

Rare-Earth Acetates as Alternative Precursors for Rare-Earth Cluster-Based Metal–Organic Frameworks

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Supplementary information

Materials

All solvents and reagents were purchased from commercial sources. N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), acetone, and nitric acid (70%) were purchased from Fisher Scientific (Fisher Chemical). Y(NO₃)₃·xH₂O, Sm(NO₃)₃·xH₂O, Eu(NO₃)₃·xH₂O, Gd(NO₃)₃·xH₂O, Tb(NO₃)₃·xH₂O, Dy(NO₃)₃·xH₂O, Ho(NO₃)₃·xH₂O, Er(NO₃)₃·xH₂O, Tm(NO₃)₃·xH₂O, Yb(NO₃)₃·xH₂O, Lu(NO₃)₃·xH₂O, Y(CH₃CO₂)₃·xH₂O, Sm(CH₃CO₂)₃·xH₂O, Eu(CH₃CO₂)₃·xH₂O, Gd(CH₃CO₂)₃·xH₂O, Tb(CH₃CO₂)₃·xH₂O, Dy(CH₃CO₂)₃·xH₂O, Ho(CH₃CO₂)₃·xH₂O, Er(CH₃CO₂)₃·xH₂O, Tm(CH₃CO₂)₃·xH₂O, Yb(CH₃CO₂)₃·xH₂O, and Lu(CH₃CO₂)₃·xH₂O were purchased from Chemicals 101. 2,6-difluorobenzoic acid (2,6-DFBA) was purchased from Ambeed. Terephthalic acid (BDC) was purchased from Acros Organics. All solvents and chemicals were used without further treatment.

Instrumentation

Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku MiniFlex diffractometer (measurements made over a range of 3° < 2θ < 40° with a 0.100 °/s scanning speed). Neat samples were smeared onto a zero-background sample holder. Data were collected using a continuous coupled θ/2θ scan with Ni-filtered CuKα (λ = 1.54178 Å).

Thermogravimetric analysis (TGA) was carried out using a TGA/DSC 1 from Mettler Toledo, from room temperature to 800 °C at a rate of 10 °C/min under air.

Samples for nitrogen adsorption/desorption were activated using a Micromeritics SmartVacPrep instrument equipped with a hybrid turbo vacuum pump. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics TriStar II Plus instrument. Activation of all RE-UiO-66 samples was performed at 80 °C for 20h.

¹H-NMR spectra were recorded on a 300 MHz Bruker spectrometer and the chemical shifts were referenced to the residual solvent peaks. Samples were digested using D₂SO₄ and then dissolved in DMSO-d⁶.

Diffuse reflectance infrared Fourier transform spectra were recorded using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with a MCT detector with a resolution of 1 cm⁻¹ in the range of 4000-450 cm⁻¹.

Synthesis

General procedure for RE-UiO-66 (RE = Y(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III))

RE-UiO-66 was synthesized solvothermally in a 6-dram vial containing the RE precursor (nitrate or acetate, 0.174 mmol), BDC (28.5 mg, 0.171 mmol), 2,6-DFBA (440 mg, 2.78 mmol), nitric acid 70% (0.1 mL), and water (0.1 mL), dissolved in DMA (8 mL). The sealed vial was heated in an oven at 120 °C for 24 hours. The solid was separated via centrifugation and washed four times with DMF over 24 hours. The DMF was removed by

washing the sample four times with acetone over 24 hours. The obtained material was activated under vacuum at 80 °C for 20 hours.

Eu-UiO-66 and Sm-UiO-66

To obtain Eu-UiO-66 and Sm-UiO-66, the same procedure was followed but no water was added. In the case of Sm-UiO-66 the amount of BDC was also increased (42 mg, 0.252 mmol).

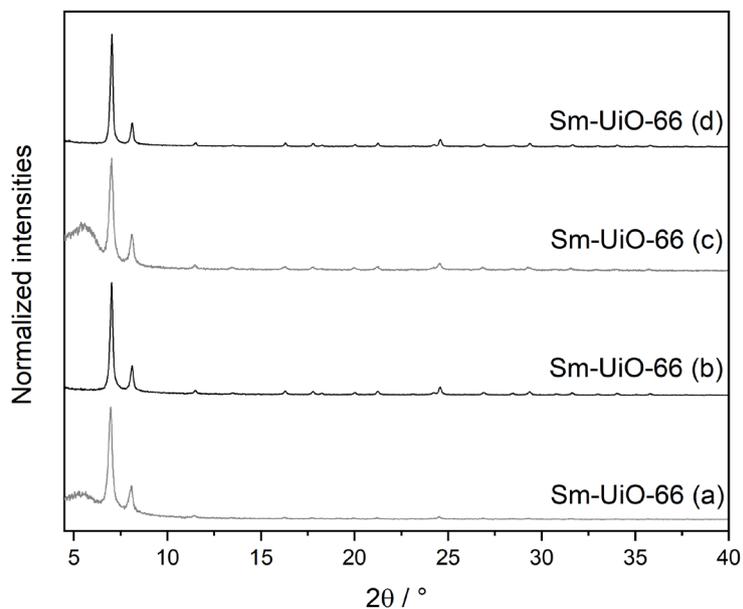


Figure S1 Stacked PXRD patterns for the products of (a) regular synthesis of Sm-UiO-66 using nitrate, (b) synthesis of Sm-UiO-66 using nitrate and increasing the amount of linker in 50 %, (c) regular synthesis of Sm-UiO-66 using acetate, (d) synthesis of Sm-UiO-66 using acetate and increasing the amount of linker in 50 %. All these syntheses were performed without the addition of water.

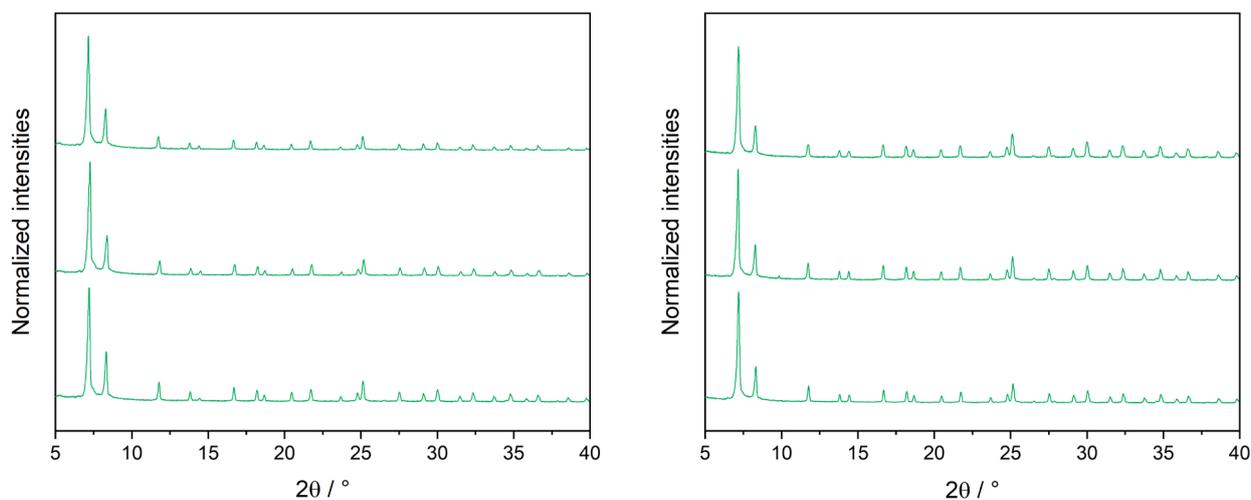


Figure S2 Stacked PXRD patterns of Yb-UiO-66 obtained using nitrate (left) and acetate (right) as precursors.

Table S1 Yield for the syntheses of RE-UiO-66 (RE = Y(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III)) after 24 hours of reaction. Theoretical yields are calculated from the exact amount of metal precursor weighed, which varies slightly in each reaction.

Metal	Yield with nitrate [mg]	Theoretical yield [mg]	Yield with nitrate [%]	Yield with acetate [mg]	Theoretical yield [mg]	Yield with acetate [%]
Y	19.9	51.0	39	21.3	44.9	47
Sm	4.5	58.8	8	5.8	53.5	11
Eu	4.9	57.0	9	3.2	59.2	5
Gd	20.0	53.5	37	15.5	52.5	30
Tb	24.6	62.5	40	33.2	55.4	60
Dy	14.4	60.2	24	15.2	68.5	22
Ho	18.3	59.4	31	21.6	58.5	37
Er	21.1	58.9	39	13.0	67.2	20
Tm	43.8	61.6	71	12.4	58.3	21
Yb	14.4	63.6	23	15.8	67.1	24
Lu	26.2	53.5	49	14.2	53.6	27

Table S2 Yield for the syntheses of Gd-UiO-66, Er-UiO-66 and Lu-UiO-66 with different amounts of water after 24 hours of reaction. Theoretical yields are calculated from the exact amount of metal precursor weighed, which varies slightly in each reaction.

MOF	Precursor	Water added [mL]	Yield [mg]	Theoretical yield [mg]	Yield [%]
Lu-UiO-66	Nitrate	0	3.3	58.4	6
Lu-UiO-66	Nitrate	0.1	26.2	53.5	49
Lu-UiO-66	Nitrate	0.2	37.1	52.5	71
Lu-UiO-66	Nitrate	0.3	45.8	61.6	74
Lu-UiO-66	Acetate	0	4.2	61.6	7
Lu-UiO-66	Acetate	0.1	14.2	53.6	27
Lu-UiO-66	Acetate	0.2	37.2	53.7	69
Lu-UiO-66	Acetate	0.3	41.8	64.4	65
Er-UiO-66	Acetate	0.1	13.0	67.2	20
Er-UiO-66	Acetate	0.2	42.3	68.7	62
Er-UiO-66	Acetate	0.3	48.5	69.5	70
Gd-UiO-66	Nitrate	0	9.0	51.4	18
Gd-UiO-66	Nitrate	0.1	20.0	53.5	37
Gd-UiO-66	Acetate	0	2.6	56.0	5
Gd-UiO-66	Acetate	0.1	15.5	52.5	30

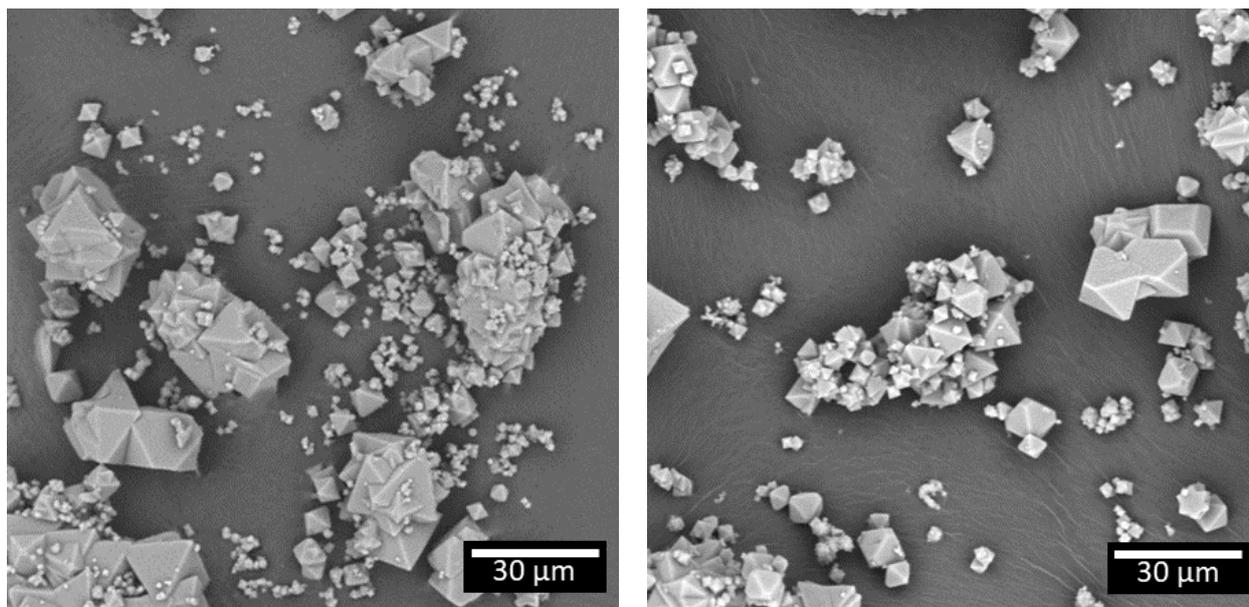
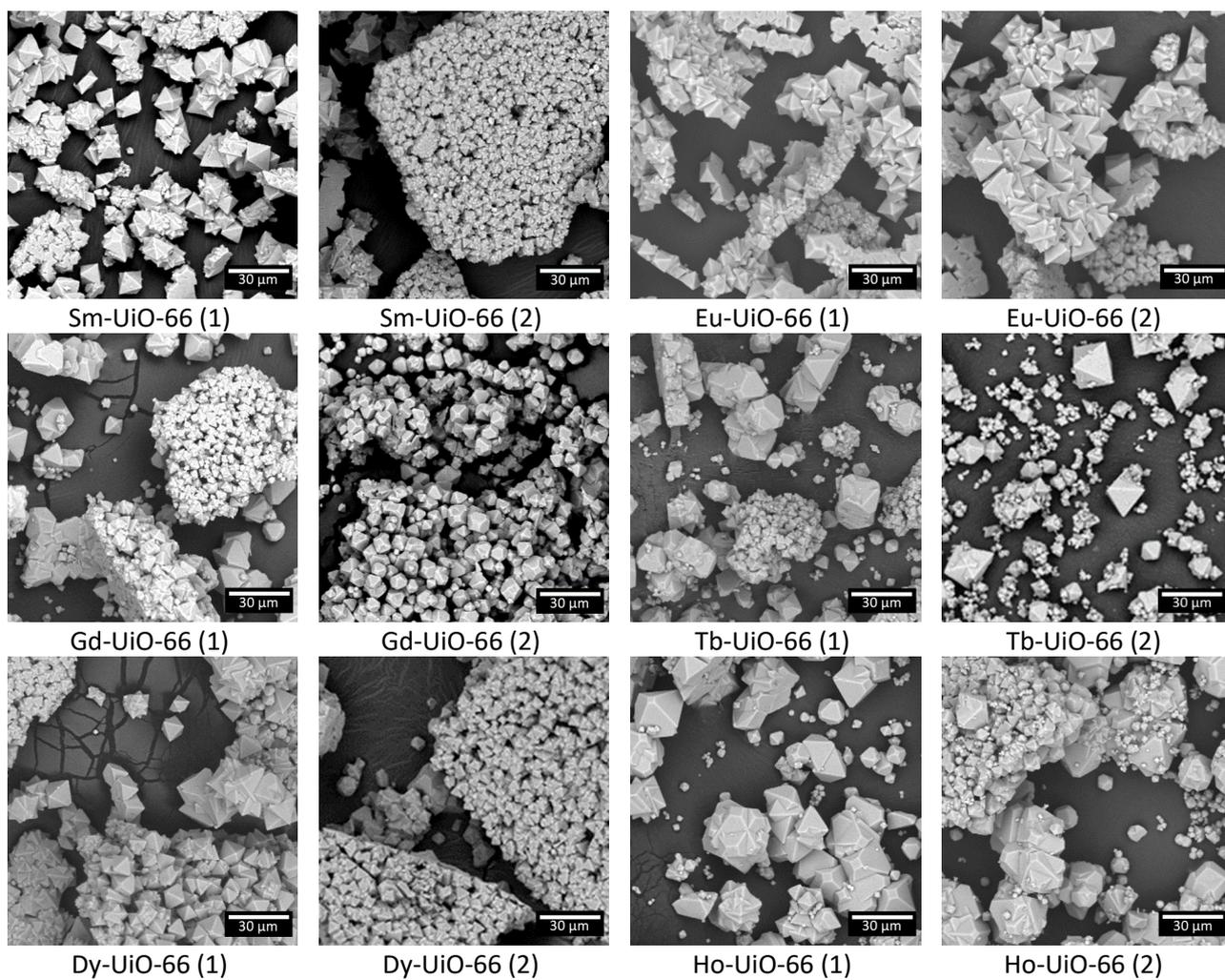


Figure S3 SEM images of Y-UiO-66 using (left) nitrate, and (right) acetate as precursors.



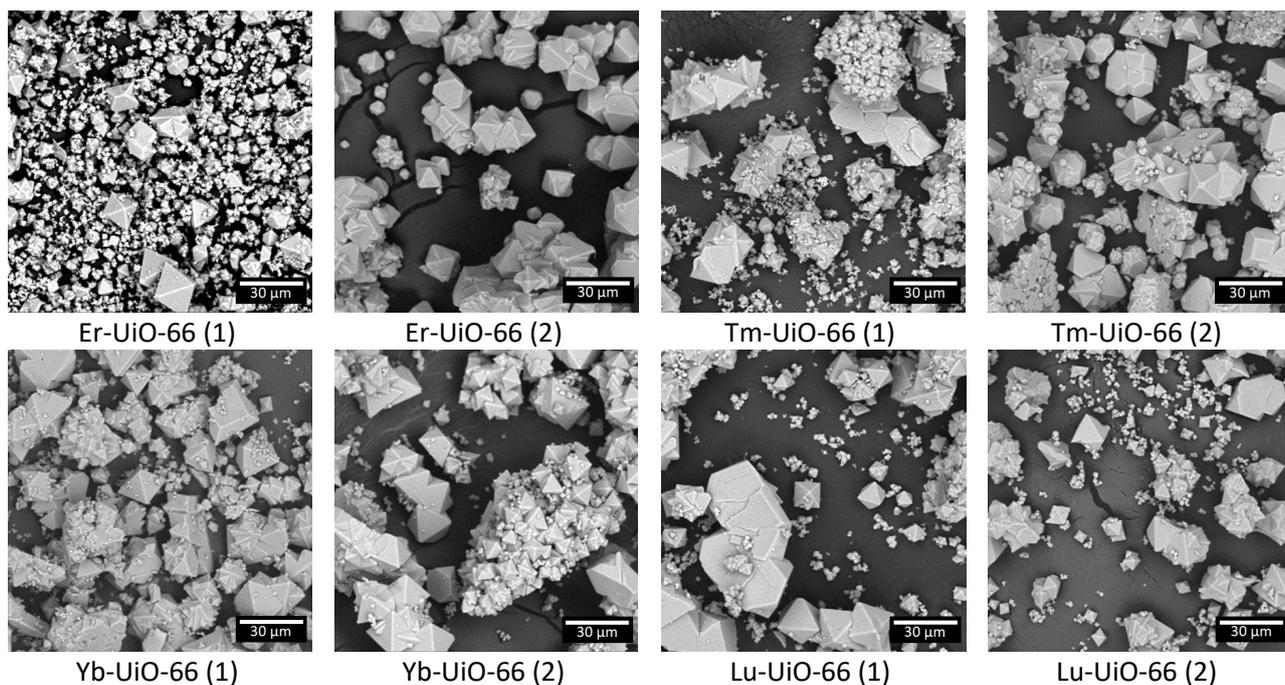


Figure S4 SEM images of RE-UiO-66 using (1) nitrate, and (2) acetate as precursor. Scale bar is 30 μm in all cases.

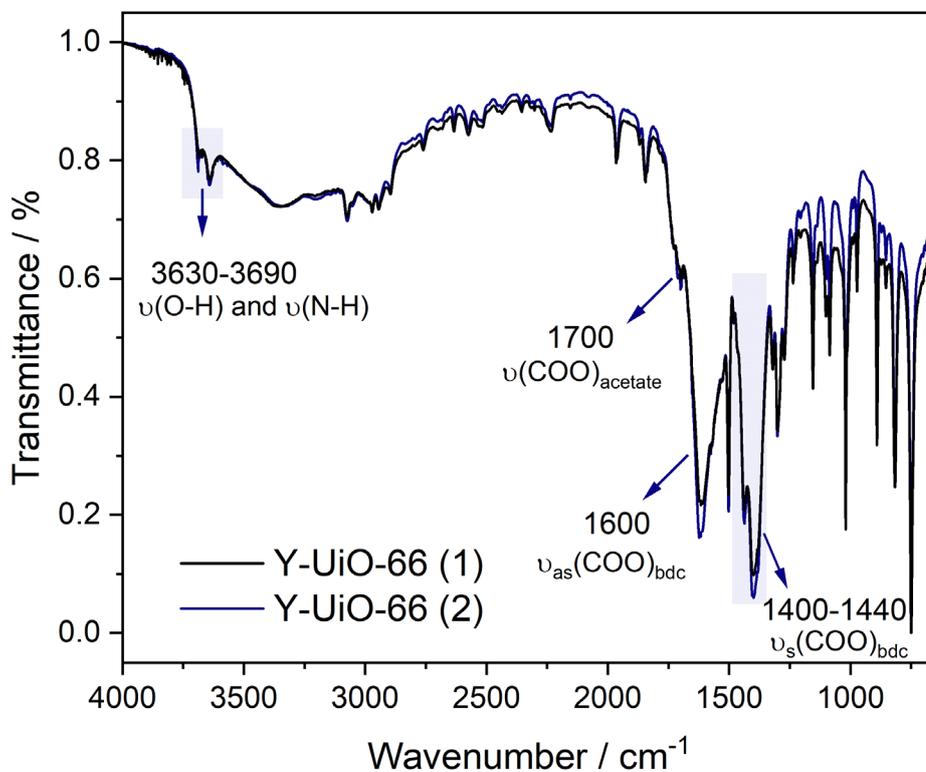
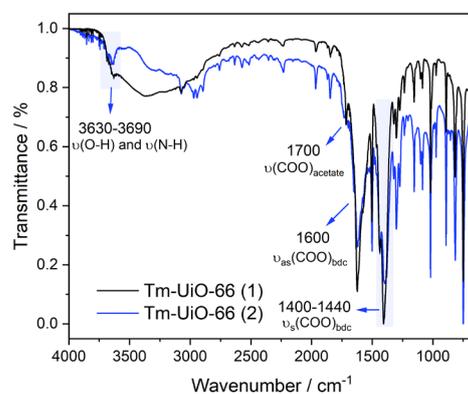
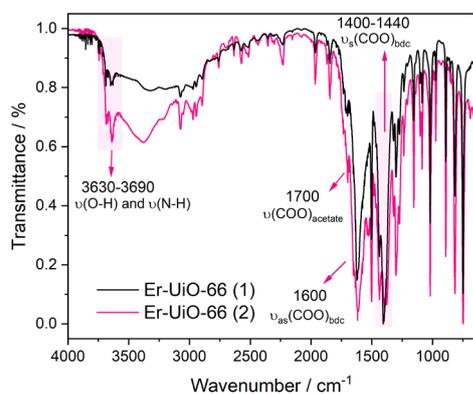
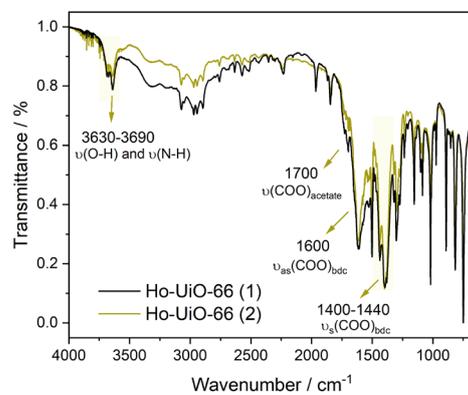
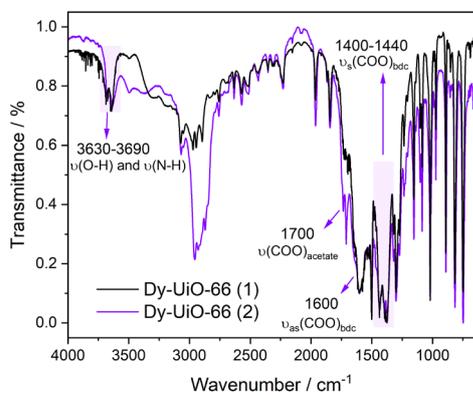
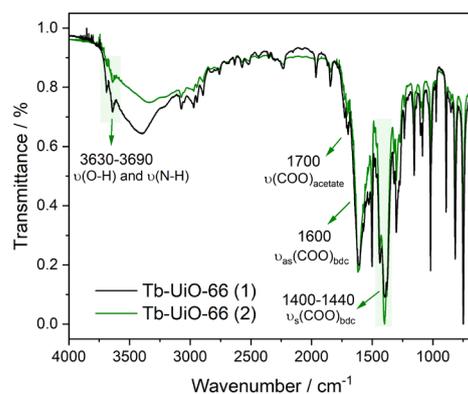
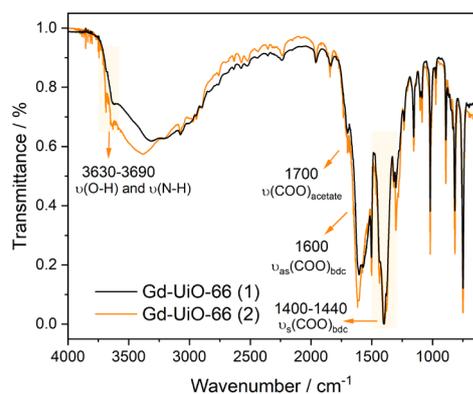
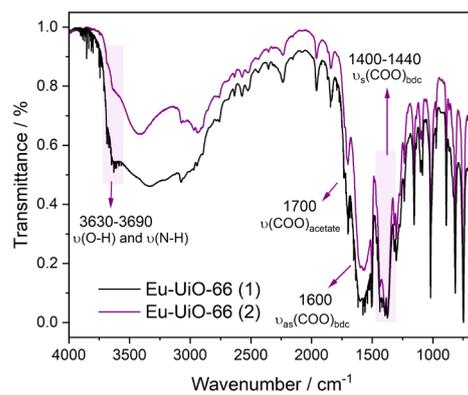
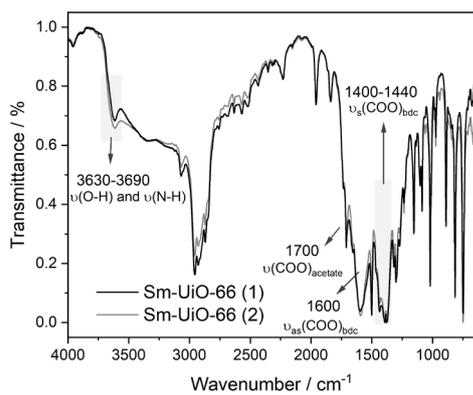


Figure S5 DRIFTS spectra of Y-UiO-66 obtained using (1) nitrate, and (2) acetate as precursor.



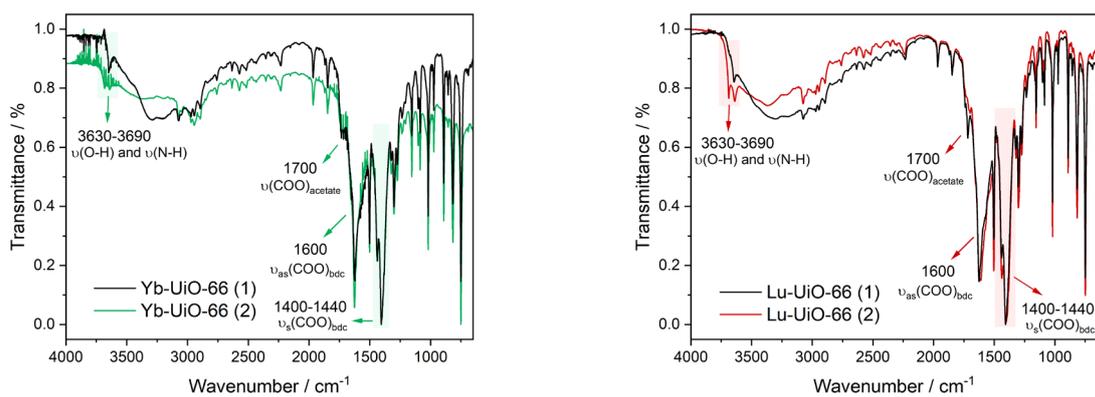


Figure S6 DRIFTS spectra of RE-UiO-66 using (1) nitrate, and (2) acetate as precursor.

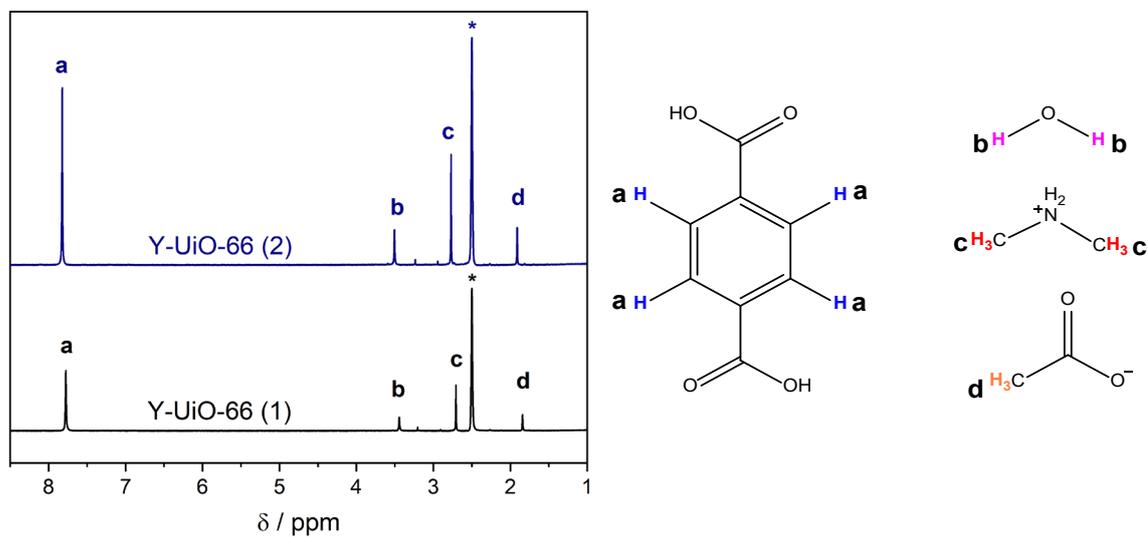


Figure S7 ^1H NMR spectra of Y-UiO-66 using (1) nitrate, and (2) acetate as precursor. Solvent (*): DMSO-d_6

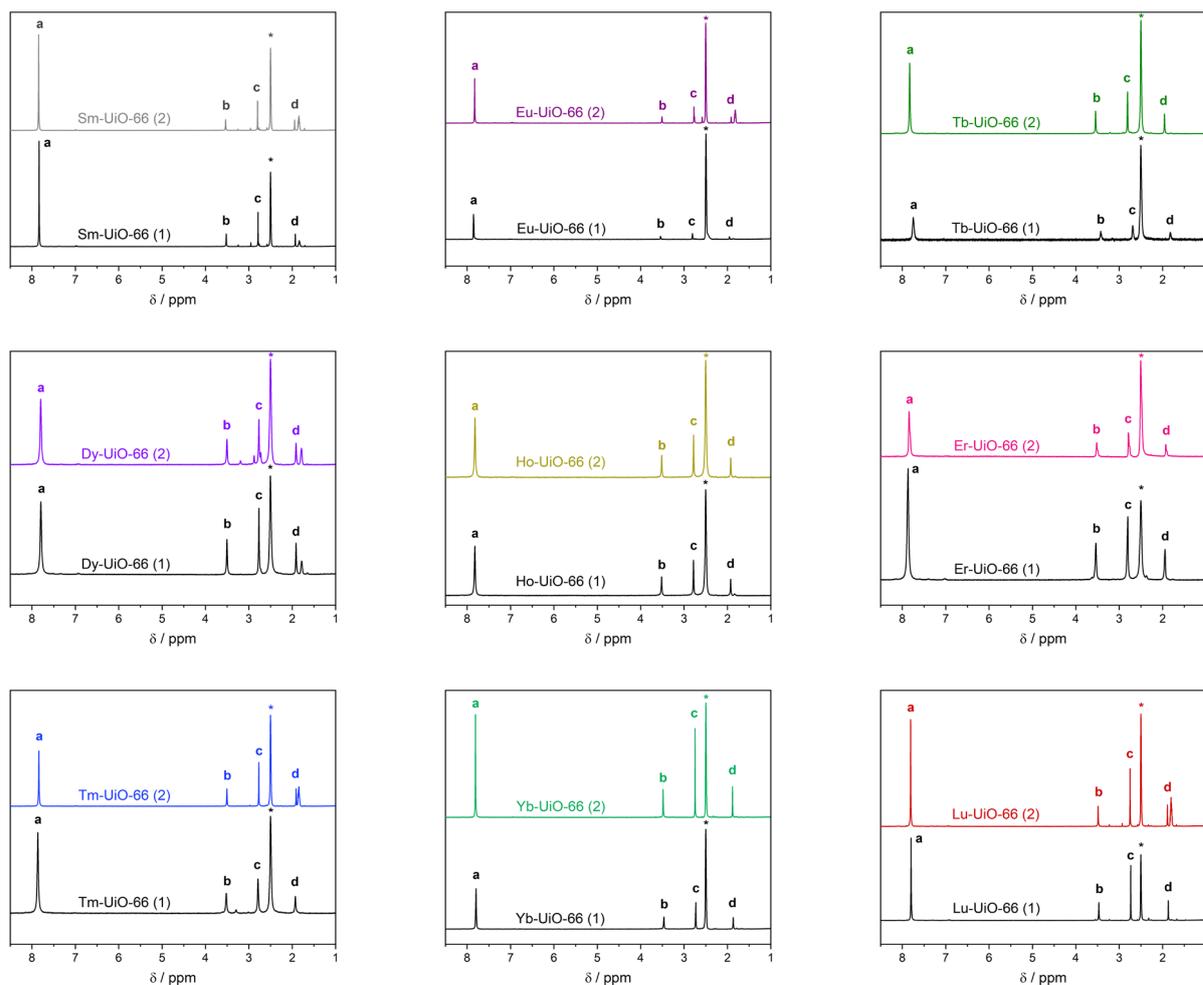


Figure S8 ^1H NMR spectra of RE-UiO-66 using (1) nitrate, and (2) acetate as precursor. Solvent: DMSO-d_6

Table S3 Integration of the peaks from ^1H NMR spectra. (1) nitrate, and (2) acetate.

Metal	BDC (1)	Cation (1)	Water (1)	Acetate (1)	BDC (2)	Cation (2)	Water (2)	Acetate (2)
Y	1	0.38	0.22	0.20	1	0.41	0.25	0.19
Sm	1	0.23	0.15	0.11	1	0.23	0.14	0.11
Eu	1	0.21	0.14	0.12	1	0.32	0.17	0.13
Tb	1	0.49	0.31	0.28	1	0.40	0.26	0.19
Dy	1	0.46	0.28	0.22	1	0.40	0.26	0.19
Ho	1	0.52	0.29	0.23	1	0.47	0.27	0.24
Er	1	0.38	0.24	0.18	1	0.39	0.25	0.21
Tm	1	0.35	0.22	0.17	1	0.46	0.29	0.23
Yb	1	0.50	0.30	0.23	1	0.47	0.30	0.23
Lu	1	0.37	0.26	0.17	1	0.35	0.22	0.17

Table S4 Calculation from ^1H NMR spectroscopy data to determine the total amount of each component in the structure. Gd is not included due to its paramagnetic properties that do not allow to obtain this information by ^1H NMR spectroscopy.

Metal	Precursor	H - BDC	Total BDC	H - cation	Total cation	H - water	Total water	H - acetate	Total acetate
Y	Nitrate	19.9	5.0	7.5	1.3	4.4	2.2	4.0	1.3
Y	Acetate	20.2	5.1	8.3	1.4	5.1	2.5	3.8	1.3
Sm	Nitrate	20.1	5.0	4.6	0.8	3.0	1.5	2.2	0.7
Sm	Acetate	20.1	5.0	4.6	0.8	2.8	1.4	2.2	0.7
Eu	Nitrate	19.8	5.0	4.2	0.7	2.8	1.4	2.4	0.8
Eu	Acetate	20.4	5.1	6.5	1.1	3.5	1.7	2.7	0.9
Tb	Nitrate	19.5	4.9	9.6	1.6	6.1	3.0	5.5	1.8
Tb	Acetate	20.1	5.0	8.1	1.3	5.2	2.6	3.8	1.3
Dy	Nitrate	20.1	5.0	9.3	1.5	5.6	2.8	4.4	1.5
Dy	Acetate	20.1	5.0	8.1	1.3	5.2	2.6	3.8	1.3
Ho	Nitrate	20.4	5.1	10.6	1.8	5.9	3.0	4.7	1.6
Ho	Acetate	19.9	5.0	9.4	1.6	5.4	2.7	4.8	1.6
Er	Nitrate	20.1	5.0	7.7	1.3	4.8	2.4	3.6	1.2
Er	Acetate	19.8	5.0	7.7	1.3	5.0	2.5	4.2	1.4
Tm	Nitrate	20.1	5.0	7.0	1.2	4.4	2.2	3.4	1.1
Tm	Acetate	20.0	5.0	9.2	1.5	5.8	2.9	4.6	1.5
Yb	Nitrate	20.3	5.1	10.1	1.7	6.1	3.0	4.7	1.6
Yb	Acetate	20.1	5.0	9.4	1.6	6.0	3.0	4.6	1.5
Lu	Nitrate	20.3	5.1	7.5	1.2	5.2	2.6	3.4	1.1
Lu	Acetate	20.1	5.0	7.0	1.2	4.4	2.2	3.4	1.1

$$10 - \frac{2x}{4} + \frac{ax}{6} - \frac{bx}{3} = 0$$

Equation S1 Used to determine the structure based on ^1H NMR spectroscopy integrations, with x being the amount of BDC protons (Table S4, H-BDC). Considering the balance of charge should be zero, the first term represents the charge of the cluster, the second one, the charge of the BDC, the third one, the charge of the acetate, and the fourth one, the charge of the cation. a and b are the integration values for $[(\text{CH}_3)_2\text{NH}_2]^+$ and acetate, respectively, obtained from the ^1H NMR spectra for each RE-UiO-66, when the BDC linker proton integration is set to 1 (values in Table S3).

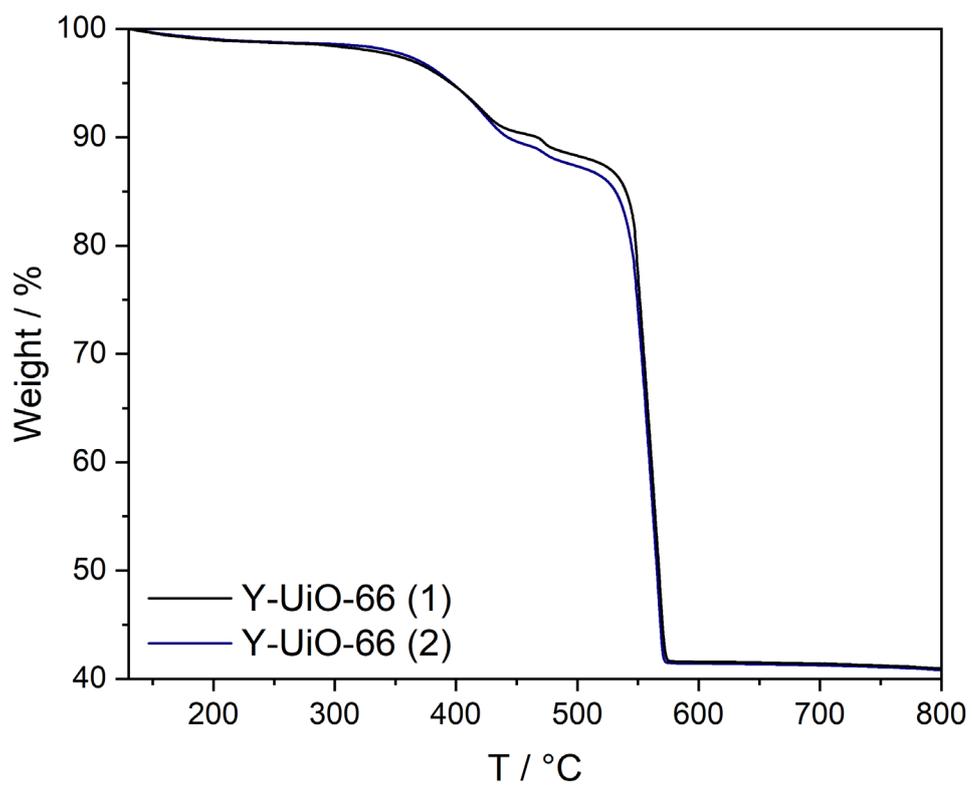


Figure S9 TGA of Y-Uio-66 using (1) nitrate, and (2) acetate as precursor.

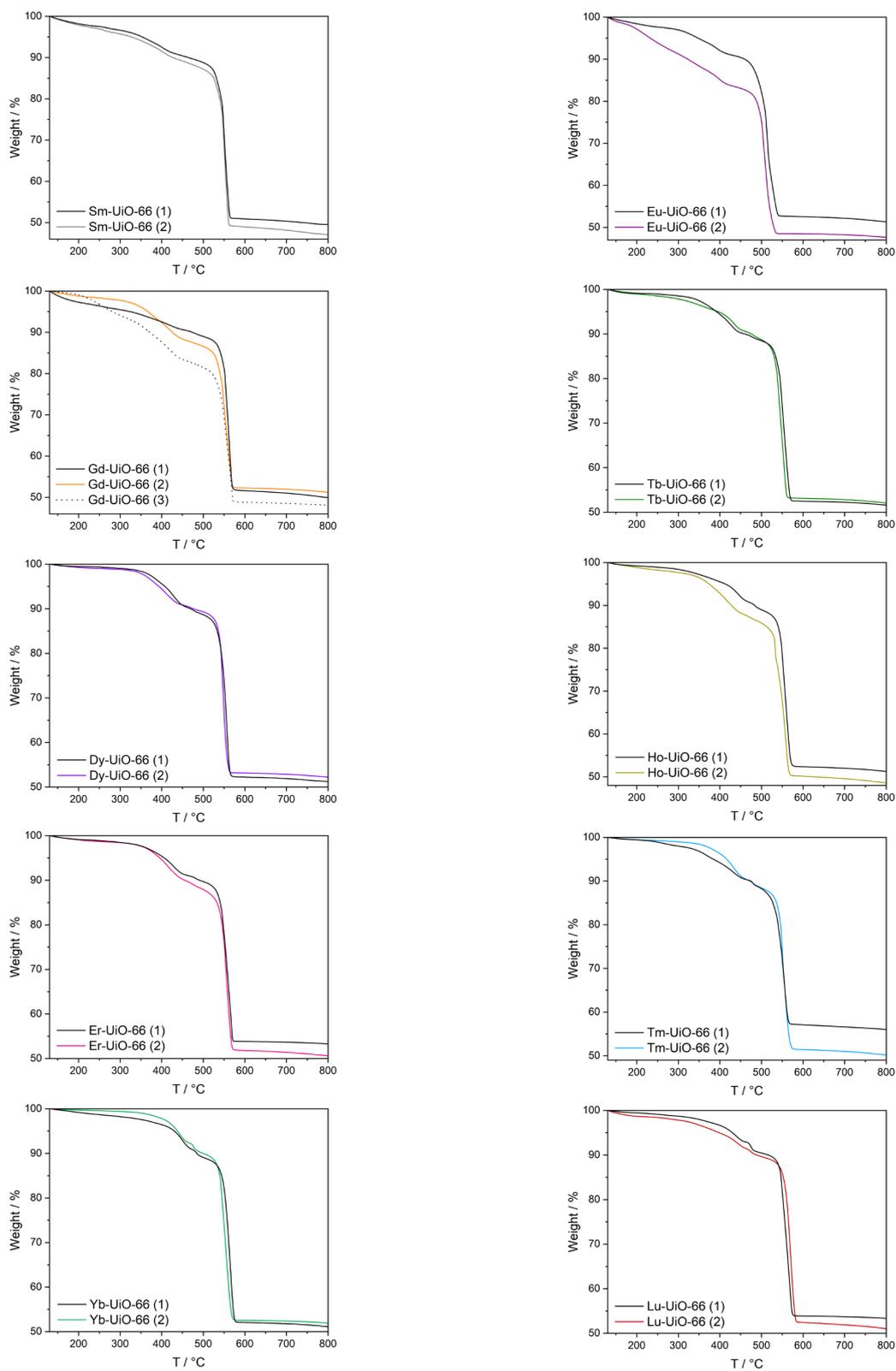


Figure S10 TGA of RE-UiO-66 using (1) nitrate, and (2) acetate as precursor. Gd-UiO-66 (3) corresponds to the reported TGA of a previous batch synthesized using nitrate as precursor.¹

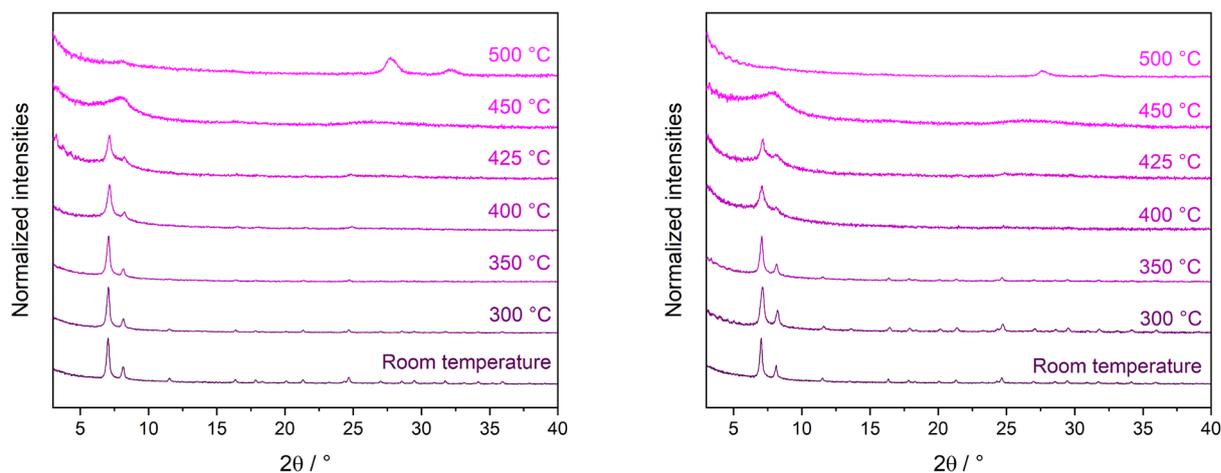


Figure S11 VT-PXRD of Eu-Uio-66 using nitrate (left) and acetate (right) as precursor.

Table S5 Calculated metal percentages in RE-Uio-66 using the information from the TGA thermograms. Samples obtained with (1) nitrate, and (2) acetate as precursor.

Metal	% metal (1) (theoretical)*	% metal TGA (1)	% metal (2) (theoretical)*	% metal TGA (2)
Y	32.9	32.8	32.6	32.6
Sm	46.5	43.9	46.5	42.3
Eu	47.0	45.3	45.9	41.9
Gd	43.5	44.8	43.5	45.4
Tb	46.0	45.6	46.5	46.1
Dy	46.5	45.5	47.0	46.3
Ho	46.3	45.7	46.9	43.7
Er	47.9	47.0	48.0	45.3
Tm	48.4	49.5	47.6	45.0
Yb	47.7	45.8	48.0	46.1
Lu	49.1	47.4	49.3	46.1

* calculated with the structure deduced from the ^1H NMR spectroscopy data, except for Gd where an ideal, defect-free, formula is used.

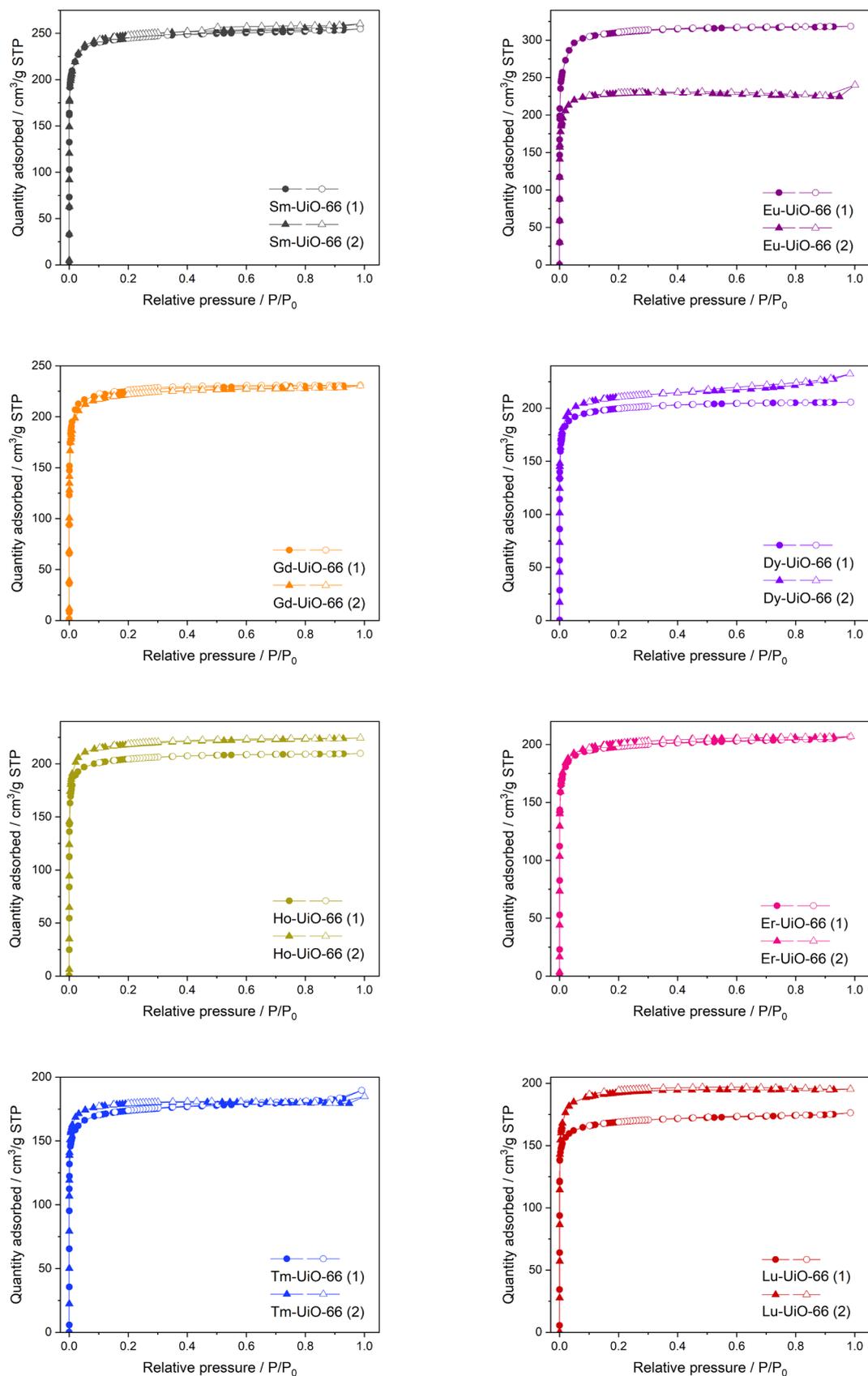
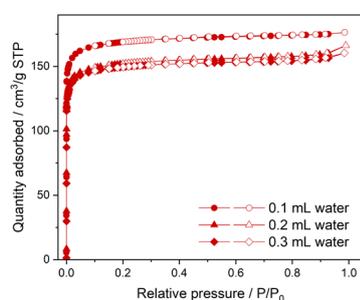


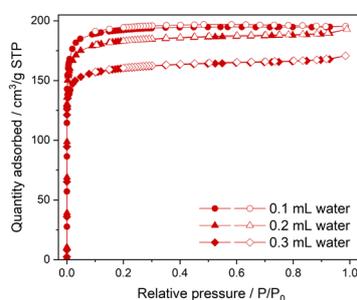
Figure S12 N₂ adsorption-desorption isotherms of RE-UiO-66 (RE = Sm(III), Eu(III), Gd(III), Dy(III), Ho(III), Er(III), Tm(III), Lu(III)) using (1) nitrate, and (2) acetate as precursor.

Table S6 Surface area of Lu-UiO-66 and Er-UiO-66, synthesized with different amounts of water.

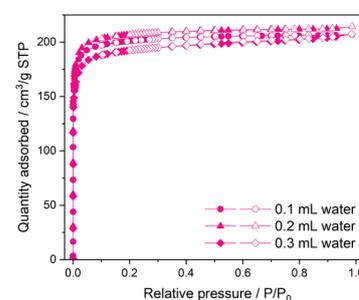
MOF	Precursor	Water added [mL]	Surface area [m ² g ⁻¹]
Lu-UiO-66	Nitrate	0.1	670
Lu-UiO-66	Nitrate	0.2	610
Lu-UiO-66	Nitrate	0.3	590
Lu-UiO-66	Acetate	0.1	780
Lu-UiO-66	Acetate	0.2	730
Lu-UiO-66	Acetate	0.3	640
Er-UiO-66	Acetate	0.1	810/870
Er-UiO-66	Acetate	0.2	830
Er-UiO-66	Acetate	0.3	760



Lu-UiO-66 (nitrate)



Lu-UiO-66 (acetate)



Er-UiO-66 (acetate)

Figure S13 N₂ adsorption-desorption isotherms of Lu-UiO-66 and Er-UiO-66 with different amounts of water.

References

1. P. R. Donnarumma, C. Copeman, M. Richezzi, J. Sardilli, H. M. Titi and A. J. Howarth, *Crys. Growth Des.*, 2024, **24**, 1619-1625.