

Chemistry–A European Journal

Supporting Information

The Earlier the Better: Structural Analysis and Separation of Lanthanides with Pyrroloquinoline Quinone

Henning Lumpe^{+, [a]} Annika Menke^{+, [a]} Christoph Haisch,^[b] Peter Mayer,^[a] Anke Kabelitz,^[c] Kirill V. Yusenko,^[c] Ana Guilherme Buzanich,^[c] Theresa Block,^[d] Rainer Pöttgen,^[d] Franziska Emmerling,^[c] and Lena J. Daumann^{*[a]}

Table of Contents

Experimental Procedures.....	2
Supporting Figures	4
Supporting Tables.....	8
References	13

Experimental Procedures

Materials

Metal salts were either purchased from abcr Germany ($\text{LnCl}_3 \cdot n\text{H}_2\text{O}$, 99.9%, Ln = Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb), Sigma-Aldrich ($\text{LnCl}_3 \cdot n\text{H}_2\text{O}$, 99.99%, Ln = La, Ce, Pr, Eu), chemPUR ($\text{LuCl}_3 \cdot n\text{H}_2\text{O}$, 99.9%). The water of crystallization of the lanthanides ($n\text{H}_2\text{O}$) was analyzed by elemental microanalysis prior to experiments and is given in the respective experimental descriptions. PQQ was extracted from Doctor's Best Science-Based Nutrition PQQ capsules, as described previously.^[1] Milli-Q-grade water (pH 5.5), received from a Millipore Synergy UV system from Merck (Darmstadt, Germany), was used for all experiments.

Methods

Eu₂ PQQ₂ crystal preparation

$\text{Na}_2\text{PQQ} \cdot \text{H}_2\text{O}$ (24.2 mg, 61.8 μmol) was completely dissolved in H_2O (4 mL) at 80 °C in an ultrasonic bath. $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (67.9 mg, 185.4 μmol , 3 equiv.) was dissolved in a small amount of water (0.2 mL) and was added to the Na_2PQQ solution at 80 °C, which caused precipitation of a grey-brown solid. The mixture was directly placed in an oven at 80 °C, which was then switched off to slowly cool down the reaction mixture. After one day, small, dark crystals grew between the bulk precipitate. The crystals grew in size over the next days while partially consuming the surrounding bulk precipitate. Due to the presence of both crystals and precipitate, reporting of an isolated yield was not possible. Crystals, suitable for x-ray diffraction analysis were then picked out of the reaction mixture.

Ln₁PQQ or Ln₁Ln₂PQQ synthesis

$\text{Na}_2\text{PQQ} \cdot \text{H}_2\text{O}$ (20 mg, 51.0 μmol , 1.0 equiv.) was completely dissolved in H_2O (8 mL) in 45 mL centrifuge tubes, resulting in a pH decrease to pH = 3.5. Stock solutions of $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ in H_2O (100 μL / equiv. Na_2PQQ) were prepared. For pure samples, 300 μL (3 equiv.) of the respective $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ was added to the Na_2PQQ solution or for mixed samples, 300 μL (3 equiv.) $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 300 μL (3 equiv.) of an additional $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ were mixed together and then added to the Na_2PQQ solution. To work-up the formed precipitate, the suspension was centrifuged (5 min at 4500 rpm in a Heraeus Megafuge 8R benchtop centrifuge with a swinging bucket), and the colorless supernatant was removed. To wash the resulting pellet, water was added (25 mL), and the suspension was first vortex mixed and then centrifuged (same configuration as above), followed by the removal of the supernatant. This washing step was repeated twice. The pellet was then lyophilized overnight (Christ Alpha) to afford a brown powder. From a washing solution the crystals were grown for the EuPQQ complex over several weeks at room temperature.

Room temperature **EPR measurements** with a Bruker EMX nano, x-band spectrometer showed for some powdered samples (with the diamagnetic lanthanides La and Lu) traces of an organic, most likely PQQ-based, radical. Further investigation of redox chemistry and radical formation was not conducted in this study.

Coordination experiments with the La/Lu couple were carried out the same way, but in addition, both Na_2PQQ and $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ solutions were either cooled to 4 °C using an ice bath or warmed up to 50 °C or 78 °C prior to addition, using a dry block heater from IKA.

For **experiments with controlled pH**, the lanthanide mixtures (300 μL / 3 equiv. $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in H_2O and 300 μL / 3 equiv. of an additional $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ in H_2O) were diluted with H_2O (3800 μL), NaCl was added (500 μL / 50 equiv. in H_2O) and the pH was set to 3.5 with few drops of HCl (0.01 M). The Ln mixtures were then added to aqueous solutions of $\text{Na}_2\text{PQQ} \cdot \text{H}_2\text{O}$ (20 mg, 51.0 μmol , 1.0 equiv.) and the formed precipitate was treated as described above.

SUPPORTING INFORMATION

For **experiments with lanthanum and the lanthanides** (except Pm) at different pH values, the pH of the Na₂PQQ solution was set to either 2.5, 3.5 or 4.5 with few drops of HCl (0.01 M) or NaOH (0.01 M) before metal addition. Stock solutions of LnCl₃·nH₂O in H₂O (200 μL / equiv. Na₂PQQ) were prepared, out of which a single stock solution including lanthanum and all lanthanides (2.8 mL equals 1 equiv. of each Ln) was prepared. The Ln mixture was then added to the aqueous solutions of Na₂PQQ·H₂O (20 mg, 51.0 μmol, 1.0 equiv.) at different pH and the formed precipitates were treated as described above. The supernatant received after the first centrifugation was used for ICP-MS analysis. The separation factor was calculated as previously described by Schelter and coworkers^[2] using the following equation:

$$\text{Separation Factor: } SF_{Ln2/Ln1} = \frac{[Ln2]_{solid} / [Ln2]_{filtrate}}{[Ln1]_{solid} / [Ln1]_{filtrate}}$$

The concentrations in solid and filtrate were determined by ICP-MS.

Elemental Microanalyses (EA) (C, H, N) were performed with a vario EL element analyzer.

Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a Nexion 350D from Perkin Elmer, measurements were performed in kinetic energy discrimination (KED) cell mode. An ICP reference standard from VWR was used for calibration, including 14 lanthanides (La-Lu, except Pm), Sc, Y and Th, each in 10 μg/mL concentration. Samples (~5-10 mg) were given in defined amounts of nitric acid (65%, Suprapur from Merck) and were diluted with water to a concentration of 3% HNO₃, which gave a sample concentration of 1.0256 mg/mL. In two additional dilution steps, concentration was set to 50.54 ppb (50 μL in 5 mL 3% HNO₃ followed by 50 μL of this solution in 10 mL 3% HNO₃, the ICP-MS data in Tables S4a and b denotes the concentrations of these final dilutions). Addition of HNO₃ caused precipitation of protonated PQQ as red solid, while the no longer coordinated metal ions stayed in solution. Two additional samples were completely digested in hot nitric acid (65%, Suprapur from Merck) at 125 °C under addition of a few drops of concentrated hydrochloric acid, and then diluted to a concentration of 50.54 ppb. ICP-MS gave similar results for both methods and therefore, the simplified work-up was used for all samples.

FT-Infrared Spectroscopy (IR) was carried out with a Jasco FT/IR-460Plus with an ATR Diamond Plate

X-ray absorption fine structure (XAFS) Samples were measured at 1.5 GeV Synchrotron BL10 DELTA in Dortmund, Germany. The EXAFS measurements were performed at the BL10 beamline at the DELTA synchrotron facility (Technische Universität Dortmund), Germany. Samples were slightly ground in an agate mortar and mixed with Boron Nitride (BN). Powders were placed in 1 mm thick polycarbonate holders between two Kapton foils. The weight ratios between samples and BN powders were calculated to obtain an optimal edge jump of 2. The measurements were performed at L₃-edges of the respective lanthanides. Eu₂O₃, TbCl₃·6H₂O and Lu₂O₃ were used as standard substances. The beam was monochromatized with a channel-cut Si (111) @L₃-edges of Lu (9,244 keV), Tb (7,514 keV), Eu (6,977 keV), La (5,483 keV). The incoming signal was optimized by adjusting Slit1 for each sample. In general, a beamsize of 1mm (V) x 0.6 mm (H) was used. For good statistics, at least 3 spectra were acquired for each sample. In the case of La more repetitions were made, as the signal to noise ratio (SNR) was not so good. For data analysis and evaluation, the open source software package Athena and Artemis based on IFEFFIT was used.^[3] For background subtraction the Rbkg value was set to 1.0. All spectra were normalized to the post-edge region, free from absorption features. A Hanning-type Fourier window for forward Fourier transform was set to the k-range between 2-8 Å⁻¹ with a dk value of 1.0. For an estimation of the coordination of the 1st shell (Ln-O), Artemis was used. The model based on PQQ-Eu single crystal data was used to fit the first shell. A CN of 9 was obtained for La- and Eu-PQQ and a CN of 7 was obtained for Tb- and Lu-PQQ.

Powder Diffraction and Total scattering (XRD/ PDF) Measurements were performed at the P02.1 beamline at the PETRA III synchrotron facility (DESY, Hamburg, Germany).^[4] The samples were slightly ground in an agate mortar and sealed in borosilicate capillaries (Müller GmbH, Berlin, Germany) of 1.0 mm diameter. Samples were measured with spinning at room temperature (λ = 0.20714 Å); LaB₆ powder was used as external standard for wavelength and sample-to-detector distances calibration. The beamsize was 1 mm in diameter. The measuring time was 1 min x 15. Detector parameters are as followed: Pixel Size 200 x 200 μm, pixel count 2048 x 2048, dynamic range 16 bit, maximum frame rate 67 ms, point spread function 1.1 pixels. An empty capillary was used for background subtraction. Data reduction and integration has been performed using DAWN software.^[5] Background subtraction, data reduction and calculation of pair distribution functions were performed using GUDRUN software.^[6] For each sample 15 scattering curves were collected and summed to obtain better data quality. Experimental Q_{max} was chosen up to 23 Å⁻¹.

For the ¹⁵¹Eu Mössbauer spectroscopic investigation of the 1:1 EuPQQ complex the 21.53 keV transition of a ¹⁵¹Sm:EuF₃ source with an activity of 50 MBq (0.91 % of the total activity; *l* = 7/2 to *l* = 5/2 transition) was used. The measurement was conducted at 6 K (continuous flow cryostat system, Janis Research Co LLC) in usual transmission geometry while the source was kept at room temperature. For the measurement the sample was placed in a thin walled PMMA container (diameter of 2 cm) with an optimized thickness corresponding to Long *et al.*^[7] For fitting the spectrum, the WinNormos for Igor software package was used.^[8]

SUPPORTING INFORMATION

Supporting Figures

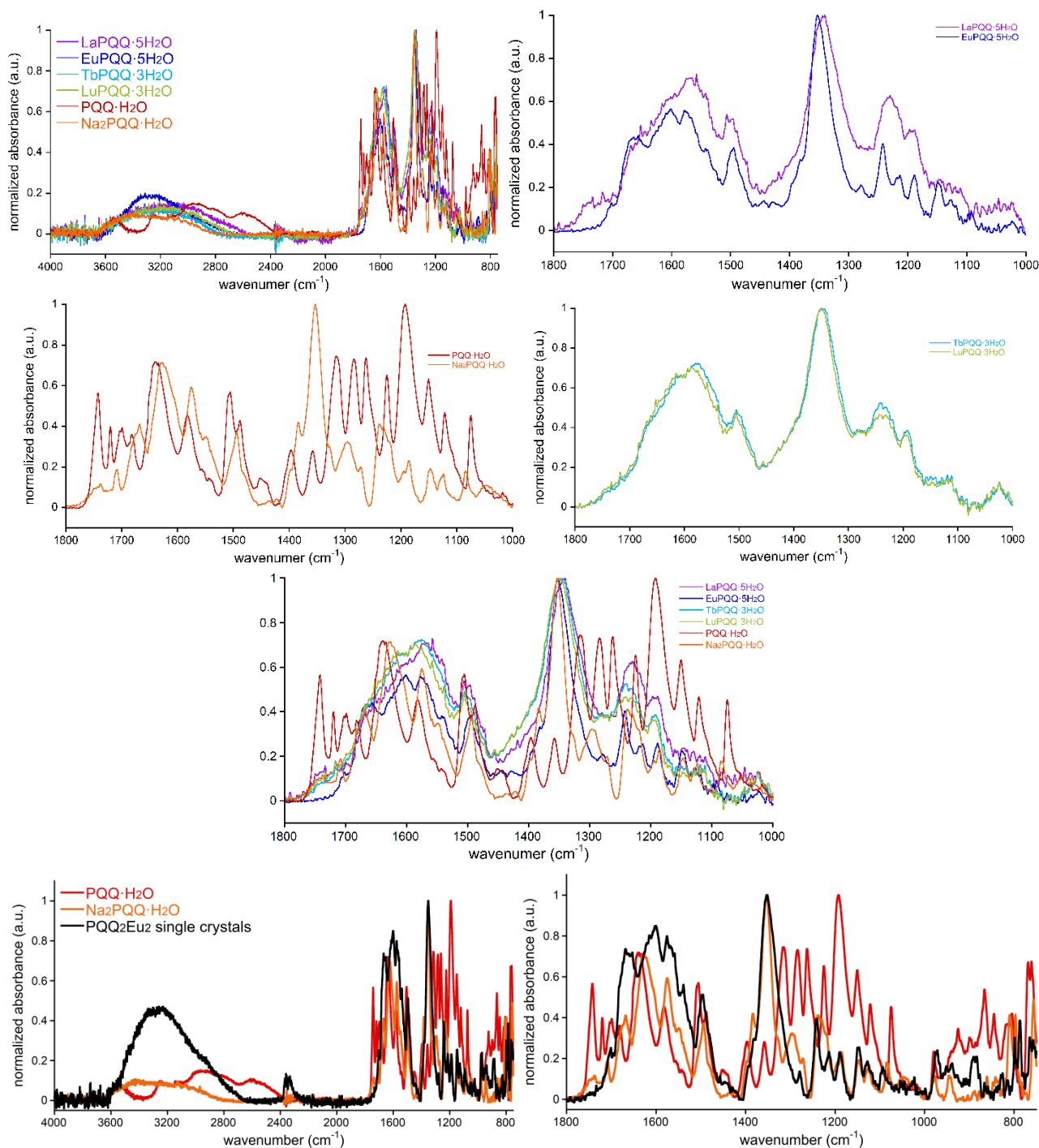


Figure S1. Normalized and superimposed IR absorption spectra of selected 1:1 LnPQQ complexes (Ln = La, Eu, Tb, Lu), Na₂PQQ·H₂O and PQQ·H₂O

SUPPORTING INFORMATION

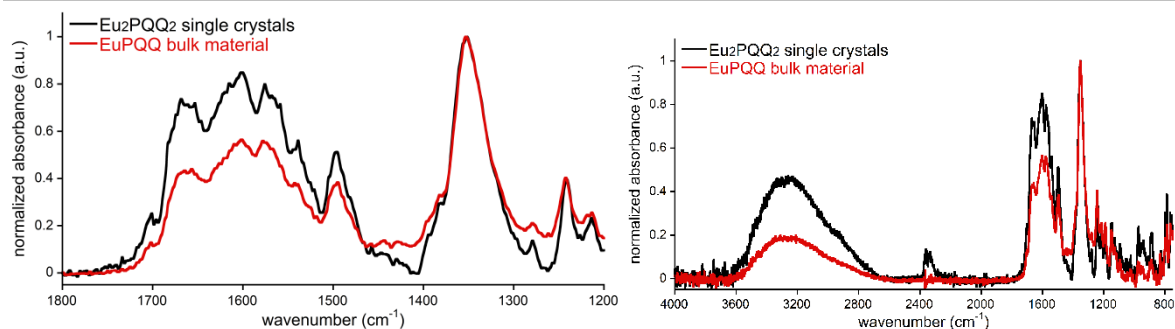


Figure S2. Normalized IR absorption spectra of 1:1 EuPQQ bulk material and the crystalline Eu_2PQQ_2 sample.

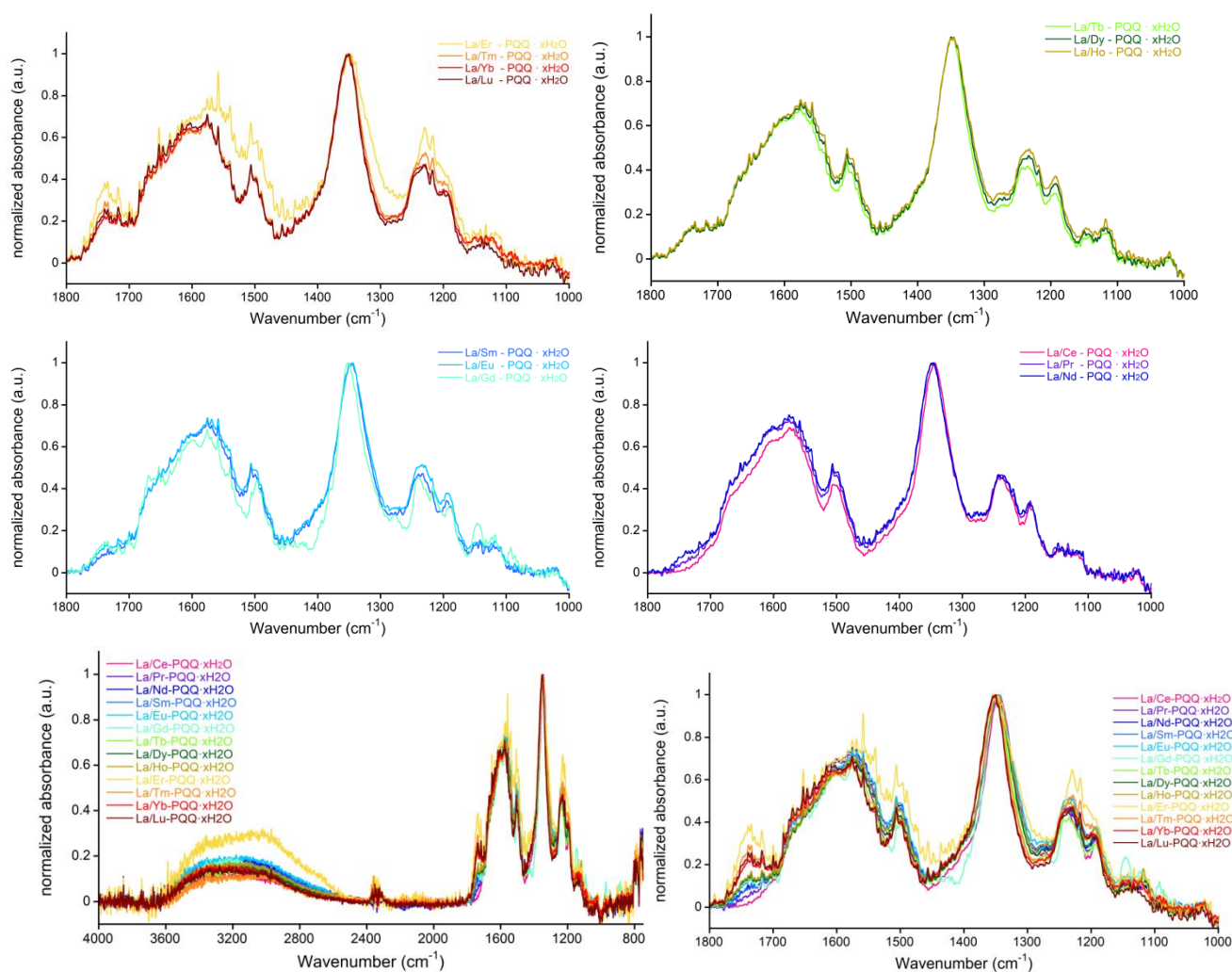


Figure S3. Normalized IR absorption spectra of 1:1 LaLnPQQ complexes ($\text{Ln} = \text{Ce-Lu}$). Differences in the height of the large IR-absorption band between 3630 – 2500 cm^{-1} might stem from different equiv. of coordinated (or co-crystallized) water.

SUPPORTING INFORMATION

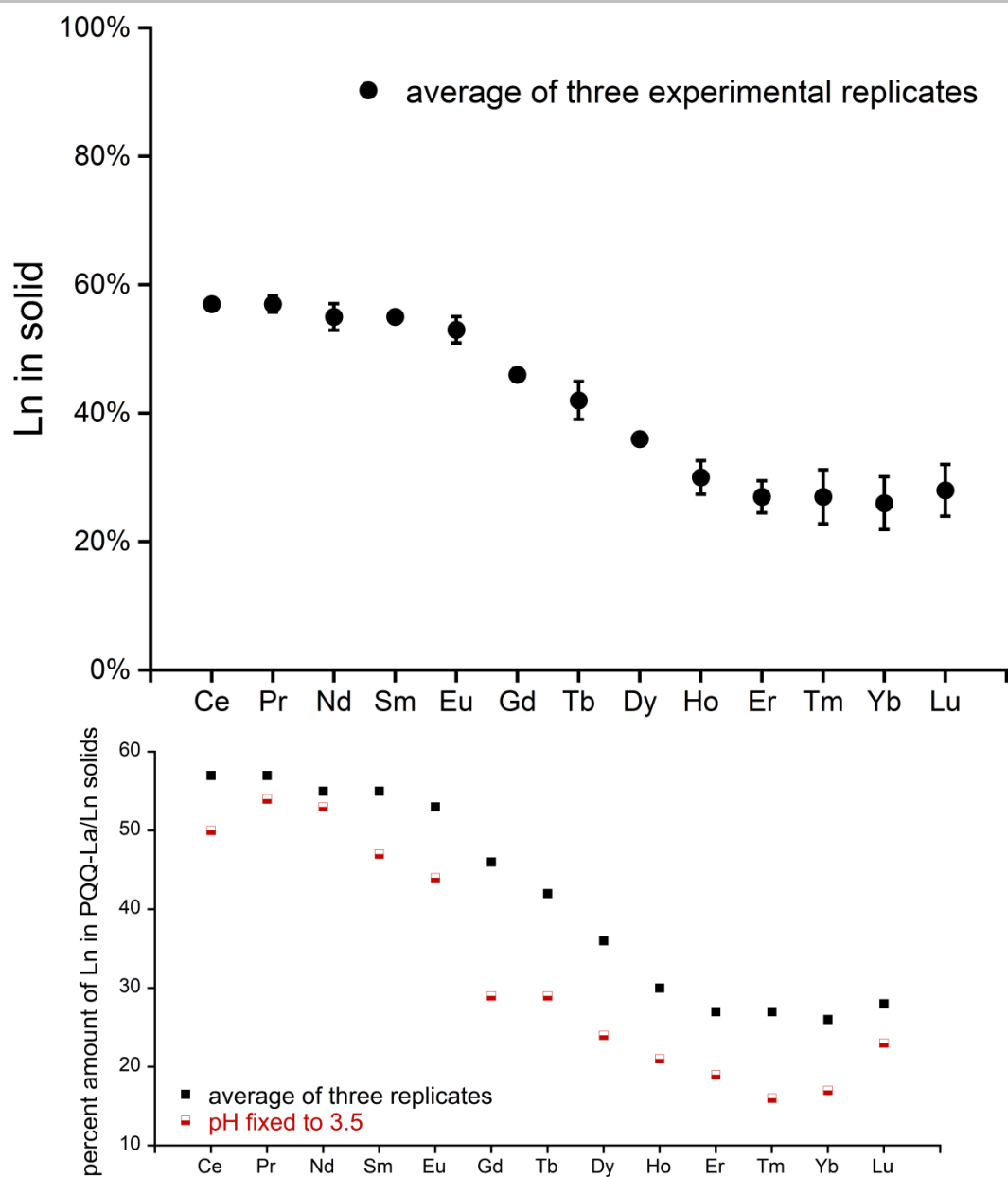


Figure S4. Percentage of Ln vs. La in 1:1 PQQ-metal complexes, precipitated from aqueous Na_2PQQ ($51 \mu\text{M}$) solutions at room temperature. Averaged values of three experiments are shown as black squares and values received from an experiment with fixed pH (= 3.5) are shown as red squares.

SUPPORTING INFORMATION

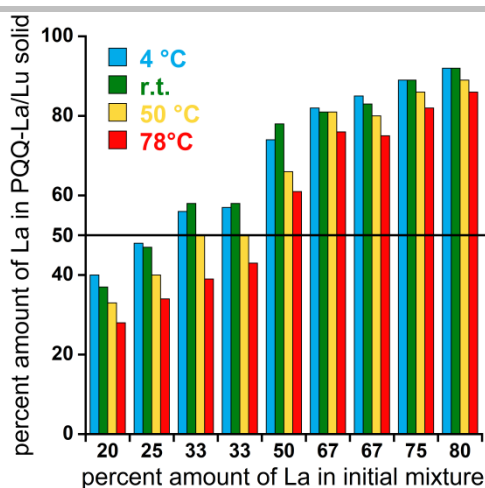


Figure S5. Percentage of lanthanum vs lutetium in a 1:1 PQQ-metal complex, depending on the amount of lanthanum in the initial mixture and the temperature. Aqueous Na_2PQQ ($51 \mu\text{M}$, 1 equiv.) solutions were used, to which aqueous mixtures of LaCl_3 and LuCl_3 were added. Due to the added stoichiometries of La and Lu (1:4; 1:3; 0.5:1; 1:2; 3:3; 1:0.5; 2:1; 3:1; 4:1 equiv.), two datasets are available for 33% and 67% La in the initial mixture.

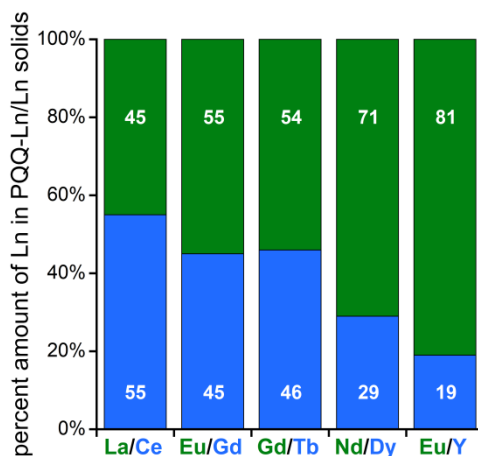


Figure S6. Percentage of different Ln couples in a 1:1 PQQ-metal complex, precipitated from an aqueous Na_2PQQ ($51 \mu\text{M}$) solution at room temperature.

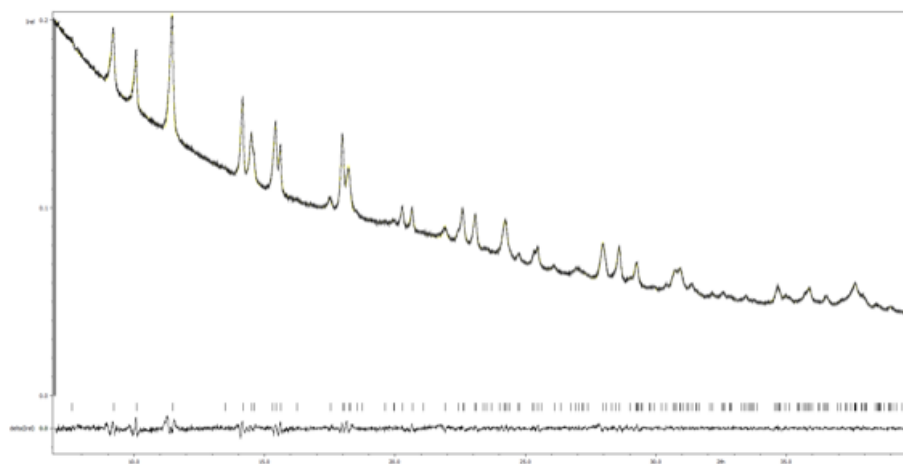
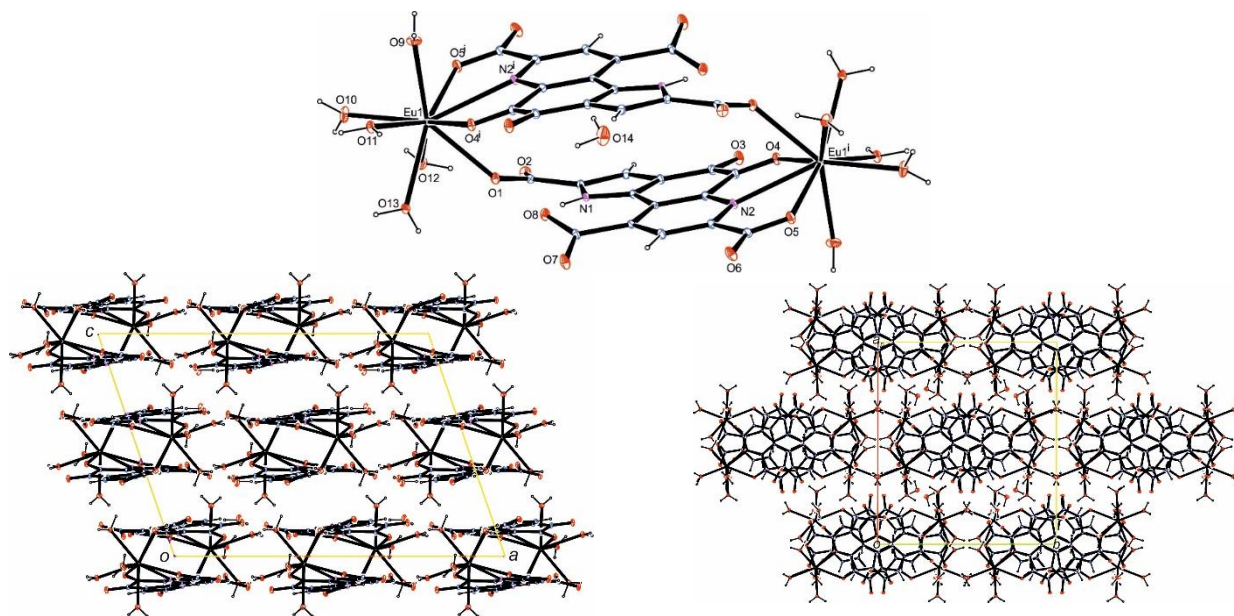


Figure S7. Model-free refinement of cell parameters for bulk powdered sample EuPQQ against single crystal data: $C2/c$, $a = 18.471(1)$, $b = 15.380(1)$, $c = 13.179(1) \text{ \AA}$, $\beta = 108.93(1)^\circ$, $V = 3541.3(4) \text{ \AA}^3$ (in house powder X-ray diffraction data, at room temperature, a D8 Discover diffractometer (Bruker AXS, Karlsruhe, Germany), $\lambda(\text{CuK}\alpha_1) = 1.5406 \text{ \AA}$, a Johansson monochromator, a position-sensitive LYNXEYE detector; sample was sealed in a 0.5 mm glass capillary (Müller GmbH, Berlin), mounted horizontally and spun at 60 min^{-1} ; $2\theta = 4\text{-}100^\circ$ with a step size of 0.009 and 9 s per step).

SUPPORTING INFORMATION

Supporting Tables

Table S1. Crystallographic Data of the Eu_2PQQ_2 complex.

Net formula	$\text{C}_{28}\text{H}_{30}\text{Eu}_2\text{N}_4\text{O}_{28}$
$M_r/\text{g mol}^{-1}$	1174.48
crystal size/mm	$0.090 \times 0.020 \times 0.020$
T/K	102.(2)
radiation	MoK α
diffractometer	'Bruker D8 Venture TXS'
crystal system	monoclinic
space group	$C2/c$
$a/\text{\AA}$	18.4171(7)
$b/\text{\AA}$	15.3960(6)
$c/\text{\AA}$	13.0961(5)
$\beta/^\circ$	108.9980(10)
$V/\text{\AA}^3$	3511.1(2)
Z	4
calc. density/ g cm^{-3}	2.22
μ/mm^{-1}	3.7
absorption correction	Multi-Scan
transmission factor range	0.82–0.93
refls. measured	39397
R_{int}	0.0452
mean $\sigma(I)/I$	0.0251
θ range	3.116–30.506
observed refls.	4937
x, y (weighting scheme)	0.0051, 21.2292
hydrogen refinement	H(C) constr, H(N,O) refxyz
refls in refinement	5346
parameters	319
restraints	81
$R(F_{obs})$	0.0303
$R_w(F^2)$	0.0607
S	1.284
shift/error _{max}	0.003
max electron density/ e \AA^{-3}	1.16
min electron density/ e \AA^{-3}	-1.28

SUPPORTING INFORMATION

selected bond lengths and distances [Å]

O5-Eu1	2.440
N2-Eu1	2.648
O4-Eu1	2.584
O1'-Eu1	2.409
H2O-Eu1	2.389 - 2.464
N1-N2'	3.732

selected bond angles

O4-Eu1-N2	59.74°
N2-Eu1-O5	61.24°

The X-ray intensity data was measured on a Bruker D8 Venture TXS system equipped with a multilayer mirror optics monochromator and a Mo K α rotating-anode X-ray tube ($\lambda = 0.71073$ Å). The frames were integrated with the Bruker SAINT software package.^[9] Data was corrected for absorption effects using the Multi-Scan method (SADABS).^[10] The structures were solved and refined using the Bruker SHELXTL Software Package.^[11] All C-bound hydrogen atoms have been calculated in ideal geometry riding on their parent atoms. Coordinates of H-atoms bound to N and O have been refined freely but restrained to be equal within a standard deviation of 0.01 Å (O-H distances) and 0.02 Å (H...H distances in water molecules). The isotropic displacement parameters of these hydrogen atoms have been calculated as $U(\text{H}) = 1.2 U(\text{N,O})$. The data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1991651) and can be obtained free of charge from: <https://www.ccdc.cam.ac.uk/structures/>. Symmetry code for the figure above: $i = 1-x, 1-y, 1-z$.

SUPPORTING INFORMATION

Table S2. Ln-L distances (r , Å) and coordination number (CN) for LnPQQ species, according to EXAFS and PDF data. H₂O equiv. according to CHN elemental analysis and ICP-MS.

Compound	EXAFS		PDF	H ₂ O (equiv.)
	CN	Ln-L distance (r , Å)	Ln-L distance (r , Å)	
LaPQQ	9	2.64(4)	2.58	5
EuPQQ	9	2.48(1)	2.50	5
TbPQQ	7	2.44(2)	2.44	3
LuPQQ	7	2.35(2)	2.34	3

Table S3. EXAFS first shell fit parameters of samples La-, Eu-, Tb- and Lu-PQQ. The root mean square error (RMSE) is presented.

Sample	Scattering path	Degeneracy	R_{model} (Å)	R_{fit} (Å)	R_{diff}^2 (Å)	RMSE (Å)
LaPQQ	La-O10	1	2.365	2.539	0.029	0.423
	La-O9	2	2.422	2.595	0.029	
	La-O1	3	2.453	2.626	0.029	
	La-O12	1	2.487	2.659	0.029	
	La-O3	1	2.575	2.748	0.029	
	La-N1	1	2.659	2.832	0.029	
EuPQQ	Eu-O10	1	2.36560	2.37225	0.00004	0.0155
	Eu-O9	2	2.42190	2.42855	0.00004	
	Eu-O1	3	2.45270	2.45935	0.00004	
	Eu-O12	1	2.48650	2.49315	0.00004	
	Eu-O3	1	2.57460	2.58125	0.00004	
	Eu-N1	1	2.65880	2.66545	0.00004	
TbPQQ	Tb-O10	1	2.3656	2.3397	0.00067	0.0578
	Tb-O9	2	2.4219	2.3960	0.00067	
	Tb-O1	2	2.4527	2.4268	0.00067	
	Tb-O3	1	2.5746	2.5487	0.00067	
	Tb-N1	1	2.6588	2.6329	0.00067	
LuPQQ	Lu-O10	1	2.366	2.243	0.0149	0.273
	Lu-O9	2	2.422	2.299	0.0149	
	Lu-O1	2	2.452	2.330	0.0149	
	Lu-O3	1	2.575	2.452	0.0149	
	Lu-N1	1	2.659	2.536	0.0149	

SUPPORTING INFORMATION

Table S4a. Complex formation of Na₂PQQ with La/Ln couples. The samples were digested in defined amounts of nitric acid (65%) and then diluted with the given amount of MilliQ water, to yield a concentration of 1.0256 mg/mL in 3% nitric acid for each sample. Values below the detection limit are marked with “-”.

	Mass Fraction (%) (EA)			µg / L (ICP-MS)														Yield (mg)	Weight of sample (mg)	Volume of added H ₂ O (mL)
	C	H	N	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
La/Ln (1)	32.78	1.94	5.56	5.4	7.3													24.4	8.7	8.091
La/Ln (1)	32.67	1.86	5.46	5.7		7.5												25.4	6.3	5.859
La/Ln (1)	31.98	1.96	5.32	5.6			7.2											24.4	9.8	9.114
La/Ln (1)	32.60	1.93	5.38	7.5				5.8										26.0	7.9	7.347
La/Ln (1)	31.83	1.81	5.33	6.2					7.7									24.0	7.0	6.510
La/Ln (1)	29.68	2.22	4.95	7.1						6.5								22.9	8.4	7.812
La/Ln (1)	31.28	1.90	5.23	8.4							5.8							21.8	5.7	5.301
La/Ln (1)	31.79	2.05	5.23	9.0								3.9						18.1	7.6	7.068
La/Ln (1)	31.59	2.05	5.21	10.4									4.7					21.0	5.8	5.394
La/Ln (1)	32.32	1.90	5.36	9.8										4.1				25.5	6.4	5.952
La/Ln (1)	27.80	2.02	4.60	9.4											5.1			28.1	6.3	5.859
La/Ln (1)	27.59	2.02	4.59	9.1												5.1		28.3	6.9	6.417
La/Ln (1)	27.05	2.08	4.50	10.4													5.9	29.0	6.6	6.138
La/Ln (2)	32.09	2.18	5.54	6.0	7.9													25.5	7.1	6.603
La/Ln (2)	30.99	2.41	5.76	6.6		8.6												25.9	7.4	6.882
La/Ln (2)	31.31	2.31	6.14	6.5			7.5											26.6	5	4.65
La/Ln (2)	30.9	2.29	5.87	6.5				6.0										25.3	5.2	4.836
La/Ln (2)	31.01	2.20	5.78	6.7					7.4									24.3	5.3	4.929
La/Ln (2)	31.10	1.87	5.38	7.0						7.1								25.0	8.4	7.812
La/Ln (2)	31.70	1.79	5.41	8.1							7.7							25.7	5.5	5.115
La/Ln (2)	31.81	1.79	5.41	9.0								5.8						25.3	9.2	8.556
La/Ln (2)	30.92	2.19	5.28	8.9									4.4					24.6	7.1	6.603
La/Ln (2)	30.68	2.34	5.24	9.8										3.7				25.6	7.7	7.161
La/Ln (2)	31.26	2.22	5.21	9.4											3.1			25.6	9.1	8.463
La/Ln (2)	31.41	2.19	5.29	9.8												3.3		25.4	6	5.580
La/Ln (2)	31.11	2.34	5.25	8.8													3.1	24.9	6.6	6.138
La/Ln (3)	31.85	2.41	5.44	4.3	6.0													24.4	10.6	9.858
La/Ln (3)	32.24	2.17	5.44	4.5		6.5												22.3	4.8	4.464
La/Ln (3)	31.00	2.57	5.34	4.6			6.5											24.9	5.5	5.115
La/Ln (3)	30.35	2.65	5.22	6.5				6.7										25.5	6.1	5.673
La/Ln (3)	30.48	2.74	5.14	5.3					7.1									26.2	13.7	12.741
La/Ln (3)	29.57	2.77	5.10	6.2							6.3							25.3	8.2	7.626
La/Ln (3)	35.97	3.21	6.17	6.7								5.8						25.7	7.4	6.882
La/Ln (3)	31.15	2.58	6.20	8.4									4.4					24.4	6	5.580
La/Ln (3)	30.78	2.37	6.04	7.9										4.9				24.9	6.1	5.673
La/Ln (3)	31.08	2.48	6.16	9.4											4.9			25.5	8.3	7.719
La/Ln (3)	31.76	2.49	3.36	8.5											3.9			25.3	6.7	6.231
La/Ln (3)	31.69	2.51	6.51	9.2												4.2		25.7	5.2	4.836
La/Ln (3)	30.72	2.56	6.08	8.3													4.5	25.1	5.8	5.394
La/Pr (digestion A)				5.3		7.1	-												6.3	5.859
La/Pr (digestion B)				5.5		7.3	-												6.2	5.766
La/Nd (digestion A)				5.3		-	6.9												9.8	9.114
La/Nd (digestion B)				4.9		-	6.3												6.0	5.580

SUPPORTING INFORMATION

Table S4b. Complex formation of Na₂PQQ with all Ln simultaneously or Ln/Ln couples. The samples were digested in defined amounts of nitric acid (65%) and then diluted with the given amount of MilliQ water, to yield a concentration of 1.0256 mg/mL in 3% nitric acid for each sample. Values below the detection limit are marked with "-".

	Mass Fraction (%) (EA)			$\mu\text{g} / \text{L}$ (ICP-MS)														Yield (mg)	Weight of sample (mg)	Volume of added H ₂ O (mL)
	C	H	N	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
all Ln (pH 2.5)	32.27	2.35	5.37	1.7	1.9	1.8	1.6	1.3	1.2	0.8	0.7	0.6	0.5	0.6	0.4	0.4	0.5	16.1	4.2	3.906
all Ln (pH 2.5) supernatant	-	-	-	26.9	26.7	25.9	27.2	30.0	30.4	32.3	31.0	33.2	32.7	33.6	32.0	35.0	34.5			
all Ln (pH 3.5)	30.17	2.18	4.88	1.5	1.6	1.6	1.7	1.9	1.7	1.2	1.0	0.8	0.7	0.7	0.6	0.6	0.7	22.1	4.8	4.464
all Ln (pH 3.5) supernatant	-	-	-	29.7	29.2	27.9	29.2	31.2	32.3	34.9	33.5	36.4	35.8	37.4	35.1	38.9	38.1			
all Ln (pH 4.5)	29.24	2.15	4.71	1.5	1.5	1.6	1.9	2.0	2.0	1.2	1.1	0.9	0.8	0.8	0.7	0.8	0.8	22.6	5.2	4.836
all Ln (pH 4.5) supernatant	-	-	-	27.3	26.7	25.5	26.2	28.0	28.9	30.9	30.2	32.6	32.2	33.1	31.5	34.3	34.1			
Ln stock solution	-	-	-	32.0	32.8	31.9	33.5	35.8	36.1	37.1	35.6	38.2	37.5	38.7	36.1	39.7	39.4			
Nd/Nd (1:1)	30.35	2.12	4.94				8.0					6.3						21.6	5.9	5.487
Nd/Nd (1:1) supernatant	-	-	-				12.8					24.4								
Nd/Nd (3:3)	30.46	2.09	4.92				9.2					5.6						23.1	5.4	5.022
Nd/Nd (3:3) supernatant	-	-	-				78.0					109.1								
Nd/Nd (6:6)	30.37	2.08	4.89				9.2					5.1						23.7	5.9	5.487
Nd/Nd (6:6) supernatant	-	-	-				151.2					202.0								

SUPPORTING INFORMATION

Table S5 Separation factors of selected pairs when PQQ is exposed to 14 lanthanides.

Ln1/Ln2	SF _{Ln2/Ln1} at pH	SF _{Ln2/Ln1} at pH	SF _{Ln2/Ln1} at pH
	2.5	3.5	4.5
Dy/Nd	3.31	2.61	2.49
Ce/La	1.12	1.13	1.03
La/Lu	4.30	2.86	2.29
La/Gd	2.54	1.47	1.38
Gd/Eu	1.59	1.56	1.69
Gd/Tb	1.15	1.14	1.13

References

- [1] H. Lumpe, L. J. Daumann, *Inorg. Chem.* **2019**, *58*, 8432-8441.
- [2] J. J. M. Nelson, T. Cheisson, H. J. Rugh, M. R. Gau, P. J. Carroll, E. J. Schelter, *Commun. Chem.* **2020**, *3*, 7.
- [3] M. Newville, B. Ravel, *J. Synchrotron Radiat.* **2005**, *12*, 537-541.
- [4] A.-C. Dippel, H.-P. Liermann, J. T. Delitz, P. Walter, H. Schulte-Schrepping, O. H. Seeck, H. Franz, *J. Synchrotron Radiat.* **2015**, *22*, 675-687.
- [5] a) M. Basham, J. Filik, M. T. Wharmby, P. C. Chang, B. El Kassaby, M. Gerring, J. Aishima, K. Levik, B. C. Pulford, I. Sikharulidze, *J. Synchrotron Radiat.* **2015**, *22*, 853-858; b) J. Filik, A. Ashton, P. Chang, P. Chater, S. Day, M. Drakopoulos, M. Gerring, M. Hart, O. Magdysyuk, S. Michalik, *J. Appl. Crystallogr.* **2017**, *50*, 959-966.
- [6] A. K. Soper, E. R. Barney, *J. Appl. Crystallogr.* **2011**, *44*, 714-726.
- [7] G. J. Long, T. Cranshaw, G. Longworth, *Mössbauer Eff. Ref. Data J.* **1983**, *6*, 42-49.
- [8] R. A. Brand, *WINNORMOS for IGOR6 (version for IGOR 6.2 or above: 22.02.2017)*, Universität Duisburg, Duisburg, Germany, 2017.
- [9] J. Nevarez, A. Turmo, J. Hu, R. P. Hausinger, *ChemCatChem* **2020**, doi.org/10.1002/cctc.202000575.
- [10] B. D. Roach, E. K. Fenske, R. H. Ilgner, C. R. Hexel, T. J. Haverlock, J. M. Giaquinto, *J. Chromatogr. A* **2019**, *1587*, 155-165.
- [11] J. Borrini, A. Favre-Reguillon, M. Lemaire, S. Gracia, G. Arrachart, G. Bernier, X. Hérés, C. Hill, S. Pellet-Rostaing, *Solvent Extr. Ion Exch.* **2015**, *33*, 224-235.