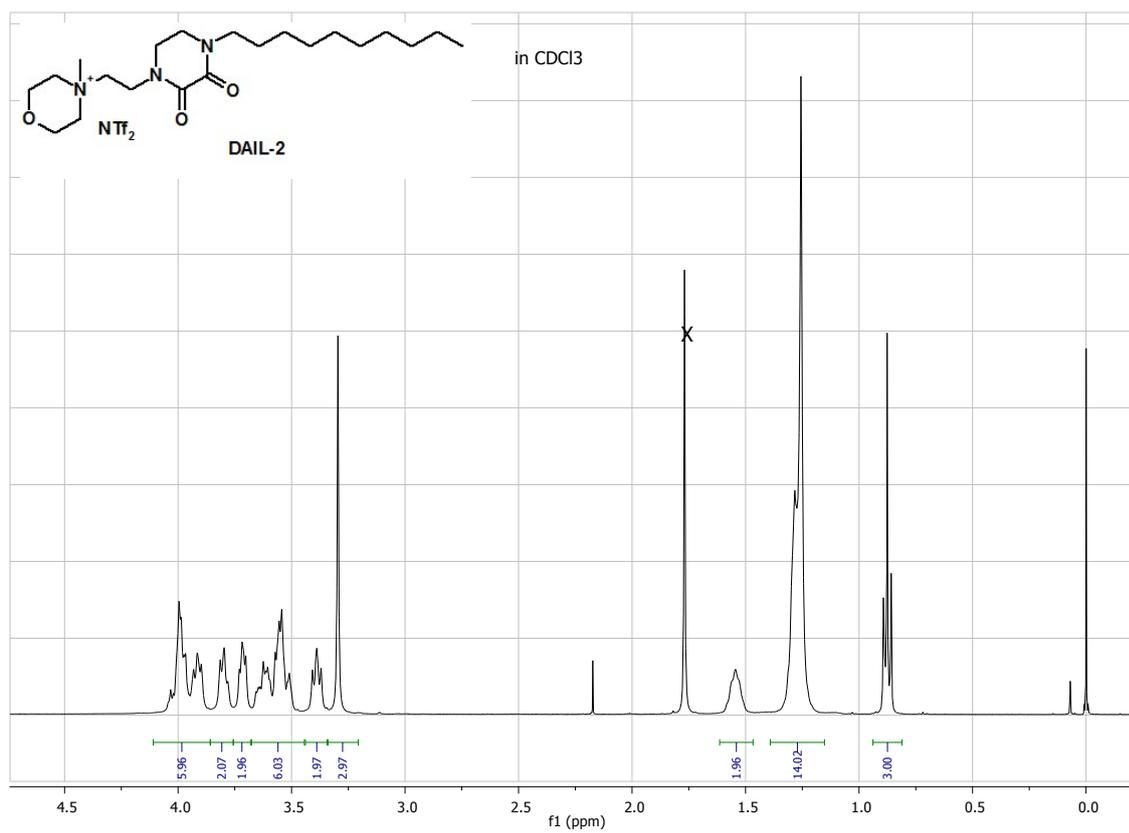


Figure-S3: <sup>1</sup>H NMR spectrum of DAIL-2 in CDCl<sub>3</sub>

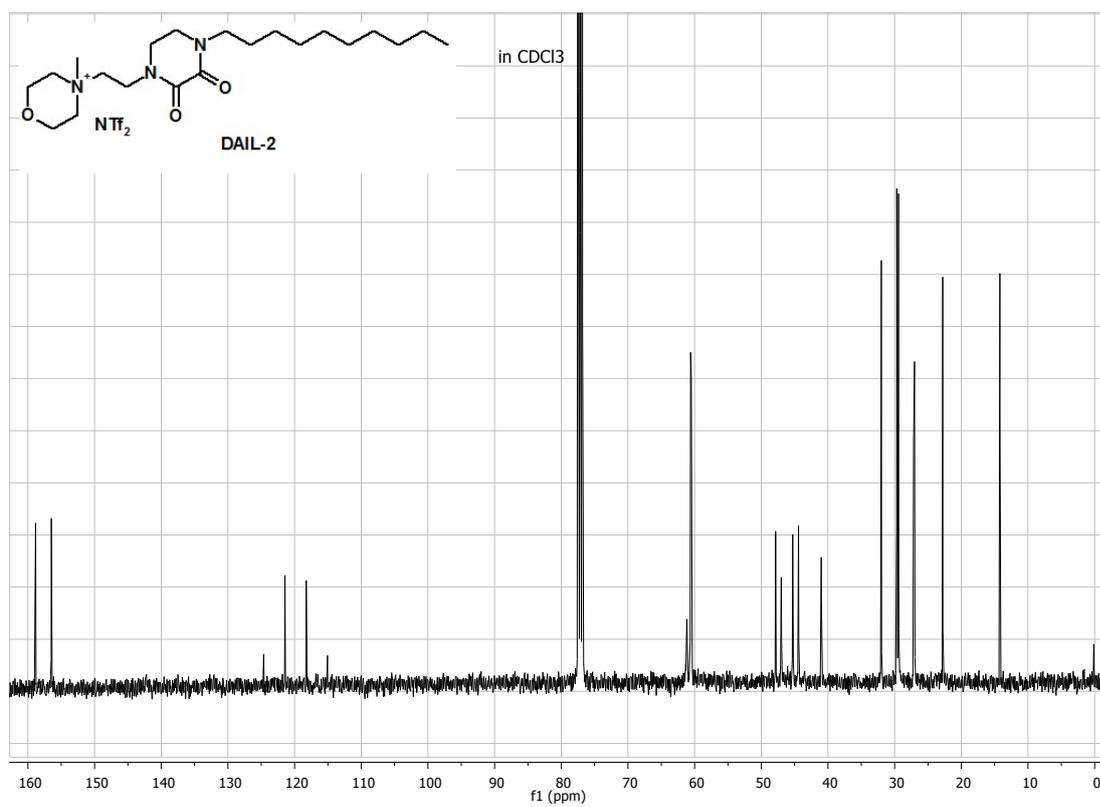
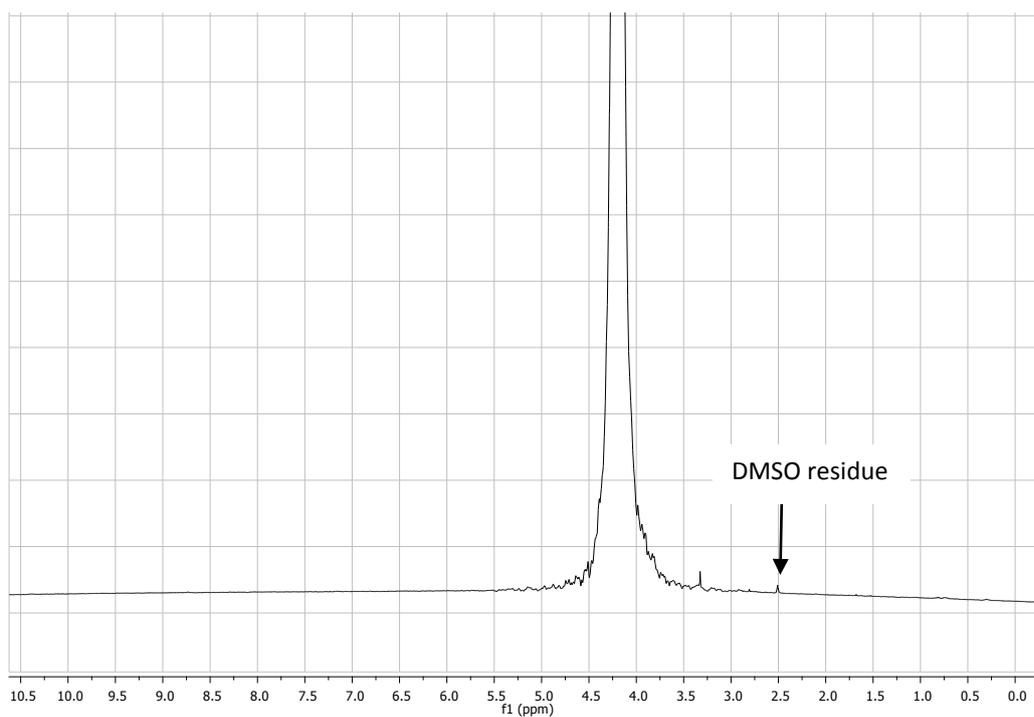
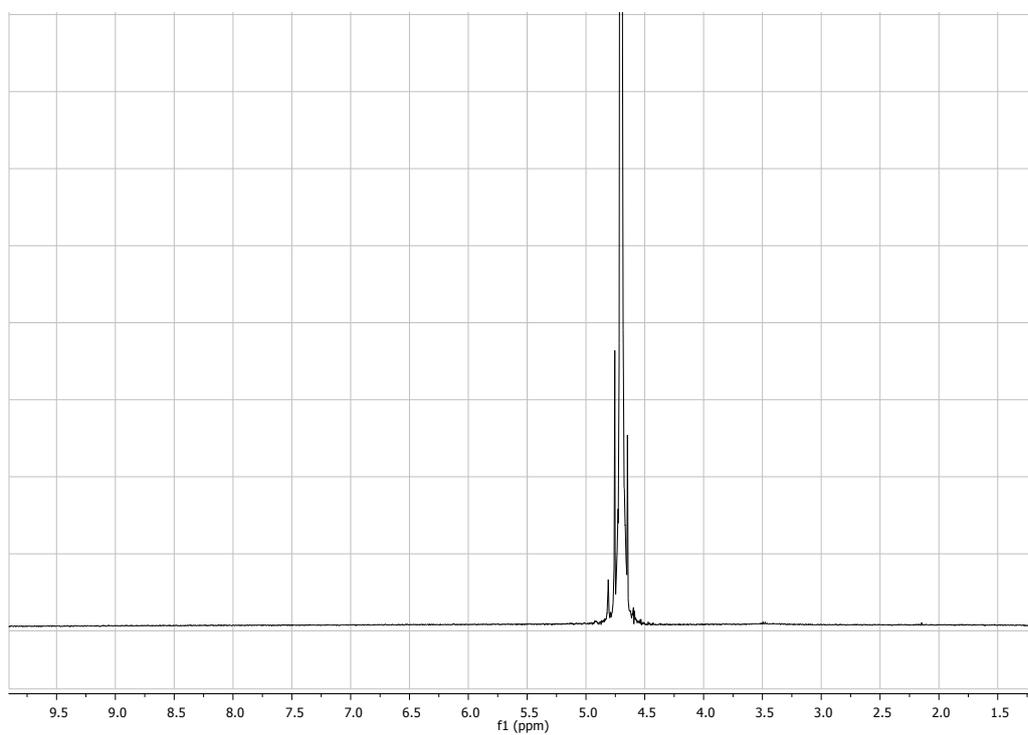


Figure-S4: <sup>13</sup>C NMR spectrum of DAIL-2 in CDCl<sub>3</sub>



**Figure-S5:**  $^1\text{H}$  NMR spectrum of the acidic water phase after shaking with DAIL-1 (a capillary tube filled with  $\text{DMSO-d}_6$  was used as the lock)



**Figure-S6:**  $^1\text{H}$  NMR spectrum of the  $\text{D}_2\text{O}$  phase after shaking with a mixture of DAIL-1 and  $[\text{P}_{6.6.6.14}][\text{NTf}_2]$  (The NMR was run after centrifuging the biphasic system)

## Metal extractions

Due to high viscosities associated with 1,2-diamide functionalised ionic liquids, they were mixed with [P<sub>66614</sub>][NTf<sub>2</sub>] to generate a 0.005M stock solution. An aliquot of this stock solution (1 ml) was mixed with aqueous solution (1 ml) of appropriate metal salts in a centrifuge tube. These centrifuge tubes were agitated in a mechanical shaker for 30 min. followed by centrifugation to obtain clear layer separation. The upper aqueous layer was separated and analysed by ICP.

## Methods and Materials

Stock solutions were prepared by dissolving the metal chloride salt (LaCl<sub>3</sub>.7H<sub>2</sub>O, SmCl<sub>3</sub>.6H<sub>2</sub>O, LuCl<sub>3</sub>.6H<sub>2</sub>O, MgCl<sub>2</sub>, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, ZnCl<sub>2</sub>) and sodium chloride (0.5 M) in HCl<sub>(aq)</sub> (pH 1 – 4).

The extracting phase was prepared by dissolving [DAIL][NTf<sub>2</sub>] (0.005 M) in [P<sub>66614</sub>][NTf<sub>2</sub>].

## Distribution experiments

A sample of organic phase was first contacted with an equal volume of 0.25 M NaCl HCl<sub>(aq)</sub> solution on a wrist-action shaker (30 mins). The sample was centrifuged and the aqueous layer discarded. Equal volumes of the acid-equilibrated organic phase and aqueous feed were contacted action shaker (30 mins) and centrifuged (15 mins) to obtain a colourless aqueous layer and cloudy ionic liquid layer. Aqueous samples were diluted as required and submitted for analysis.

Metal ion	Distribution coefficient	pH
La <sup>3+</sup>	0.368	4.0
Sm <sup>3+</sup>	65.67	4.0
Lu <sup>3+</sup>	All extracted <sup>#</sup>	4.0
Ni <sup>2+</sup>	0.009442	4.0
Zn <sup>2+</sup>	0.077	4.0
Mg <sup>2+</sup>	Unable to calculate*	4.0
Co <sup>2+</sup>	Unable to calculate*	4.0

**Table S1:** Distribution coefficients of various metal ions obtained with DAIL-1

\*No detectable amount of metal ions extracted; # no detectable metal ions present in the aqueous phase after extraction

**Table S2: A table showing comparison of D-values for lanthanide metal ions with DAIL-1 Vs diamides reported in literature:**

Metal ion	pH	D values for DAIL-1	D values for diamides reported in ref. b	D values for Diamide functionalised ionic liquid system in ref. c	D values reported in ref. d
La <sup>3+</sup>	1	0.04	3	7.82 (3M HNO <sub>3</sub> )	not reported
	2	0.20	3.6		
	3	0.35	2		
	4	0.37	1		
Sm <sup>3+</sup>	1	0.21	3	380 (3M HNO <sub>3</sub> )	not reported
	2	1.89	3.7		
	3	47.95	3.2		
	4	65.67	2.8		
Lu <sup>3+</sup>	1	21.94	4	not reported	200
	2	1077.7	2.2		not reported
	3	a	4.4		not reported
	4	a	20		not reported

a; D value could not be obtained due to the amount of metal ions in the aqueous phase was below the detection level of measurement (all metal ions were extracted).

b; A. Shimada, T. Yaita, H. Narita, S. Tachimori and K. Okuno, *Solvent Extraction and Ion Exchange*, 2004, **22**, 147-161.

c; A. Sengupta, P. K. Mohapatra, R. M. Kadam, D. Manna, T. K. Ghanty, M. Iqbal, J. Huskens and W. Verboom, *RSC Adv.*, 2014, **4**, 46613

d; M. S. Tyumentsev, Ph.D Thesis, *Tetradentate amide extraction agents for trivalent lanthanides*, 2018

## Recycling Study

### Materials and methods

A stock solution of La(III) (37 ppm) containing NaCl (0.5 M) was prepared by dissolving La(III)Cl<sub>3</sub>·7H<sub>2</sub>O and NaCl in dilute HCl (pH4). A stock solution of Arsenazo III with concentration 0.01 % (w/v) was prepared by weighing and dissolving the appropriate amount of Arsenazo III in deionised water. Buffer solution at pH 3.35 was prepared by mixing of diluted hydrochloric acid with a solution of 0.1M glycine.

### Extraction procedure

A sample of extracting phase (1 ml) was contacted with dilute HCl (pH4, 1 ml) containing NaCl (0.5M) on a wrist-action shaker (30 mins). The sample was centrifuged (10 mins, 4400

rpm) and the aqueous layer discarded. The acid-equilibrated extracting phase (1 ml) and aqueous La(III) feed (pH4) were contacted on a wrist-action shaker (30 mins) and centrifuged (10 mins, 4400 rpm). The aqueous layer was extracted using a pipette and stored for analysis. The extracting phase was stripped by contacting with dilute HCl (pH0.5, 1 ml) containing NaCl (0.5 M) on a wrist-action shaker (30 mins) and centrifuging (10 mins, 4400 rpm). The aqueous layer was extracted and stored for analysis. The previous stripping step was repeated to ensure complete stripping. The stripped extracting phase was contacted with deionised water (1 ml) containing NaCl (0.5 ml) on a wrist-action shaker (30 mins) and centrifuged (10 mins, 4400 rpm). The aqueous layer was discarded, and the deionised water wash step was repeated. The recycled extracting phase was contacted with La(III) feed as described above and the steps were repeated until a total of 3 extractions had been carried out.

### Analysis

Buffer (1 ml), ethanol (1 ml), dye solution (0.25 ml) and aqueous sample, from extraction, (0.12 ml) were added to a flask and shaken thoroughly. The absorbance of this solution at  $652\text{ cm}^{-1}$  was measured against a blank. The La(III) concentration was determined from a calibration curve, prepared from known amounts of La(III) (5-20 ppm).

### NMR Titration

Stock solutions of [DAIL][NTf<sub>2</sub>] (0.05 M) and LuCl<sub>3</sub>·6H<sub>2</sub>O (0.1 M) in deuterated methanol were prepared and added to NMR tubes according to the following table.

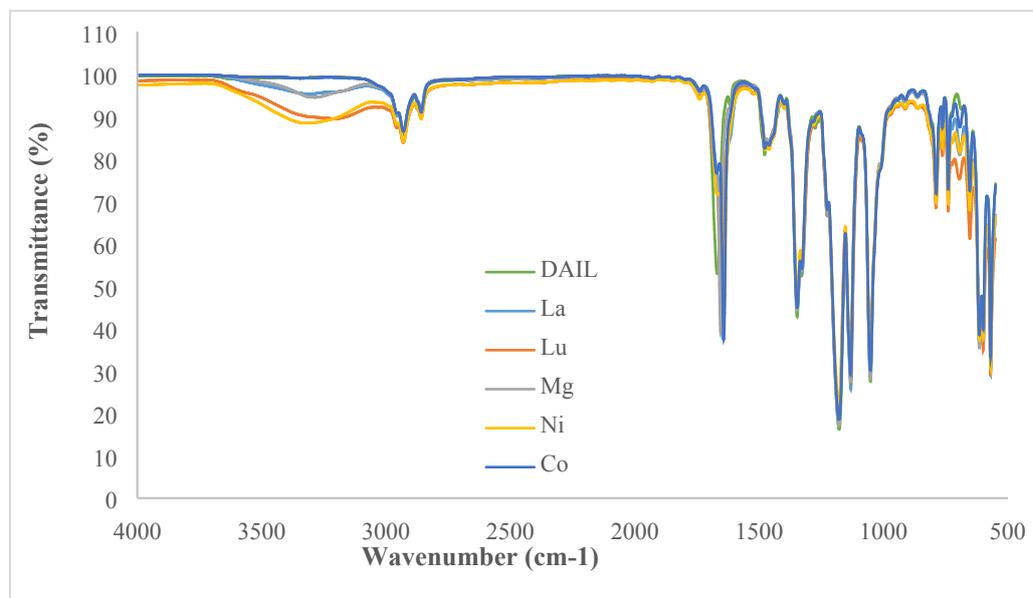
**Table S3**

Code	Ratio (L:M)	Volume of DAIL sol. (μl)	Volume of Lu sol. (μl)	Volume of MD <sub>3</sub> OD (μl)
N0	1	500	0	0
N1	1:1	500	250	0
N2	1:2	500	125	125
N3	1:3	500	83.33	166.7
N4	1:4	500	62.50	187.5
N5	1:5	500	50	200
N6	1:6	500	41.67	208.3
N7	1:7	500	35.71	214.3
N8	1:8	500	31.25	218.8

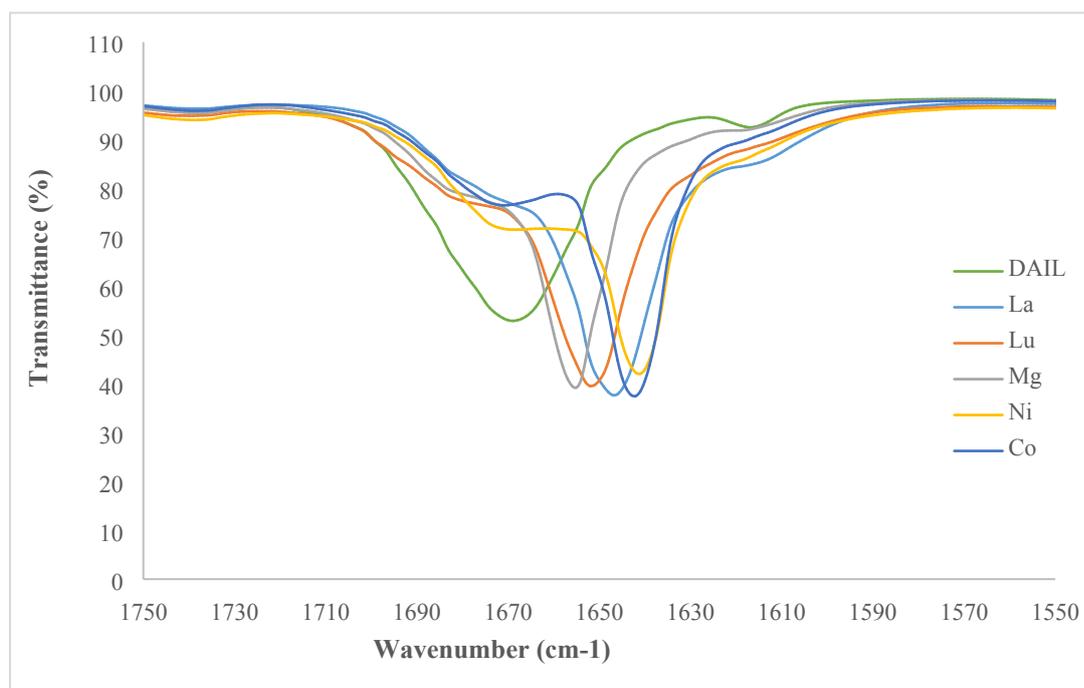
Samples were analysed on a Bruker Advance III 400.

## IR Study

[DAIL][NTf<sub>2</sub>] and metal salt (LaCl<sub>3</sub>·7H<sub>2</sub>O, LuCl<sub>3</sub>·6H<sub>2</sub>O, MgCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, ZnCl<sub>2</sub>) were dissolved in methanol and mixed together (1:3 ligand to metal ratio). Samples were placed in a sand bath and heated to remove methanol. Samples analysed on a PerkinElmer Spectrum 100.

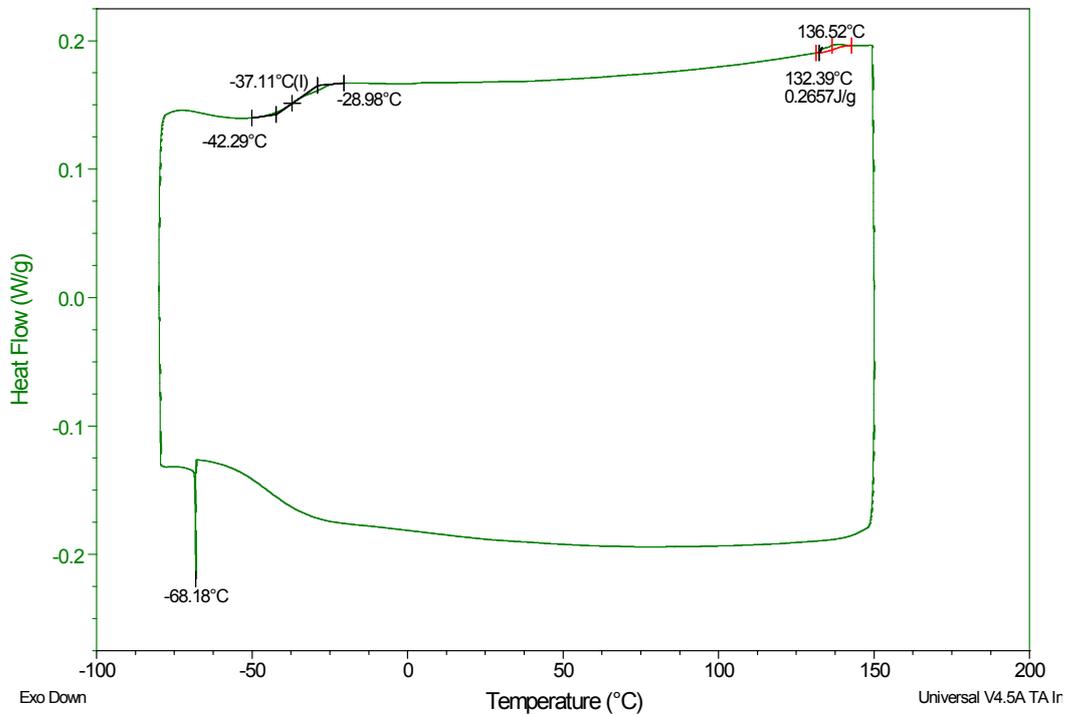


**Figure S7:** Changes observed in the whole FTIR spectra on complexation with various metals, as shown inside the figure.

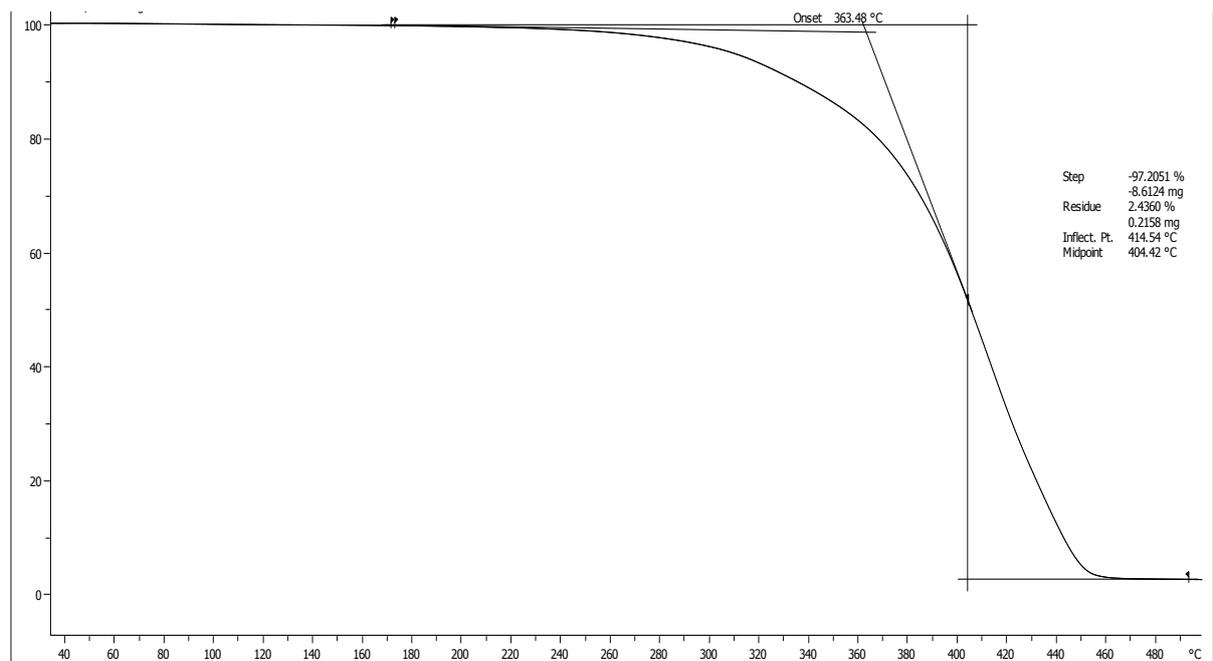


**Figure S8:** Changes observed in the C=O stretching band on complexation with various metals, as shown inside the figure.

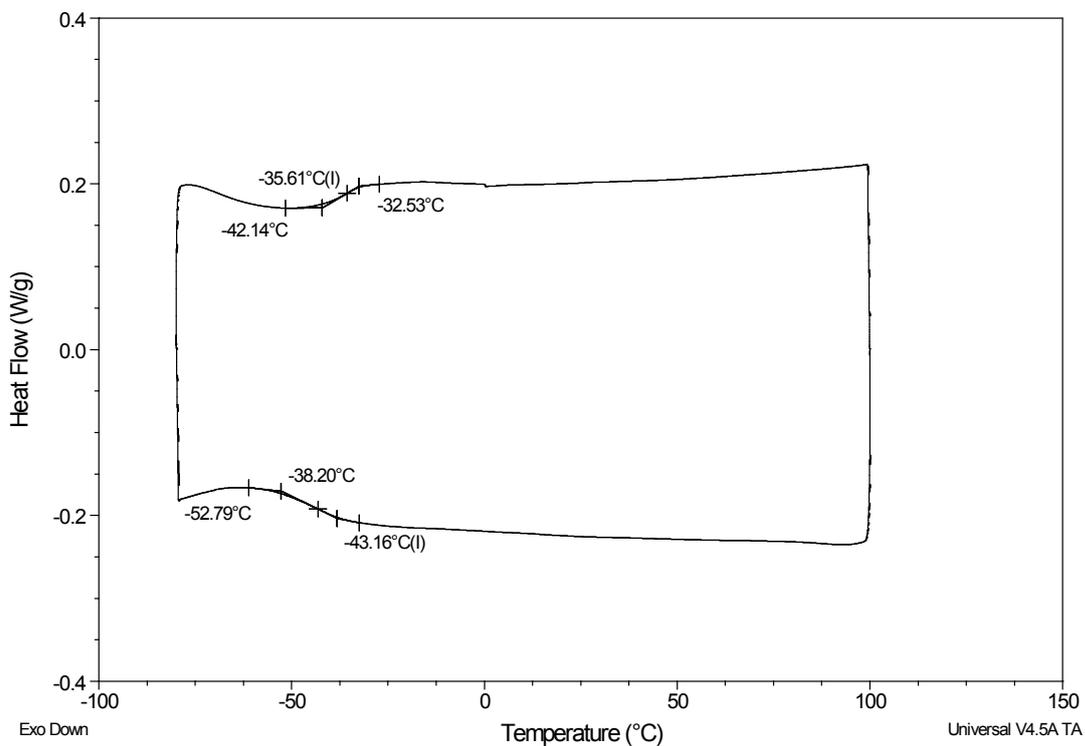
### DSCs and TGAs of DAIL-1 and DAIL-2



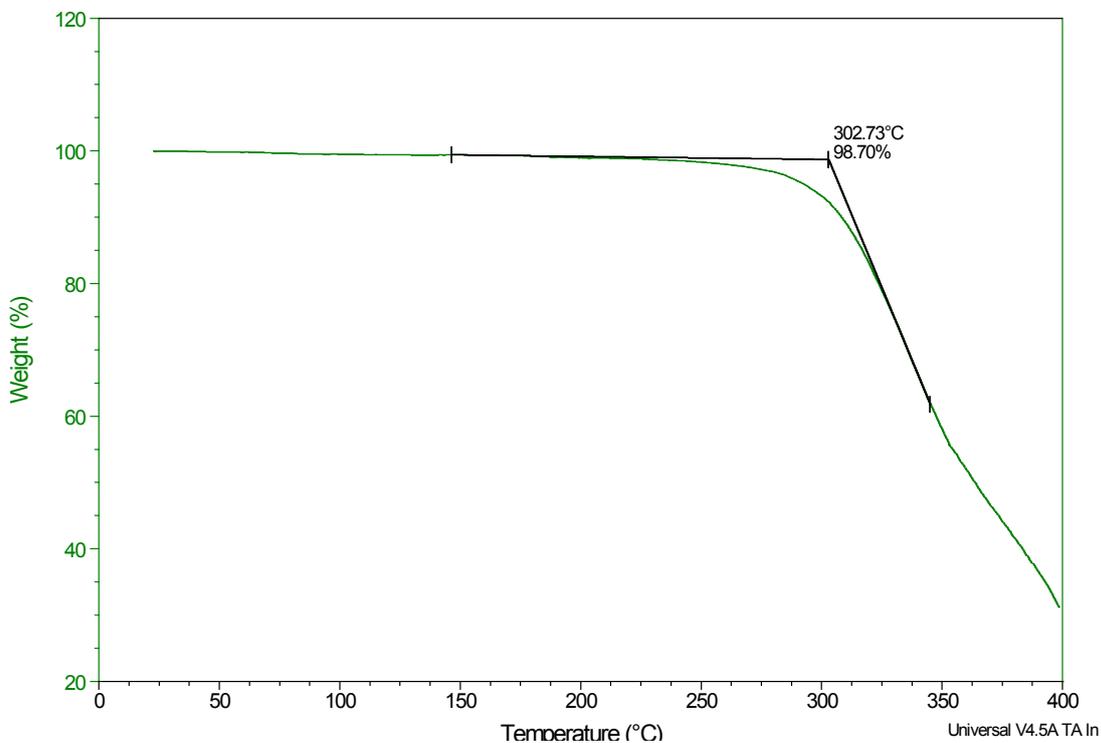
**Figure S9:** Differential scanning calorimetry of DAIL-1 (scan rate 5 °C m<sup>-1</sup>)



**Figure S10:** The Thermogravimetric analysis data of DAIL-1 (scan rate was set at 10 °C m<sup>-1</sup>)



**Figure S11:** Differential scanning calorimetry of DAIL-2 (scan rate 5 °C m<sup>-1</sup>)



**Figure S12:** The Thermogravimetric analysis data of DAIL-1 (scan rate was set at 10 °C m<sup>-1</sup>)

## Structure optimisation study

Optimization the charged (+5) DAIL complex geometry was done using NWChem 6.6 [NWChem] using the BP86 functional with Def2-SVP basis set for each element except lanthanum, for which the Def2-ECP was used. Dispersion (van der Waals) interaction were also accounted for using the Grimme's D3 correction [D3]. The charged complex was subsequently micro-solvated by adding 5 bistriflimide anions leading to a neutral cluster. The optimisation of the neutral cluster geometry was done using MOPAC 2016 [MOPAC] using the sparkle/PM7 semiempirical method [SPARKLE/PM7]. The optimized cluster geometry was then subjected to vibrational frequency determination wherein the absence of imaginary harmonic frequencies confirmed the attainment of a local minimum of the total energy. To ease the electronic structure calculations, the bulkier alkyl groups (e.g. octyl or decyl) were replaced by methyl groups. The files containing the coordinates of both optimised geometries can be provided on request.

References:

[NWChem]

M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J.J. van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, W.A. de Jong, "NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations" *Comput. Phys. Commun.* 181, 1477 (2010) DOI: 10.1016/j.cpc.2010.04.018

[D3]

Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg, "A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu" *J. Chem. Phys.* 132, 154104 (2010) DOI: 10.1063/1.3382344

[MOPAC]

MOPAC2016, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, [HTTP://OpenMOPAC.net](http://OpenMOPAC.net) (2016).

[SPARKLE/PM7]

José Diogo L. Dutra, Manoel A. M. Filho, Gerd B. Rocha, Ricardo O. Freire, Alfredo M. Simas, and James J. P. Stewart, "Sparkle/PM7 Lanthanide Parameters for the Modeling of Complexes and Materials" *Journal of Chemical Theory and Computation* 9, 3333 (2013) DOI: 10.1021/ct301012h