Crystal structures of $[Eu(CF_3CF_2OCF_2CF_2SO_3)_3(H_2O)_5]\ H_2O$ (**1**) and $Na[Eu(CF_3CF_2OCF_2CF_2SO_3)_2(H_2O)_6](CF_3CF_2OCF_2CF_2SO_3)_2\ H_2O$ (**2**)

Crystals of both substances were found in the electrolyzer, when the reduction regime was relaxed. They were of bad quality. Synthesis of $Na[Eu(CF_3CF_2OCF_2CF_2SO_3)_2(H_2O)_6]$-$(CF_3CF_2OCF_2CF_2SO_3)_2\ H_2O$ was repeated. 0.176 g of Eu_2O_3 (0.5 mmol), 0.040 g of NaOH (1 mmol) and 1.280 g of were reacted together in appr. 3 ml of water. The solution was evaporated to appr. 1 ml and 4 ml of 1-propanol were added. The crystal for the data collection was selected after a week's evaporation at ambient conditions. An attempt to prepare $[Eu(CF_3CF_2OCF_2CF_2SO_3)_3(H_2O)_5]\ H_2O$ crystals of better quality was unsuccessful. The crystals were mounted on a Rigaku SYNERGY diffractometer equipped with a CCD camera. The structure was solved with SHELXS[1] and refined with SHELXL-2017.[2] The H atoms were not located. The non-H atoms were refined anisotropically. The investigated crystal of $[Eu(CF_3CF_2OCF_2CF_2SO_3)_3(H_2O)_5]\ H_2O$ (**1**)was twinned. The data collection and refinement details for **1** and **2** are given in Table S1 and the respective Eu-O distances – in Table S2.

Table S1. Data collection and refinement details for **1** and **2.**

	1	**2**
Chemical formula	$C_{12}H_{12}EuF_{27}O_{18}S_3$	$C_{16}H_{14}EuF_{36}NaO_{23}S_4$
M_r	1205.36	1561.46
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
Temperature (K)	100	100
a, b, c (Å)	16.934 (6), 12.916 (4), 32.216 (16)	17.953 (4), 24.722 (6), 10.768 (3)
β (°)	96.17 (6)	103.58 (3)
V (Å^3)	7005 (5)	4646 (2)
Z	8	4
Radiation type	Mo $K\alpha$	Mo Kα
μ (mm^{-1})	2.18	1.76
Crystal size (mm)	0.31 × 0.16 × 0.05	0.14 × 0.10 × 0.03
Absorption correction	multi-scan	analytical
T_{min}, T_{max}	0.928, 1.000	0.831, 0.964
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	84091, 84091, 51179	67942, 13646, 9704
R_{int}	not merged	0.102

$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.052	0.705
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.093, 0.248, 1.06	0.052, 0.139, 1.02
No. of reflections	84091	13646
No. of parameters	1096	730
No. of restraints	8	0
Weights	$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 60.9735P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 10.4835P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	8.86, −2.70	3.72, −1.18

Table S2. Eu-O distances in **1** and **2.**

		1	
Eu1—O21	2.375 (4)	Eu2—OW10	2.381 (4)
Eu1—OW1	2.384 (4)	Eu2—O51	2.381 (4)
Eu1—OW3	2.383 (4)	Eu2—OW7	2.383 (4)
Eu1—OW5	2.389 (5)	Eu2—O61	2.386 (5)
Eu1—O11	2.399 (4)	Eu2—OW8	2.389 (5)
Eu1—O31	2.397 (4)	Eu2—O41	2.409 (4)
Eu1—OW2	2.415 (4)	Eu2—OW9	2.418 (4)
Eu1—OW4	2.425 (4)	Eu2—OW6	2.433 (4)
		2	
Eu—OW5	2.385 (3)	Eu—O11	2.396 (3)
Eu—OW1	2.391 (3)	Eu—OW3	2.415 (3)
Eu—OW4	2.395 (3)	Eu—OW2	2.421 (3)
Eu—OW6	2.396 (3)	Eu—O21	2.437 (3)

Brief description of the structures

In **1** there are two independent Eu sites and the $CF_3CF_2OCF_2CF_2SO_3$ anion generated by S1 is partially disordered. In **2** there are four anions and the charge is compensated by a Na^+ cation which was present in the reaction mixture as impurity. All the Eu^{3+} cations in both structures are 8-coordinate and contrary to the Eu(II) compound, described in the main part of the paper, they are more hydrated: the cations in **1** are bonded to 5 water molecules each ant that in **2** – to 6 ones.

The sulfonate ligands in **1** are monodentate and in **2** the ligands generated by S1 and S2 form bridges between Eu and Na, that generated by S3 is monodentate, being bonded to Na, and

the sulfonate group generated by S4 bridges two Na cations. The structure fragments are shown in Figs. S1 and S2, and the packing diagrams – in Figs. S3 and S4.

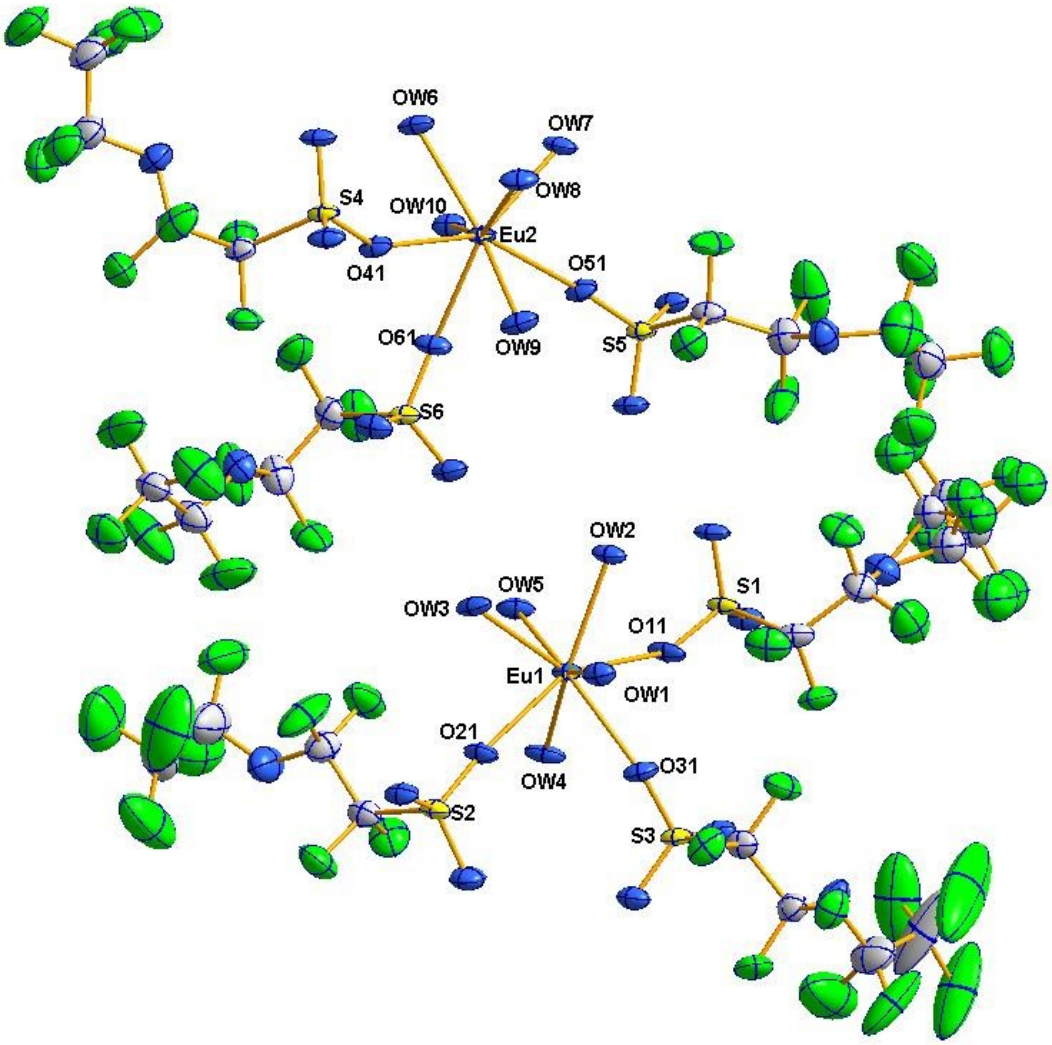

Fig. S1. Fragment of the structure in **1**. The labels are shown for Eu, S and coordinated O atoms. Uncoordinated water molecules (OW11 and OW12) are not shown.

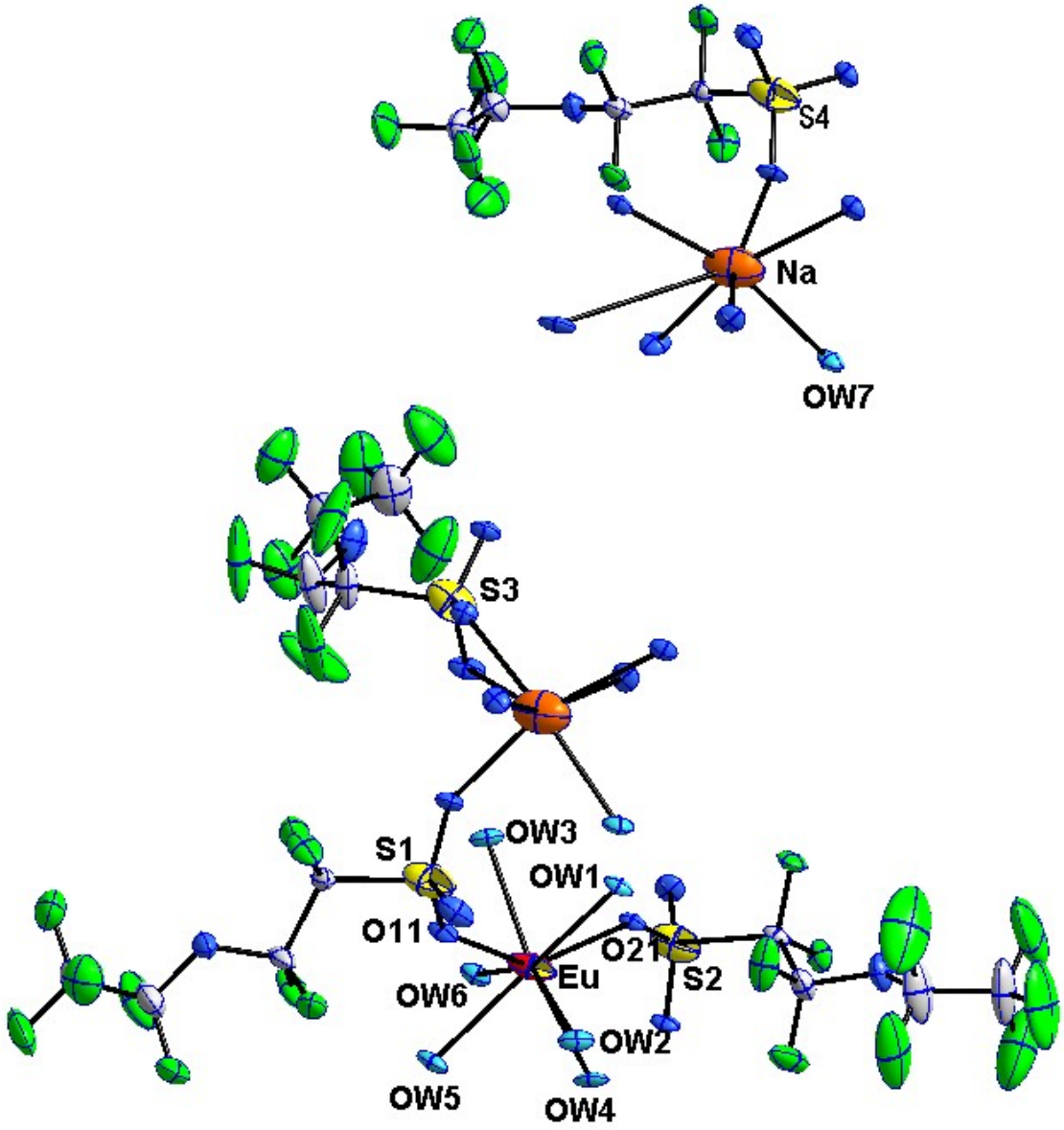

Fig. S2. Fragment of the structure in **2**. The labels are shown for Eu, S and symmetry independent Na and coordinated O atoms. The sulfonate O atoms are blue, the water molecules are turquoise.

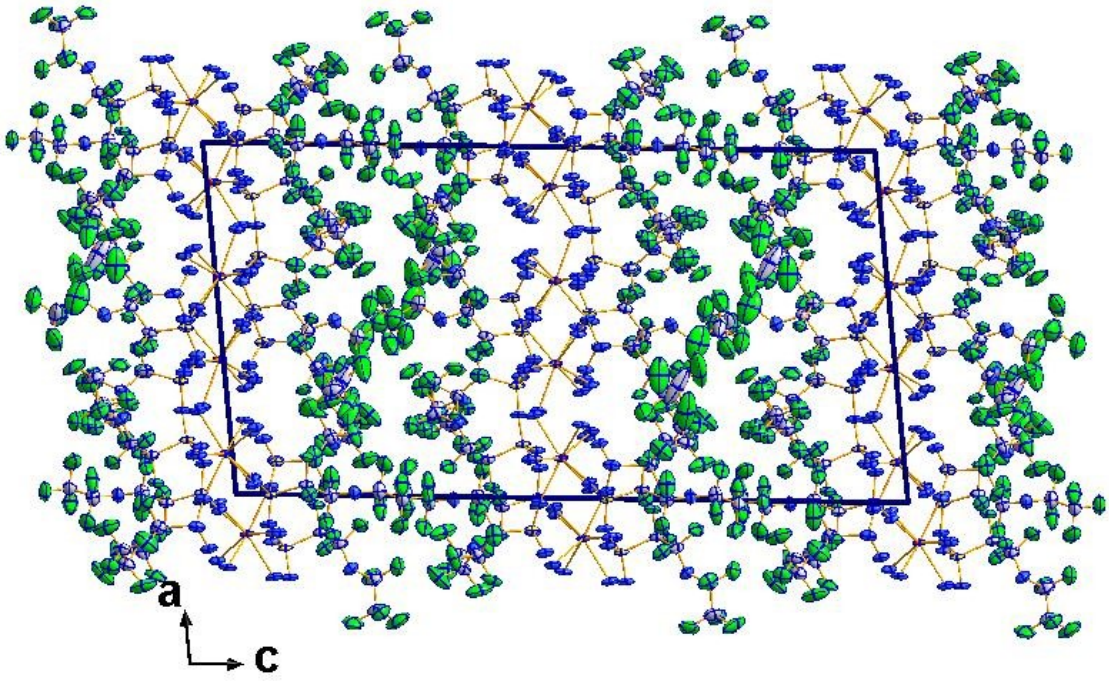

Fig. S3. Packing diagram of **1**.

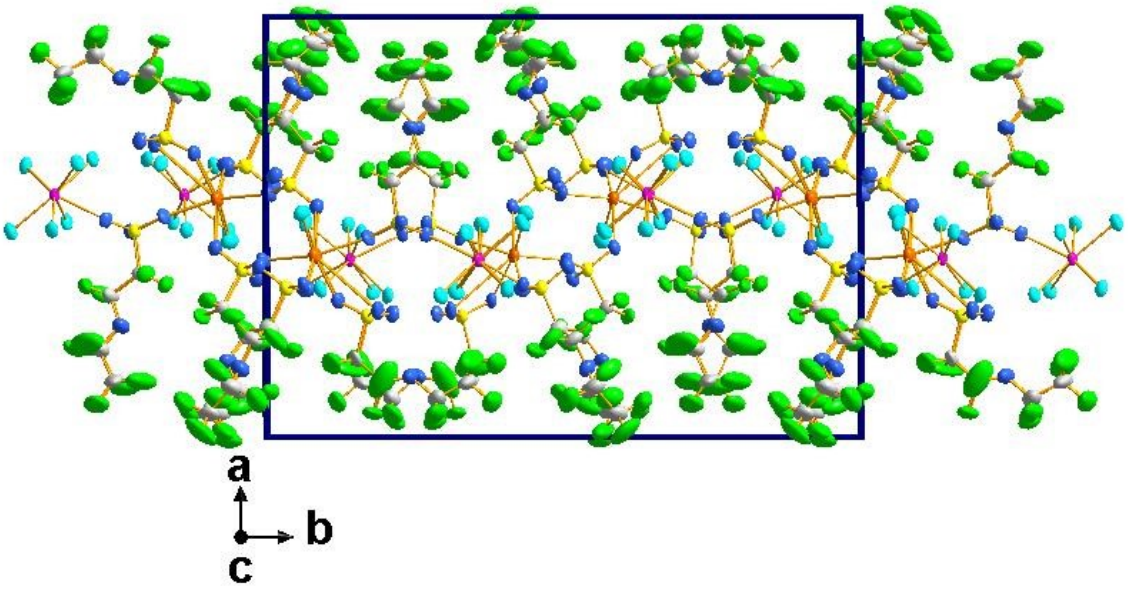

Fig. S4. Packing diagram of **2**. The Eu atoms are pink, the Na ones – orange, other colours are attributed as in Fig. S2.

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[1] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

[2] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.