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Oxidation of europium with ammonium perfluorocarboxylates in liquid ammonia: Pathways to europium(II) carboxylates and hexanuclear europium(III) fluoridocarboxylate complexes

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Table of contents

1 Equations 3

1.1 Equations for the synthesis of 1 3
1.2 Equations for the synthesis of 2 and 3 3

2 Selected structural parameters 3

2.1 $[Eu(O_2CCF_3)_2(dmf)_2]_\infty$ (1) 3
2.2 $(NH_4)_2[Eu_6F_8(O_2CCF_3)_{12}(CF_3COOH)_6]$ (2) 4
2.3 $(NH_4)_2[Eu_6F_8(O_2CC_2F_5)_{12}(C_2F_5COOH)_6]\cdot 8C_2F_5COOH$ (3) 5

3 Thermal analysis 7

4 Spectroscopy 10

4.1 IR and Raman spectra 11
4.2 ^{19}F NMR spectra 15

5 Packing diagrams and crystal morphology 16

References 18

1 Equations

1.1 Equations for the synthesis of 1

$$Eu + 2\ NH_4O_2CC_nF_{2n+1} \rightarrow Eu(O_2CC_nF_{2n+1})_2 + H_2 + 2\ NH_3$$

Equation S1 Idealized reaction between europium metal and ammonium perfluorocarboxylates.

$$Eu(O_2CCF_3)_2 + 2\ C_3H_7NO \rightarrow [Eu(O_2CF_3)_2(C_3H_7NO)_2]_\infty\ (\mathbf{1})$$

Equation S2 Formation of **1**.

1.2 Equations for the synthesis of 2 and 3

$$6\ Eu(O_2CR)_2 + 12\ RCO_2H + 8\ NH_4F \rightarrow (NH_4)_2[Eu_6F_8(O_2CR)_{12}(RCO_2H)_6] + 6\ NH_4O_2CCF_3 + 3\ H_2$$

Equation S3 1st assumption for the formation of **2** (R = CF_3) and **3** (R = C_2F_5).

$$6\ Eu(O_2CR)_2 + 1½\ O_2 + 12\ RCO_2H + 8\ NH_4F \rightarrow (NH_4)_2[Eu_6F_8(O_2CR)_{12}(RCO_2H)_6] + 6\ NH_4O_2CCF_3 + 3\ H_2O$$

Equation S4 2nd assumption for the formation of **2** (R = CF_3) and **3** (R = C_2F_5).

2 Selected structural parameters

2.1 $[Eu(O_2CCF_3)_2(dmf)_2]_\infty$ (1)

Table S1 Selected structural parameters for **1** (Å, °).

Parameters	d_i	s_i
Bond lengths		
Eu1—O4	2.542(6)	0.30
Eu1—O2^{i}	2.546(6)	0.30
Eu1—O1	2.562(6)	0.29
Eu1—O3^{ii}	2.565(7)	0.29
Eu1—O6^{i}	2.598(6)	0.26
Eu1—O6	2.614(6)	0.25
Eu1—O5^{ii}	2.621(6)	0.25
Eu1—O5	2.623(6)	0.24
Eu1—O19	2.383(17)	0.43
		S **1.92**
Eu1···Eu1^{i}	4.0839(13)	
Eu1···Eu1^{ii}	4.1049(13)	
Bond angles		
O1—C1—O2	130.8(10)	
O3—C3—O4	131.7(10)	
Eu1—O5—Eu1^{ii}	103.0(2)	
Eu1—O6—Eu1^{i}	103.2(2)	

$S = \Sigma\ s_i = \Sigma\ \exp[(d_0 - d_i) \div B]$;[1] $d_0(Eu^{II}—O)$ = 2.102 Å, B = 0.37.[2]
Symmetry codes: (i) 1–x, 1–y, 1–z; (ii) –x, 1–y, 1–z.

2.2 $(NH_4)_2[Eu_6F_8(O_2CCF_3)_{12}(CF_3COOH)_6]$ (2)

Table S2 Selected structural parameters for **2** (Å).

Bond lengths	d_i	s_i	Bond lengths	d_i	s_i
Eu1—F1	2.400(13)	0.31	Eu4—F2	2.426(13)	0.28
Eu1—F2	2.382(13)	0.37	Eu4—F3	2.417(15)	0.29
Eu1—F3	2.382(13)	0.32	Eu4—F6	2.403(12)	0.30
Eu1—F4	2.406(13)	0.30	Eu4—F7	2.390(12)	0.31
Eu1—O1	**2.751(19)**	0.16	**Eu4—O7**	**2.566(17)**	0.27
Eu1—O13	2.355(17)	0.46	Eu4—O18	2.367(17)	0.46
Eu1—O15	2.42(2)	0.30	Eu4—O24	2.488(16)	0.33
Eu1—O17	2.497(17)	0.32	Eu4—O25	2.385(18)	0.43
Eu1—O19	2.383(17)	0.43	Eu4—O33	2.384(17)	0.43
		S **3.07**			*S* **3.11**
Eu2—F1	2.378(13)	0.32	Eu5—F3	2.361(14)	0.34
Eu2—F4	2.377(12)	0.33	Eu5—F4	2.368(13)	0.33
Eu2—F5	2.402(12)	0.30	Eu5—F7	2.364(12)	0.34
Eu2—F8	2.391(11)	0.31	Eu5—F8	2.413(14)	0.30
Eu2—O3	**2.528(17)**	0.29	**Eu5—O9**	**2.720(18)**	0.18
Eu2—O14	2.388(17)	0.43	Eu5—O20	2.454(17)	0.36
Eu2—O21	2.368(19)	0.46	Eu5—O26	2.380(17)	0.44
Eu2—O28	2.469(17)	0.34	Eu5—O27	2.359(18)	0.46
Eu2—O29	2.373(15)	0.44	Eu5—O35	2.412(17)	0.40
		S **3.23**			*S* **3.11**
Eu3—F1	2.377(14)	0.33	Eu6—F5	2.390(12)	0.31
Eu3—F2	2.390(13)	0.32	Eu6—F6	2.404(13)	0.30
Eu3—F5	2.380(12)	0.32	Eu6—F7	2.399(13)	0.31
Eu3—F6	2.346(12)	0.35	Eu6—F8	2.363(12)	0.34
Eu3—O5	**2.688(19)**	0.19	**Eu6—O11**	**2.766(19)**	0.15
Eu3—O16	2.406(17)	0.41	Eu6—O30	2.502(17)	0.32
Eu3—O22	2.357(18)	0.47	Eu6—O32	2.373(17)	0.45
Eu3—O23	2.351(18)	0.47	Eu6—O34	2.337(18)	0.49
Eu3—O31	2.439(17)	0.37	Eu6—O36	2.431(17)	0.38
		S **3.22**			*S* **3.04**

$S = \Sigma s_i = \Sigma \exp[(d_0 - d_i) \div B]$;[1] $d_0(Eu^{III}—F) = 1.961$ Å, $B = 0.37$;[3] $d_0(Eu^{III}—O) = 2.074$ Å, $B = 0.37$.[1]
Eu—O bonds located at the octahedral vertices are set in bold in the table.

Table S3 Hydrogen-bond geometry in **2** (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.91	2.51	2.82(3)	100.5
N1—H3···O13	0.91	2.17	2.85(3)	131.1
N1—H4···O9^{i}	0.91	2.11	2.91(3)	146.1
N2—H8···O11	0.91	2.11	2.85(3)	137.3
N2—H5···O5^{ii}	0.91	2.06	2.89(3)	150.6
N2—H7···O34	0.91	2.22	2.95(3)	136.6
N2—H6···O22^{ii}	0.91	2.34	3.00(3)	128.9
O2—H9···O17	0.83	1.83	2.64(2)	163.6
O12—H14···O30	0.83	1.84	2.65(3)	164.0
O6—H11···O31	0.83	1.85	2.66(3)	163.6
O4—H10···O28	0.83	1.90	2.68(3)	155.9
O10—H13···O20	0.83	1.90	2.68(3)	155.3
O8—H12···O24	0.83	1.92	2.70(3)	156.4

Symmetry codes: (i) x+1, y, z; (ii) x−1, y, z.

2.3 $(NH_4)_2[Eu_6F_8(O_2CC_2F_5)_{12}(C_2F_5COOH)_6]\cdot 8C_2F_5COOH$ (3)

Table S4 Selected structural parameters for **3** (Å).

Bond lengths	d_i	s_i	Bond lengths	d_i	s_i
Eu1—F1	2.349(3)	0.35	Eu4—F5	2.353(3)	0.35
Eu1—F2	2.417(3)	0.29	Eu4—F6	2.390(3)	0.31
Eu1—F5	2.370(3)	0.33	Eu4—F7	2.372(3)	0.33
Eu1—F6	2.369(3)	0.33	Eu4—F8	2.381(3)	0.32
Eu1—O1	**2.655(4)**	0.21	**Eu4—O7**	**2.657(4)**	0.21
Eu1—O13	2.370(4)	0.45	Eu4—O18	2.387(4)	0.43
Eu1—O15	2.462(4)	0.35	Eu4—O26	2.367(4)	0.45
Eu1—O17	2.358(4)	0.46	Eu4—O27	2.363(4)	0.46
Eu1—O19	2.388(4)	0.43	Eu4—O36	2.446(4)	0.37
		S **3.20**			*S* **3.22**
Eu2—F1	2.391(3)	0.31	Eu5—F2	2.344(3)	0.36
Eu2—F2	2.378(3)	0.32	Eu5—F3	2.373(3)	0.33
Eu2—F3	2.375(3)	0.33	Eu5—F5	2.381(3)	0.32
Eu2—F4	2.376(3)	0.33	Eu5—F8	2.358(3)	0.34
Eu2—O3	**2.701(4)**	0.18	**Eu5—O9**	**2.644(4)**	0.21
Eu2—O14	2.446(4)	0.37	Eu5—O20	2.370(4)	0.45
Eu2—O22	2.378(4)	0.44	Eu5—O21	2.453(4)	0.36
Eu2—O23	2.365(4)	0.46	Eu5—O28	2.380(4)	0.44
Eu2—O32	2.389(4)	0.43	Eu5—O34	2.383(4)	0.43
		S **3.16**			*S* **3.24**
Eu3—F1	2.364(3)	0.34	Eu6—F3	2.370(3)	0.33
Eu3—F4	2.365(3)	0.34	Eu6—F4	2.377(3)	0.32
Eu3—F6	2.385(3)	0.32	Eu6—F7	2.402(3)	0.30
Eu3—F7	2.344(3)	0.36	Eu6—F8	2.358(3)	0.34
Eu3—O5	**2.650(4)**	0.21	**Eu6—O11**	**2.672(4)**	0.20
Eu3—O16	2.375(4)	0.44	Eu6—O29	2.362(4)	0.46
Eu3—O24	2.388(4)	0.43	Eu6—O31	2.359(4)	0.46
Eu3—O25	2.494(4)	0.32	Eu6—O33	2.424(4)	0.39
Eu3—O30	2.374(4)	0.44	Eu6—O35	2.411(4)	0.40
		S **3.19**			*S* **3.21**

$S = \Sigma\, s_i = \Sigma \exp[(d_0 - d_i) \div B]$;[1] $d_0(Eu^{III}—F) = 1.961$ Å, $B = 0.37$;[3] $d_0(Eu^{III}—O) = 2.074$ Å, $B = 0.37$.[1]
Eu—O bonds located at the octahedral vertices are set in bold in the table.

Table S5 Hydrogen-bond geometry in **3** (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···O47	0.91	2.15	2.909(8)	139.8
N1—H2···O45	0.91	2.29	2.921(8)	126.2
N1—H3···O24	0.91	2.11	2.933(6)	149.6
N1—H4···O37	0.91	2.10	2.989(7)	165.9
N1—H1···O30	0.91	2.56	3.034(6)	113.3
N1—H3···O5	0.91	2.43	3.081(7)	128.2
N2—H8···O28	0.91	2.25	2.590(7)	132.9
N2—H6···O49	0.91	2.41	2.874(8)	111.7
N2—H5···O51	0.91	2.04	2.917(8)	162.0
N2—H7···O43	0.91	2.18	3.034(7)	155.1
N2—H8···O9	0.91	2.19	3.034(7)	153.1
Acid molecules, int.				
O4—H10···O14	0.84	1.91	2.669(6)	149.9
O6—H11···O25	0.84	1.87	2.680(6)	160.8
O10—H13···O21	0.84	1.92	2.723(6)	160.1
O2—H9···O15	0.84	1.92	2.725(6)	158.9
O8—H12···O36	0.84	1.92	2.727(6)	160.7
O12—H14···O33	0.84	2.28	2.863(7)	127.2
O12—H14···O35	0.84	2.25	2.904(7)	134.5
Acid molecules, ext.				
O44—H18···O41	0.84	1.77	2.577(8)	159.6
O38—H15···O39	0.84	1.78	2.613(11)	171.5
O42—H17···O43	0.84	1.86	2.701(7)	179.7
O40—H16···O37	0.84	1.94	2.752(9)	163.4
O48—H20···O3	0.84	2.20	2.902(6)	140.4
O50—H21···O1	0.84	2.35	2.962(6)	130.3
O52—H22···O7	0.84	2.24	2.970(6)	145.7
O46—H19···O11	0.84	2.27	3.003(6)	146.2
O50—H21···O19	0.84	2.24	3.038(6)	157.9
O52—H22···O18	0.84	2.40	3.081(7)	136.0

3 Thermal analysis

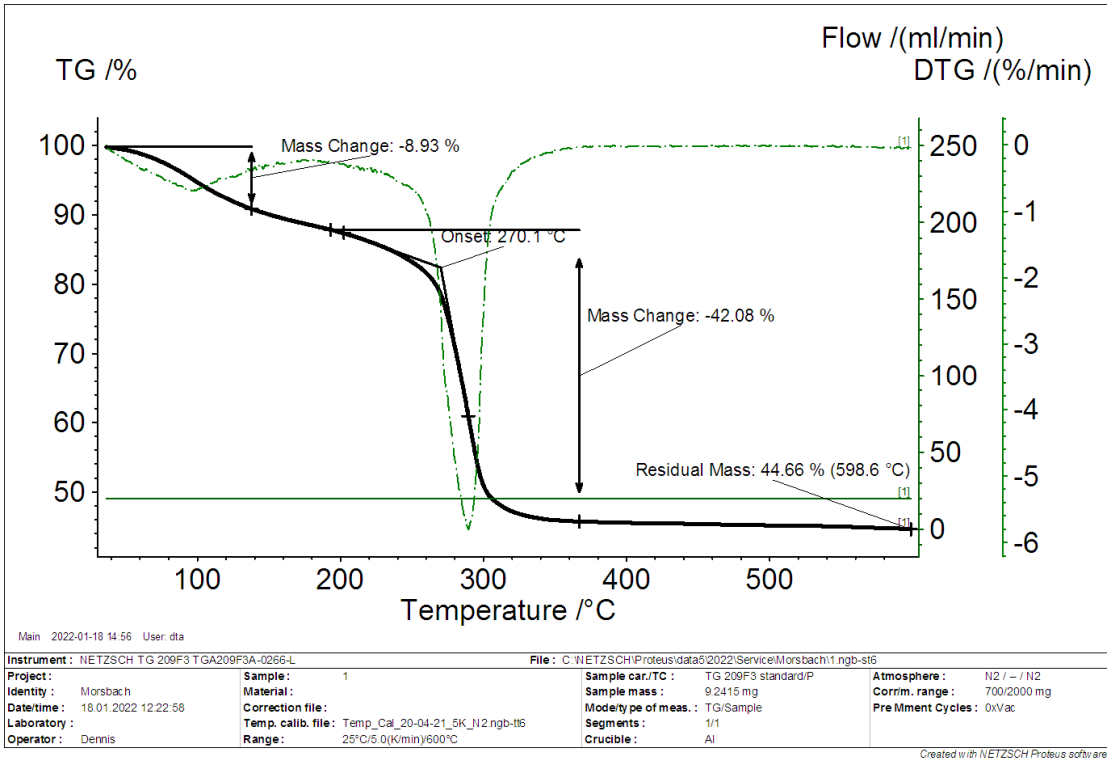

Fig. S1 TGA curve of **1**, $[Eu(O_2CCF_3)_2(dmf)_2]_\infty$.

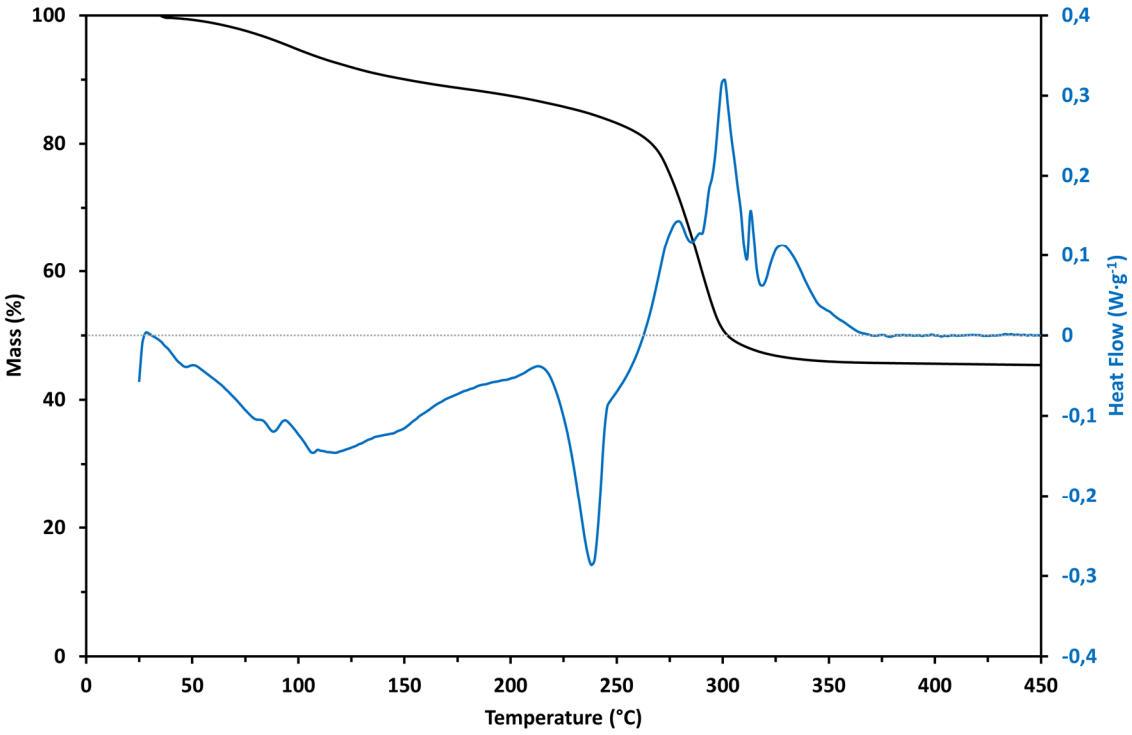

Fig. S2 DSC curve of **1**, $[Eu(O_2CCF_3)_2(dmf)_2]_\infty$, with overlayed TGA curve.

Thermal analysis (continued)

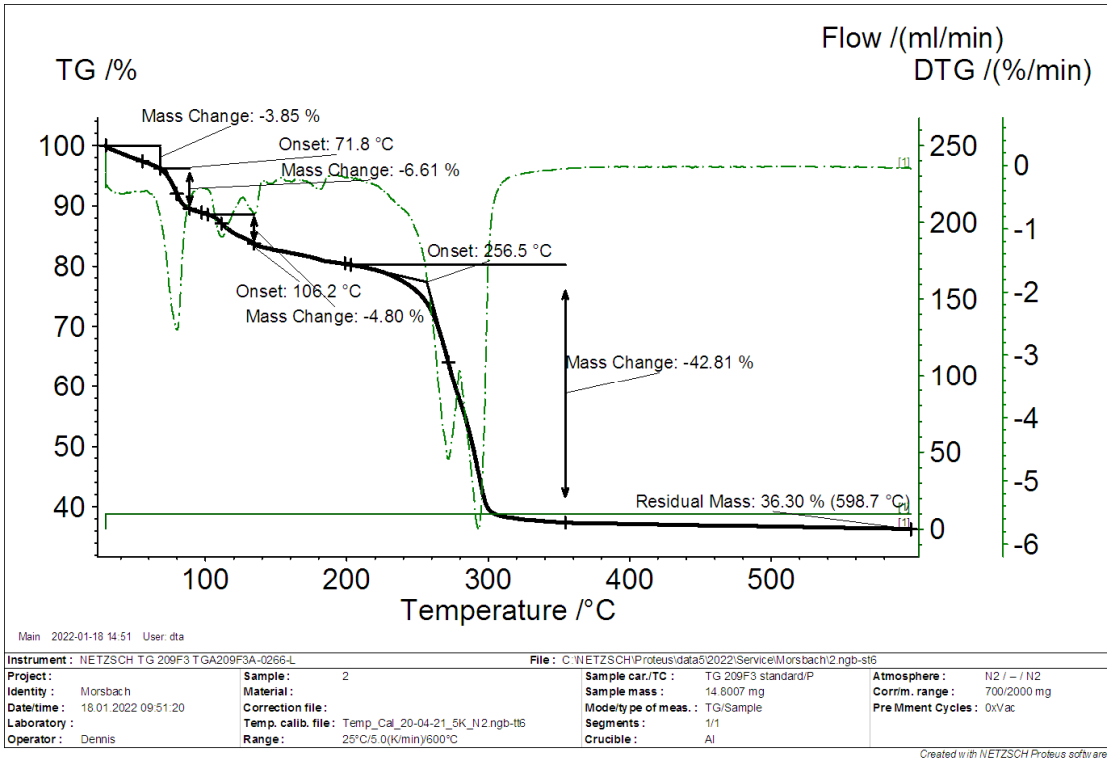

Fig. S3 TGA curve of **2**, $(NH_4)_2[Eu_6F_8(O_2CCF_3)_{12}(CF_3COOH)_6]$.

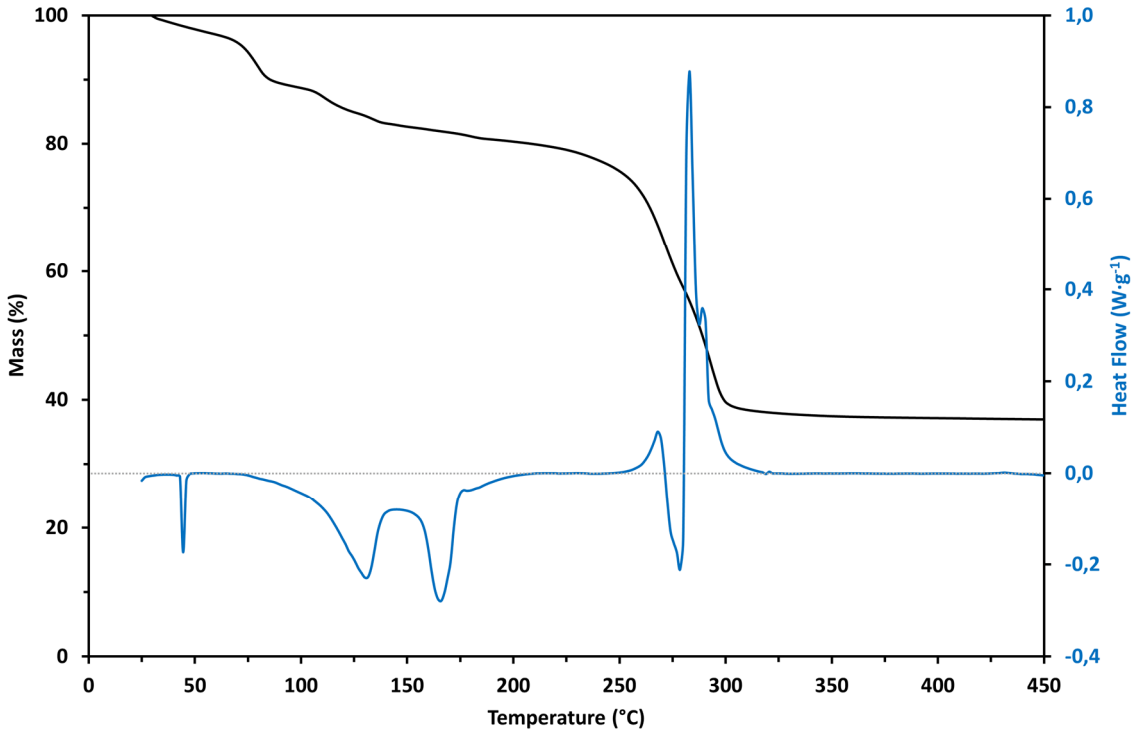

Fig. S4 DSC curve of **2**, $(NH_4)_2[Eu_6F_8(O_2CCF_3)_{12}(CF_3COOH)_6]$, with overlayed TGA curve.

Thermal analysis (continued)

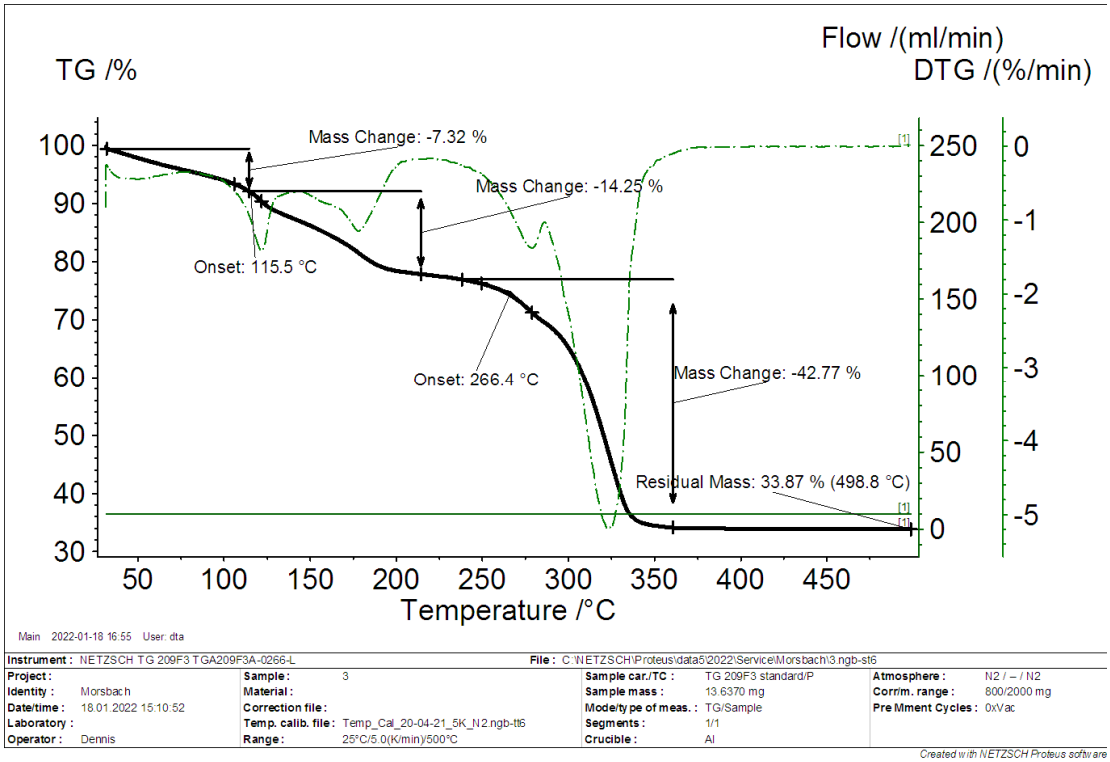

Fig. S5 TGA curve of **3** – 8 C_2F_5COOH, $(NH_4)_2[Eu_6F_8(O_2CCF_3)_{12}(CF_3COOH)_6]$.

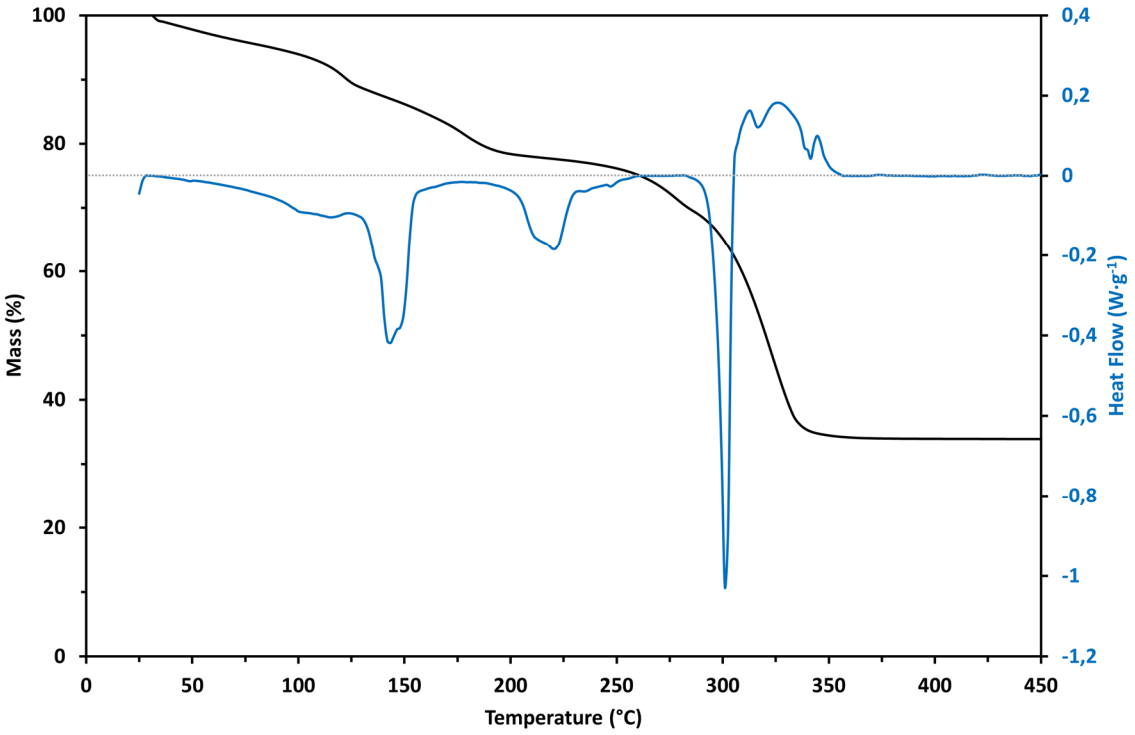

Fig. S6 DSC curve of **3** – 8 C_2F_5COOH, $(NH_4)_2[Eu_6F_8(O_2CC_2F_5)_{12}(C_2F_5COOH)_6]$, with overlayed TGA curve.

Thermal analysis (continued)

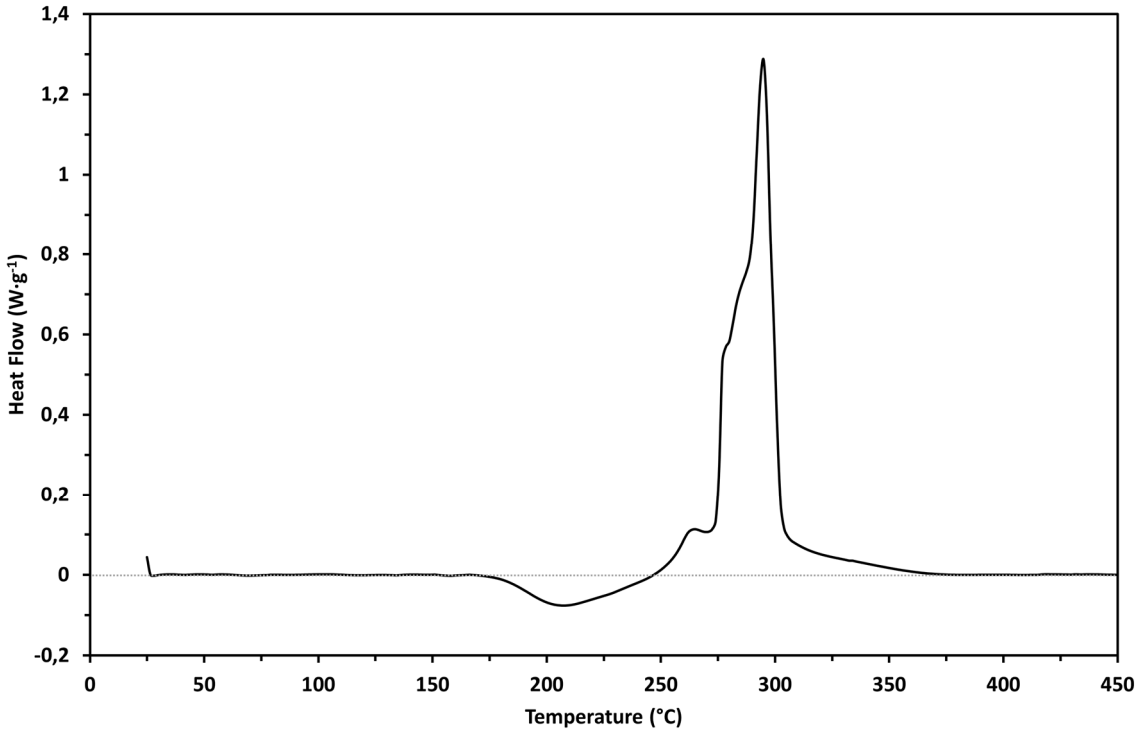

Fig. S7 DSC curve of the $Eu(O_2CCF_3)_2$-containing substance (precursor for **1** and **2**).

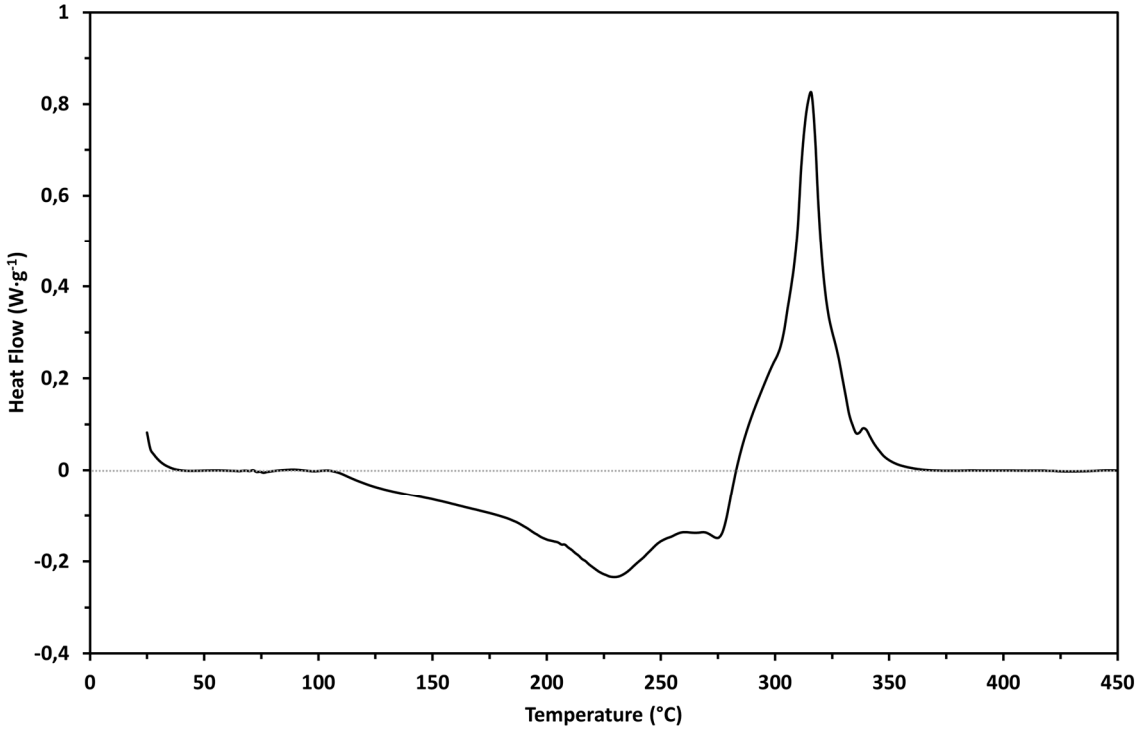

Fig. S8 DSC curve of the $Eu(O_2CC_2F_5)_2$-containing substance (precursor for **3**).

4 Spectroscopy

4.1 IR and Raman spectra

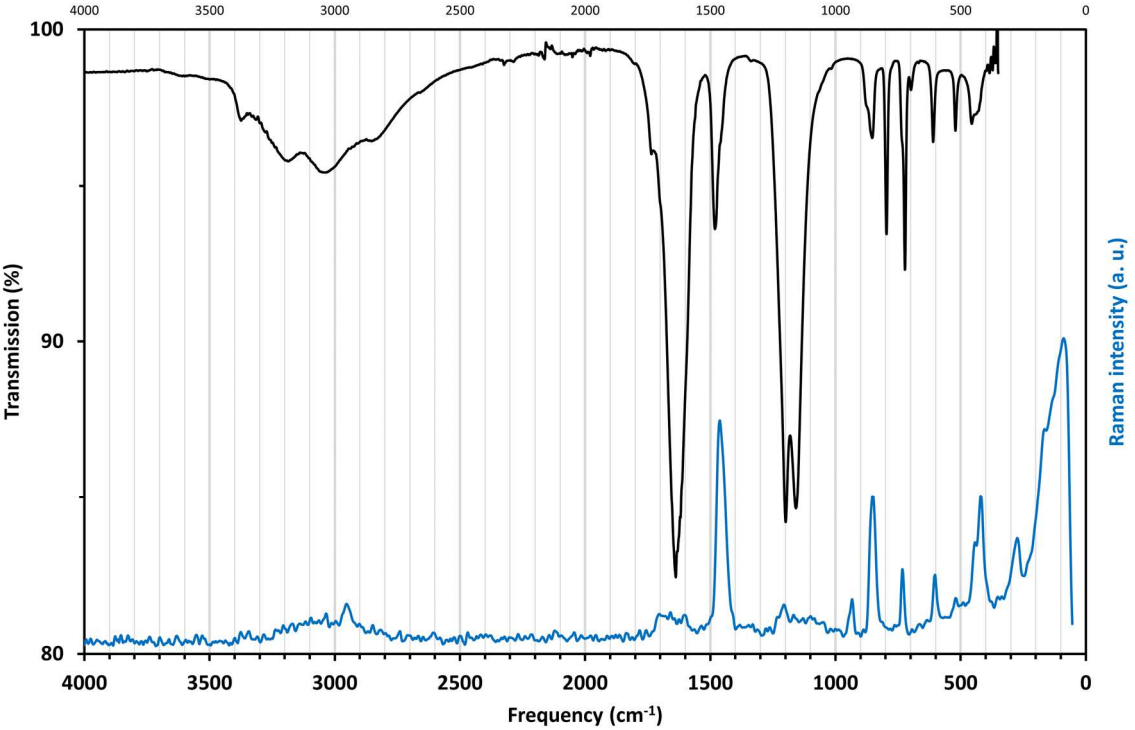

Fig. S9 IR and Raman spectra of the $Eu(O_2CCF_3)_2$-containing substance (precursor for **1** and **2**).

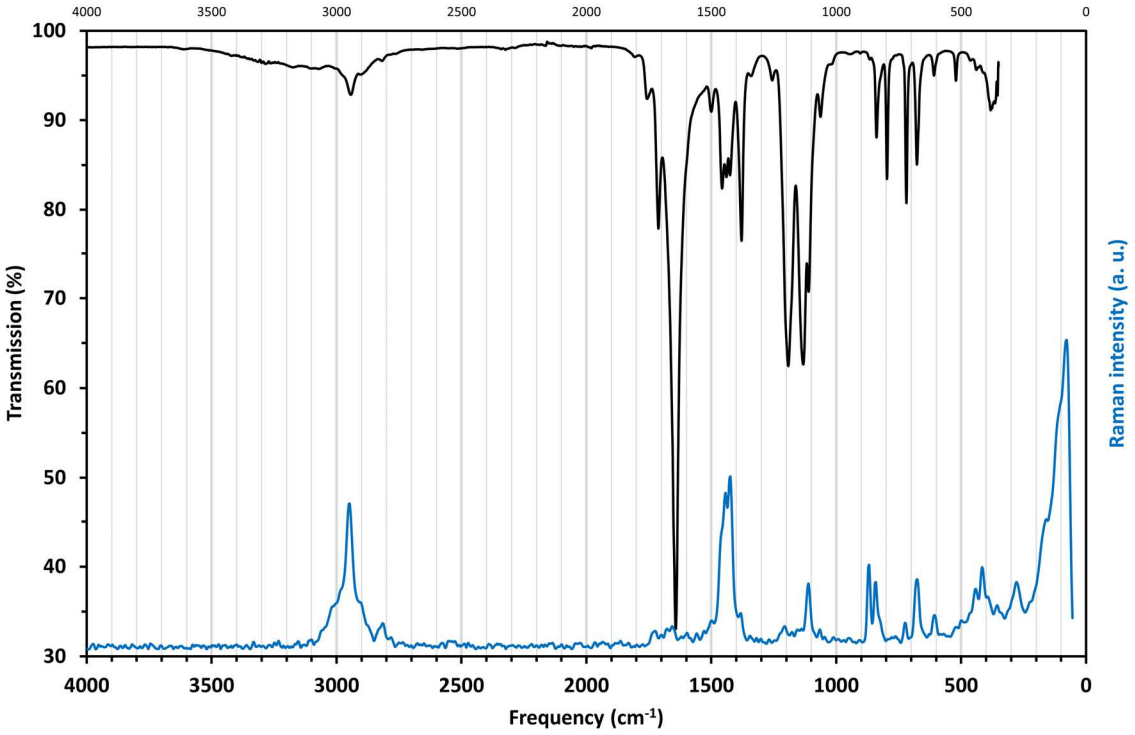

Fig. S10 IR and Raman spectra of **1**, $[Eu(O_2CCF_3)_2(dmf)_2]_\infty$.

IR and Raman spectra (continued)

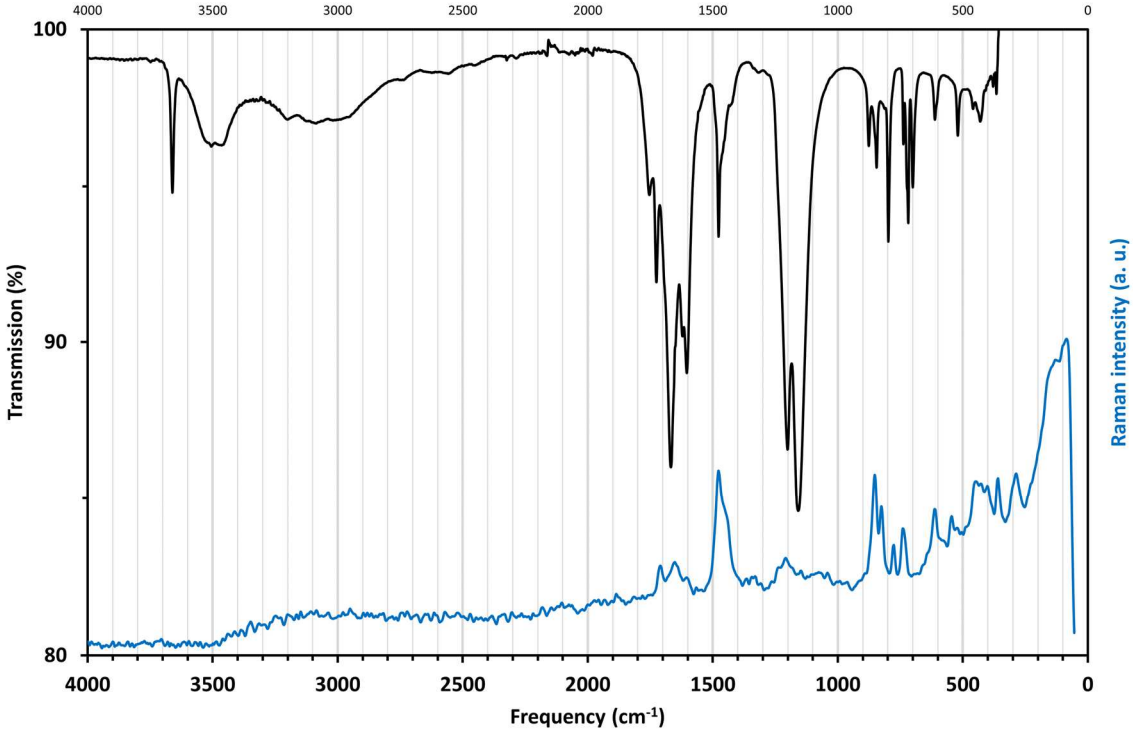

Fig. S11 IR and Raman spectra of **2**, $(NH_4)_2[Eu_6F_8(O_2CCF_3)_{12}(CF_3COOH)_6]$.

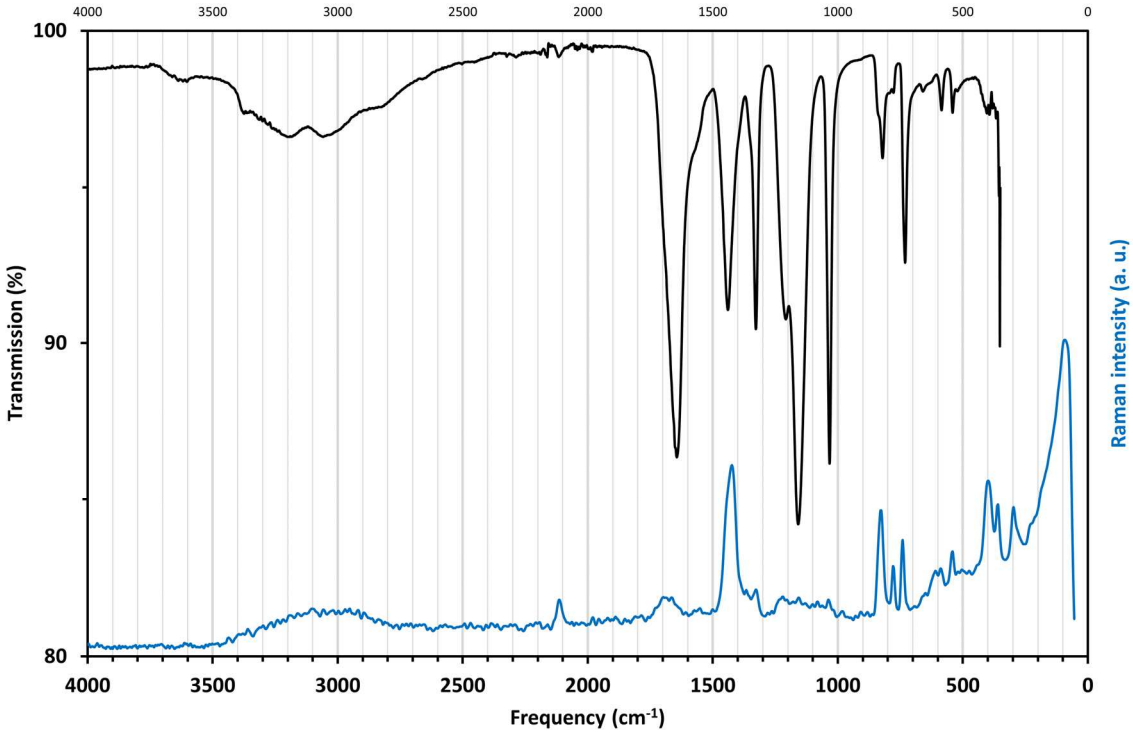

Fig. S12 IR and Raman spectra of the $Eu(O_2CC_2F_5)_2$-containing substance (precursor for **3**).

IR and Raman spectra (continued)

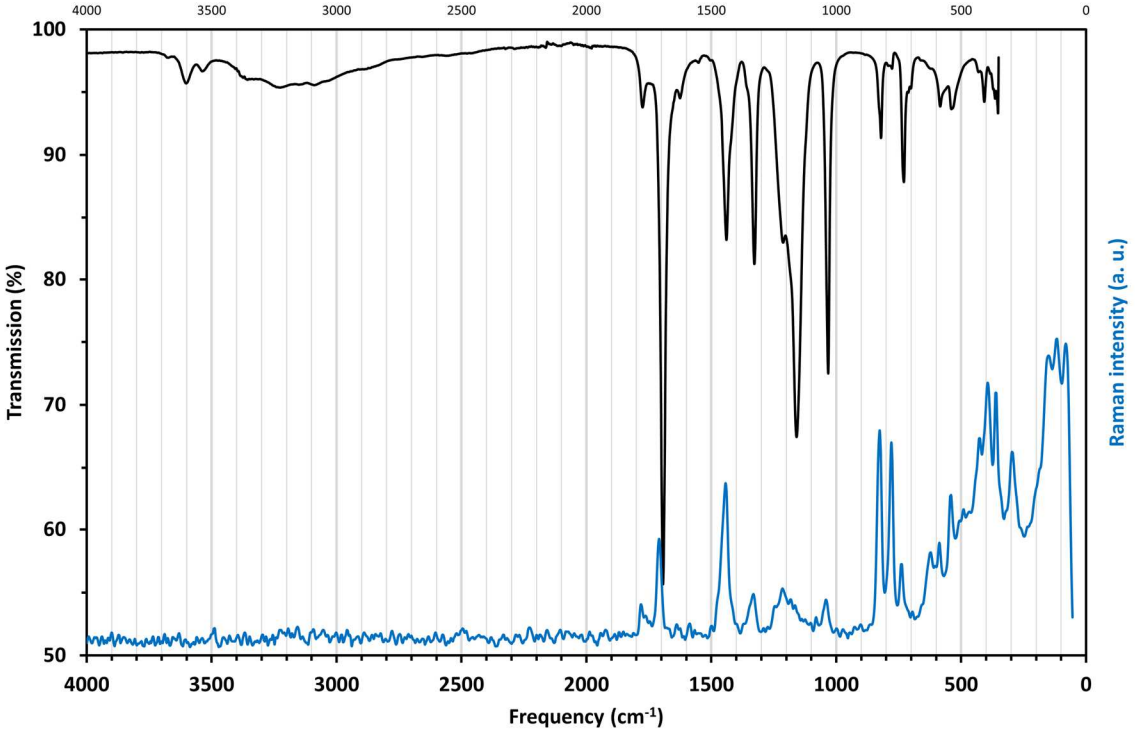

Fig. S13 IR and Raman spectra of **3**, $(NH_4)_2[Eu_6F_8(O_2CC_2F_5)_{12}(C_2F_5COOH)_6]\cdot 8C_2F_5COOH$.

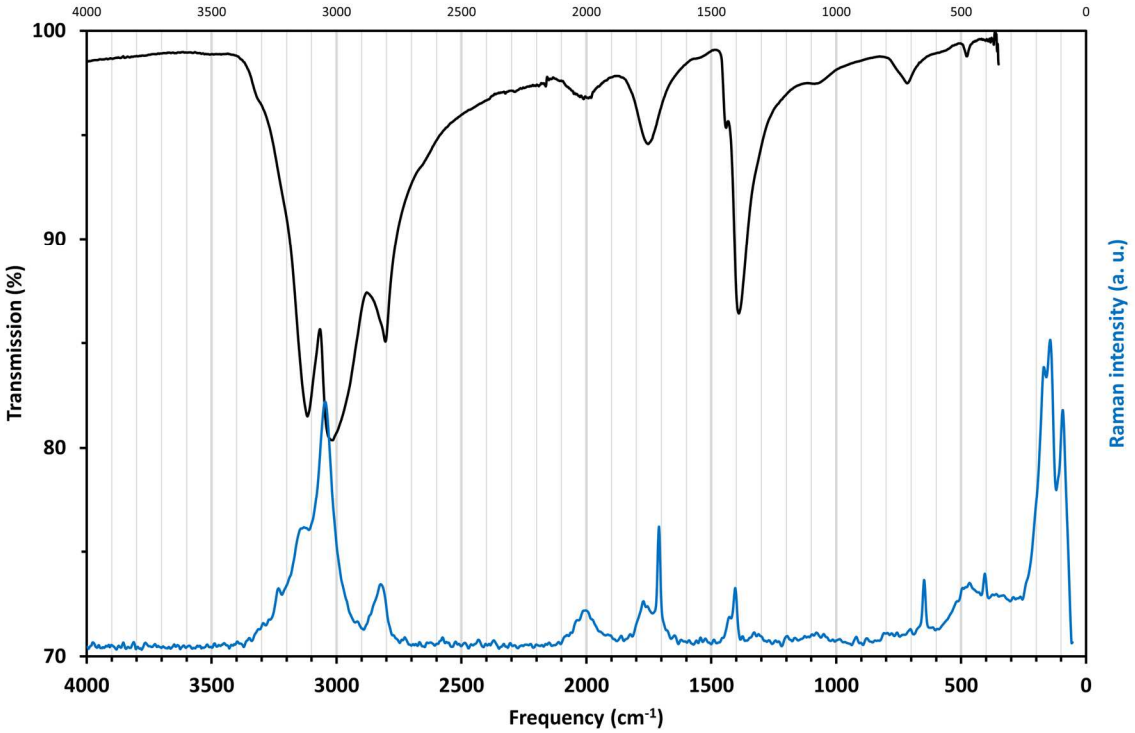

Fig. S14 IR and Raman spectra of ammonium fluoride, NH_4F.

IR and Raman spectra (continued)

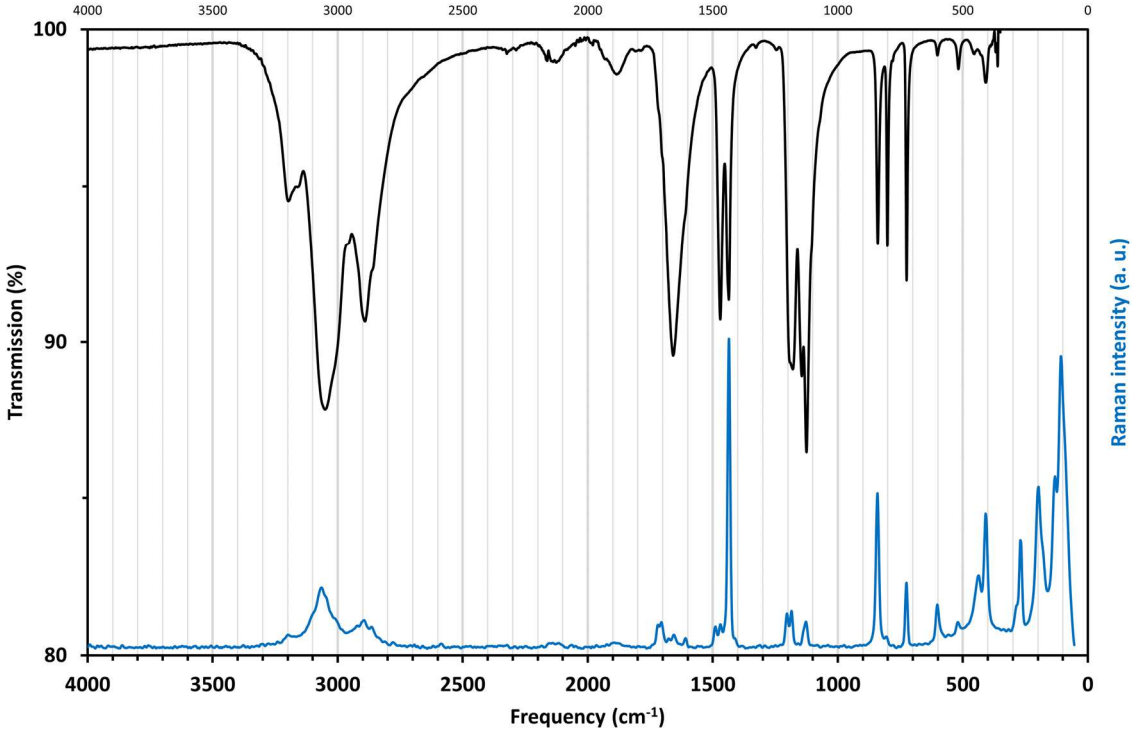

Fig. S15 IR and Raman spectra of ammonium trifluoroacetate, $NH_4O_2CCF_3$.

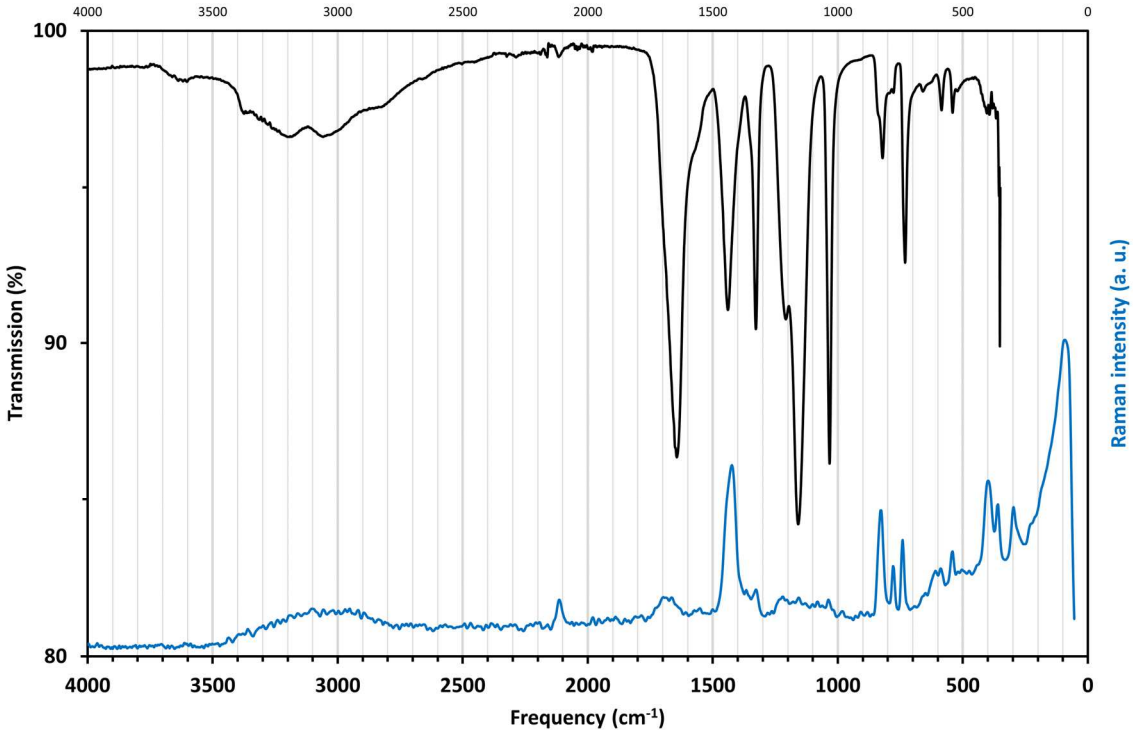

Fig. S16 IR and Raman spectra of ammonium pentafluoropropionate, $NH_4O_2CC_2F_5$.

4.2 ^{19}F NMR spectra

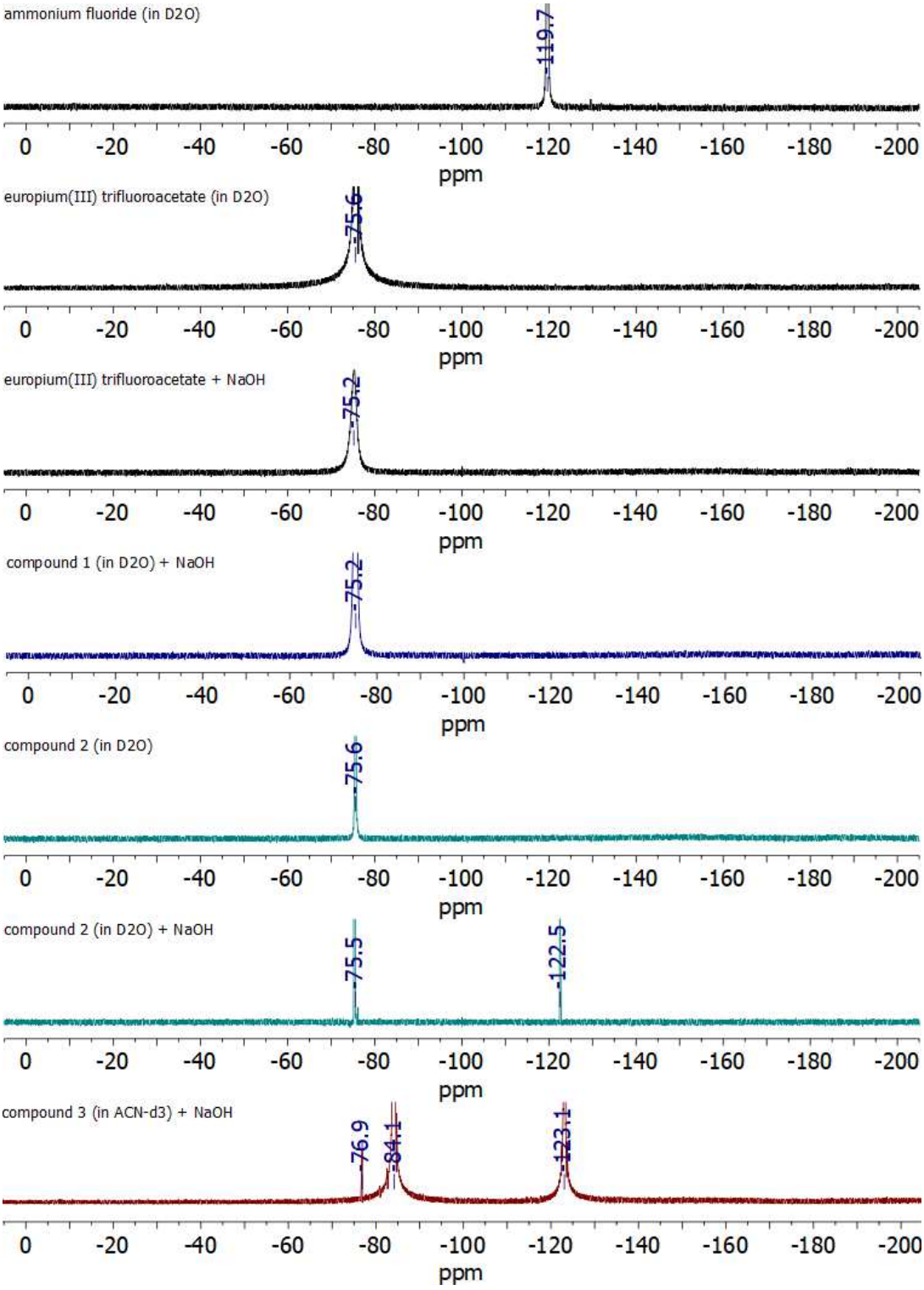

Fig. S17 ^{19}F NMR spectra of **1** and **2** (in D_2O) and of **3** (in acetonitrile-d_3). The chemical shift of free fluoride ions depends on the solvent and is about –123 ppm in deuterium oxide and about –77 ppm in acetonitrile.[4]

5 Packing diagrams and crystal morphology

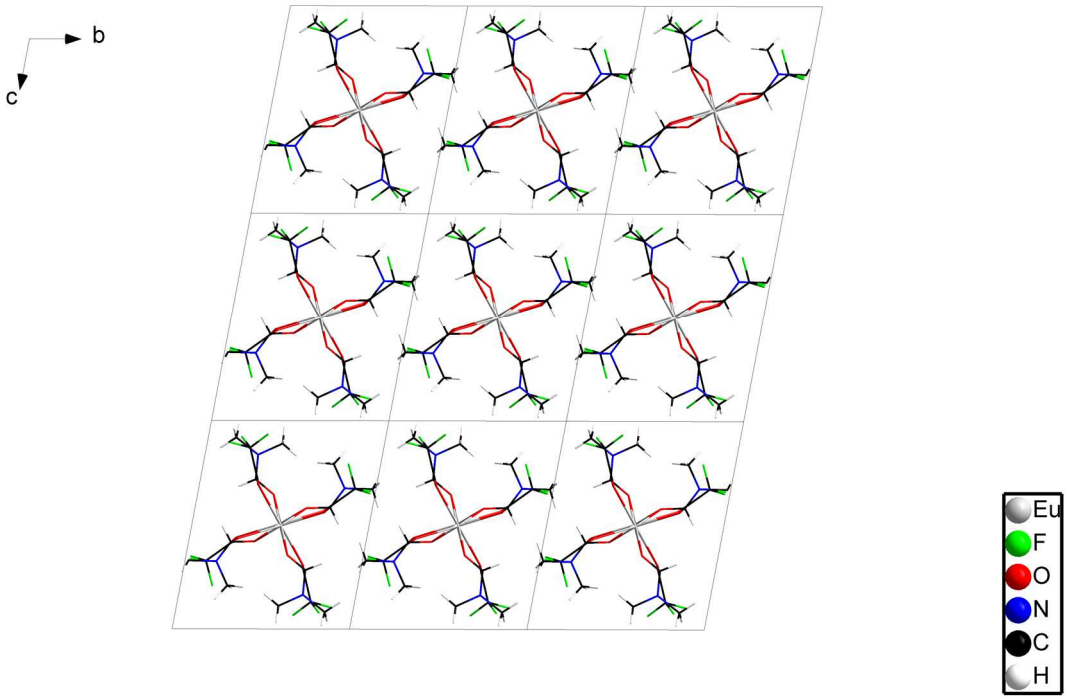

Fig. S18 Packing diagram of **1**. Direction of view along the crystallographic *a*-axis [100].

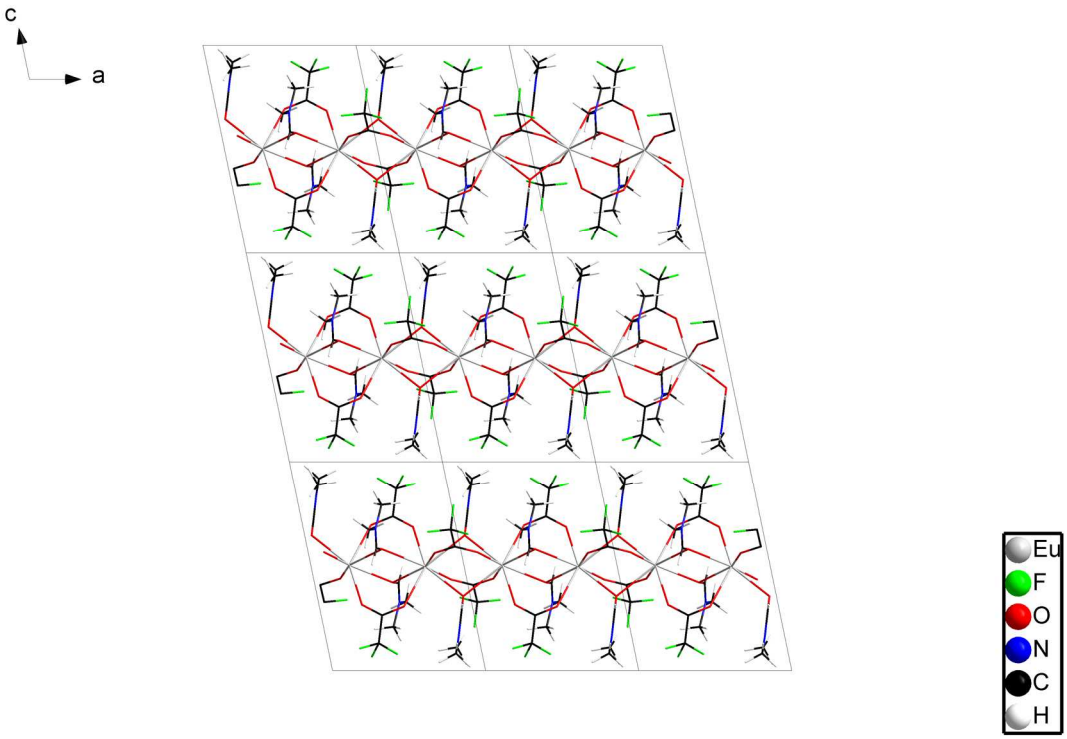

Fig. S19 Packing diagram of **1**. Direction of view along the crystallographic *b*-axis [010].

Packing diagrams (continued)

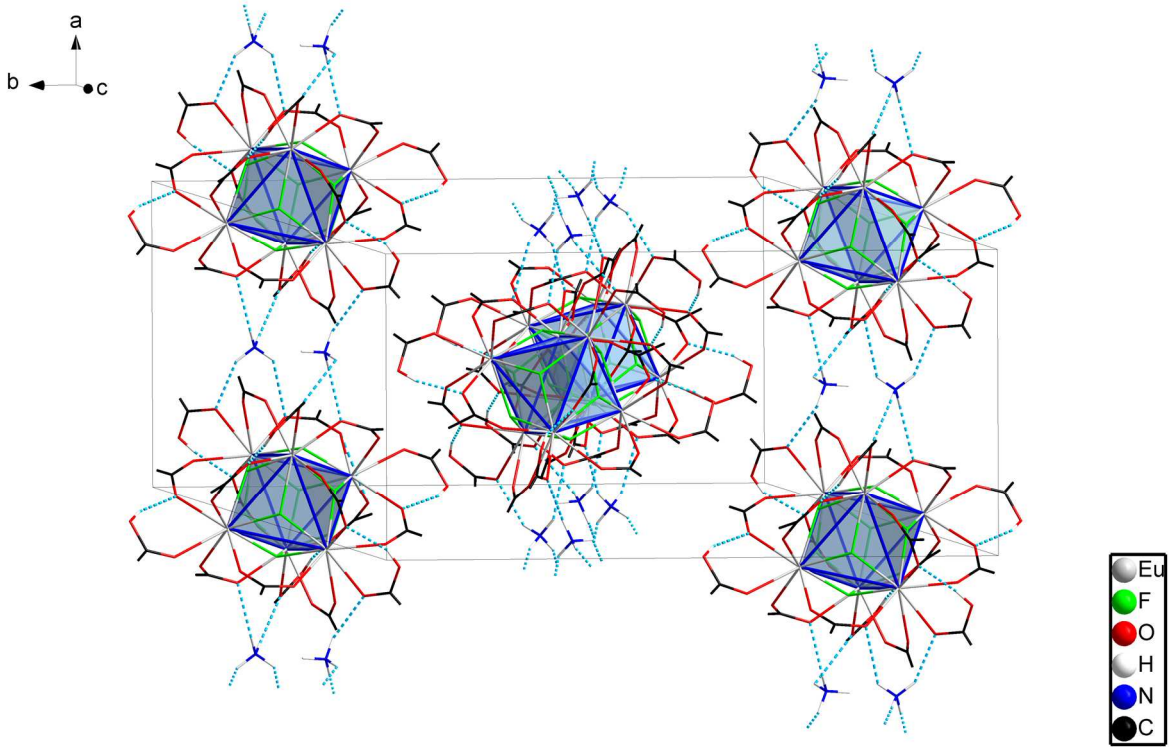

Fig. S20 Packing diagram of **2**. Note the connection of the complex ions along the crystallographic *a*-axis [100].

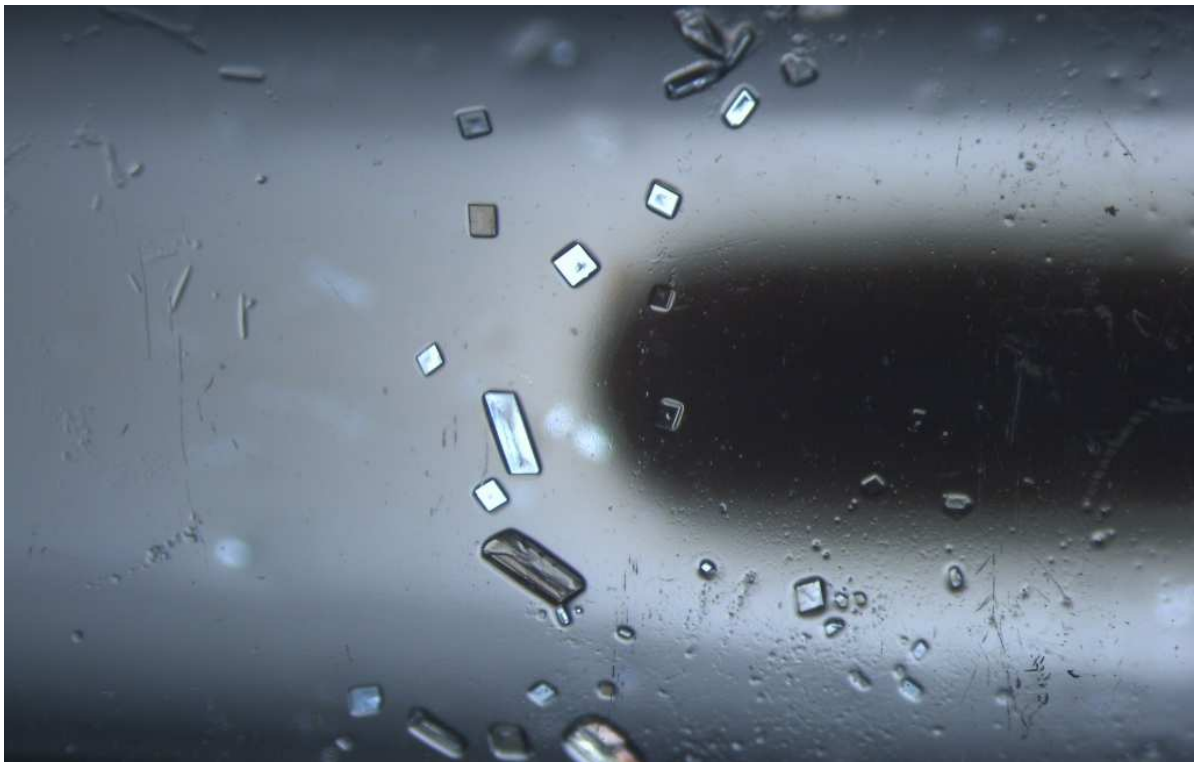

Fig. S21 Crystals of **2** (that are also representative for **3**) under a microscope in polarized light.

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