Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers. This journal is © the Partner Organisations 2022

The Chemistry behind Room Temperature Synthesis of Hafnium and Cerium UiO-66 Derivatives

Orysia Zaremba,[a] Jacopo Andreo [a] and Stefan Wuttke *[ab]

[a] *BCMaterials, Bld. Martina Casiano, 3rd. Floor, UPV/EHU Science Park, Leioa, Spain*

[b] *Ikerbasque, Basque Foundation for Science, Bilbao, Spain*

Email: stefan.wuttke@bcmaterials.net

1. Materials

All chemicals were purchased from commercial suppliers and used as received without further purification. Ammonium Cerium (IV) nitrate, >98%, TCI; Hafnium (IV) chloride, 98%, Sigma Aldrich; 2-Aminoterephthalic acid (BDC-NH_2), 99%, Acros Organics; 2-Nitroterephthalic acid (BDC-NO_2), >97%, BLDpharm; 1,2,4-Benzenetricarboxylic acid (BDC-COOH), 98%, BLDpharm; 2-Bromoterephtalic acid (BDC-Br), 98%, BLDpharm; 2,5-Dihydroxyterephtalic acid (BDC-$(OH)_2$), 95%, Fluorochem; 95 % Formic acid, >99%, LABKEM; 98% Acetic acid, > 99.8%, Acros Organics; Benzoic acid, ≥ 99.5%, Acros Organics; 2M Hydrochloric acid, LABKEM; Ethanol absolute, ≥ 99%, Carl Roth; DMF, >99.9%, LABKEM; MilliQ water, Millipore system.

2. Characterization techniques

X-ray powder diffraction patterns were collected by a Philips X'pert PRO automatic diffractometer operating at 40 kV and 40 mA, in theta-theta configuration, secondary monochromator with Cu K-α radiation (λ = 1.5418 Å) and a Pixel solid-state detector (active length in 2θ - 3.347°). Data were collected from 5 to 75° 2θ with a step size of 0.026° and a time per step of 700s at RT (total time 2h). 1° fixed soller and divergence slits giving a constant volume of sample illumination were used. SEM images were recorded with a Hitachi S-4800 FEG-SEM operating at an accelerating voltage of 5 kV. Samples were coated with a 10 nm gold layer in an Emitech K550x ion sputter. Thermogravimetric analyses (TGA) were carried out from 30 °C to 800 °C at a rate of 5 °C min^{-1} on a Mettler-Toledo TGA/SDTA 851e thermobalance under a 50 cm^3 min^{-1} flow of synthetic air.

3. Synthetic procedures

3.1 Two-step H_2O synthesis of Hf UiO-66 derivatives

Synthesis of Hf UiO-66-COOH: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to hafnium (IV) chloride (245 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 80 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 1,2,4-benzenetricarboxylic acid (0.75 mmol, 161 mg) was added. The resulting white suspension was stirred for 24 h at 300 rpm. The white solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 93% based on the Hf salt.

Synthesis of Hf UiO-66-NO_2: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to hafnium (IV) chloride (245 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 80 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-nitroterephthalic acid (0.75 mmol, 163 mg) was added. The resulting white suspension was stirred for 24 h at 300 rpm. The white solid was recovered by centrifugation (15

000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Hf salt.

Synthesis of Hf UiO-66-NH_2, Hf UiO-66-Br, Hf UiO-66-$(OH)_2$: Unsuccessful by this method.

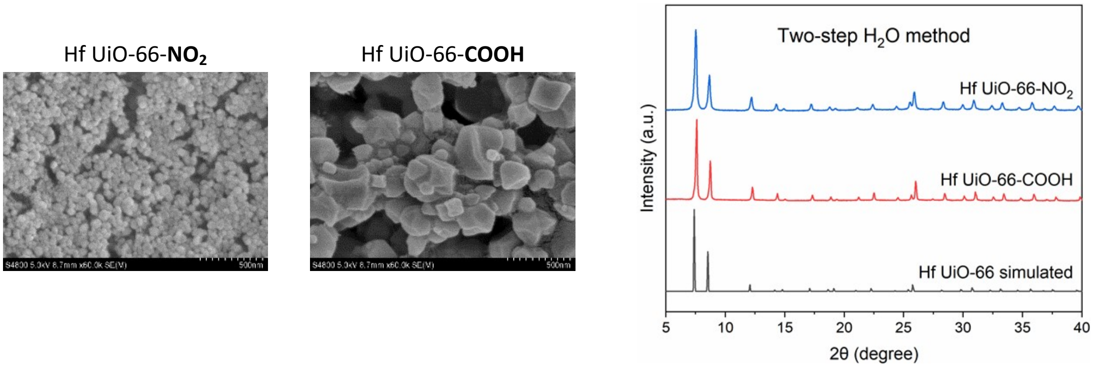


Figure S1. SEM and PXRD of Hf UiO-66-X (X= -NO_2, -COOH) synthesized by the two-step H_2O method with pre-heating at 80 °C.

3.2 Linker solubility

163 mg BDC-NO_2, 161 mg BDC-COOH, 137 mg BDC-NH_2, 188 mg BDC-Br, or 156 mg BDC-$(OH)_2$ were dissolved in (a) 4 ml of water; (b) 4 ml water and 1.5 ml formic acid; (c) 4 ml DMF and 2 ml formic acid.

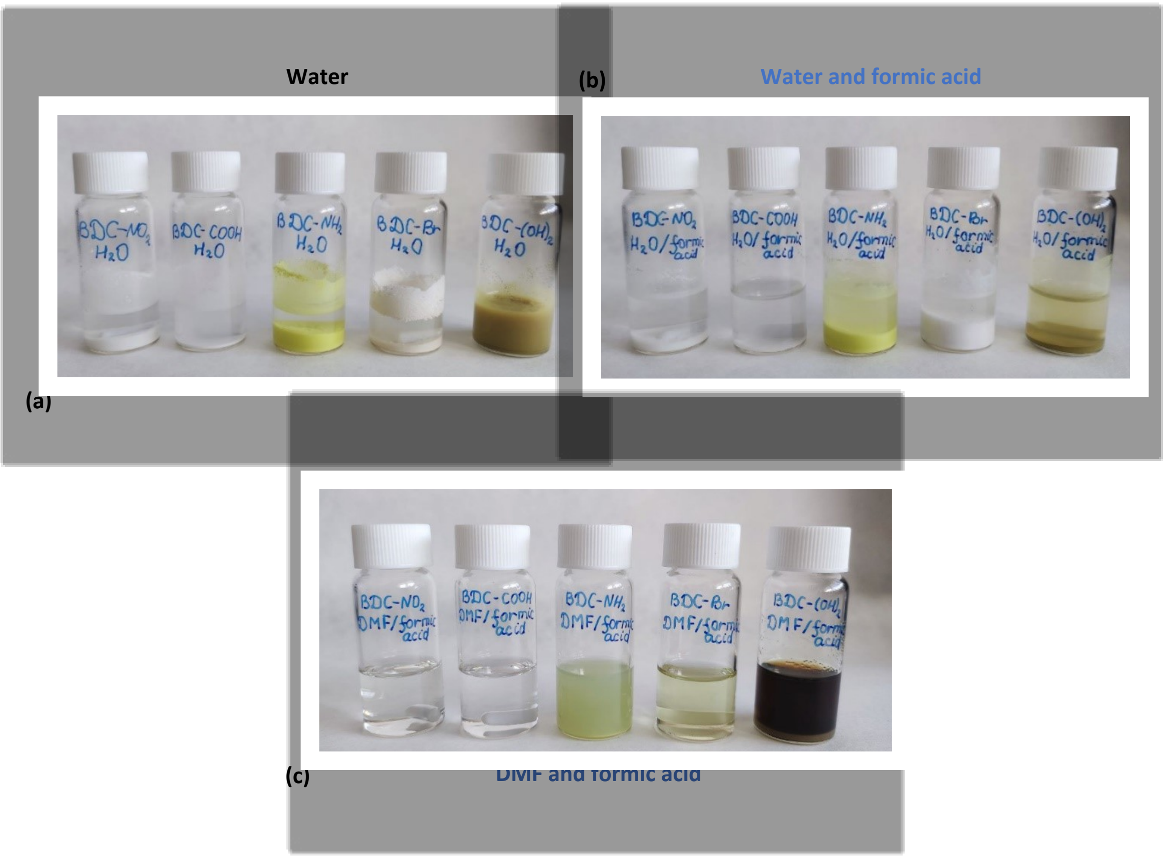


Figure S2. Solubility of BDC-NO_2, BDC-COOH, BDC-NH_2, BDC-Br, BDC-$(OH)_2$ in (a) water; (b) water and formic acid; (c) DMF and formic acid.

3.3 Two-step DMF synthesis of Hf UiO-66 derivatives using equimolar reactants

Synthesis of Hf UiO-66-NO_2: Formic acid (1.5 mL) and DMF (4 mL) were added sequentially to hafnium (IV) chloride (245 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-nitroterephthalic acid (0.75 mmol, 163 mg) was added. The resulting white suspension was stirred for 24 h at 300 rpm. The white solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 20% based on the Hf salt.

Synthesis of Hf UiO-66-NH_2: Formic acid (1.5 mL) and DMF (4 mL) were added sequentially to hafnium (IV) chloride (245 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-aminoterephthalic acid (0.75 mmol, 137 mg) was added. The resulting yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 11% based on the Hf salt.

Synthesis of Hf UiO-66-Br: Formic acid (1.5 mL) and DMF (4 mL) were added sequentially to hafnium (IV) chloride (245 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-bromoterephthalic acid (0.75 mmol, 188 mg) was added. The resulting white suspension was stirred for 24 h at 300 rpm. The white solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 47% based on the Hf salt.

Synthesis of Hf UiO-66-$(OH)_2$: Formic acid (1.5 mL) and DMF (4 mL) were added sequentially to hafnium (IV) chloride (245 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2,5-dihydroxyterephthalic acid (0.75 mmol, 156 mg) was added. The resulting dark green suspension was stirred for 24 h at 300 rpm. The grey solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 16% based on the Hf salt.

Synthesis of Hf UiO-66-COOH: Unsuccessful by this method.

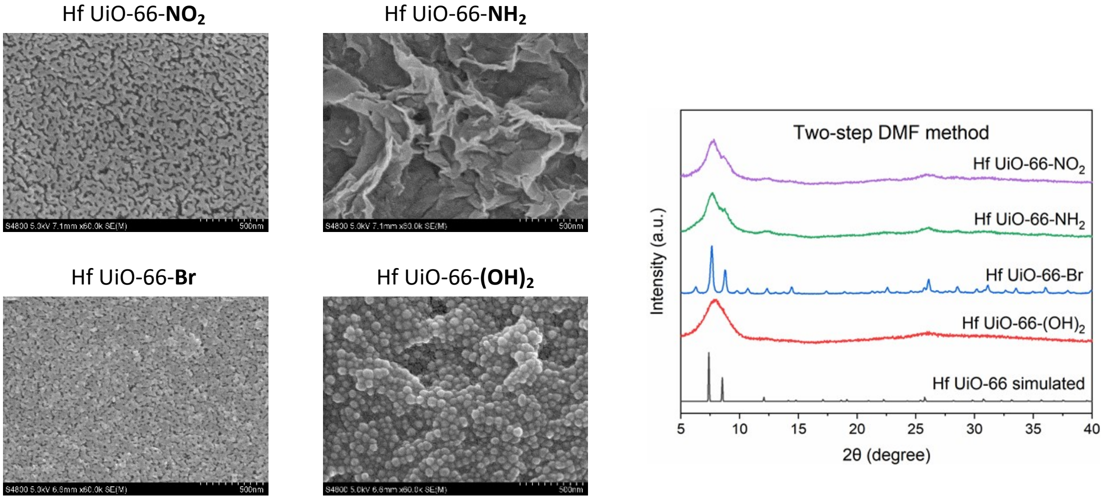


Figure S3. SEM and PXRD of Hf UiO-66-X (X= $-NO_2$, $-NH_2$, -Br, $-(OH)_2$) synthesized by the two-step DMF method with pre-heating at 120 °C using equimolar amounts of the linker and metal salt.

3.4 Two-step DMF synthesis of Hf UiO-66 derivatives with excess linker

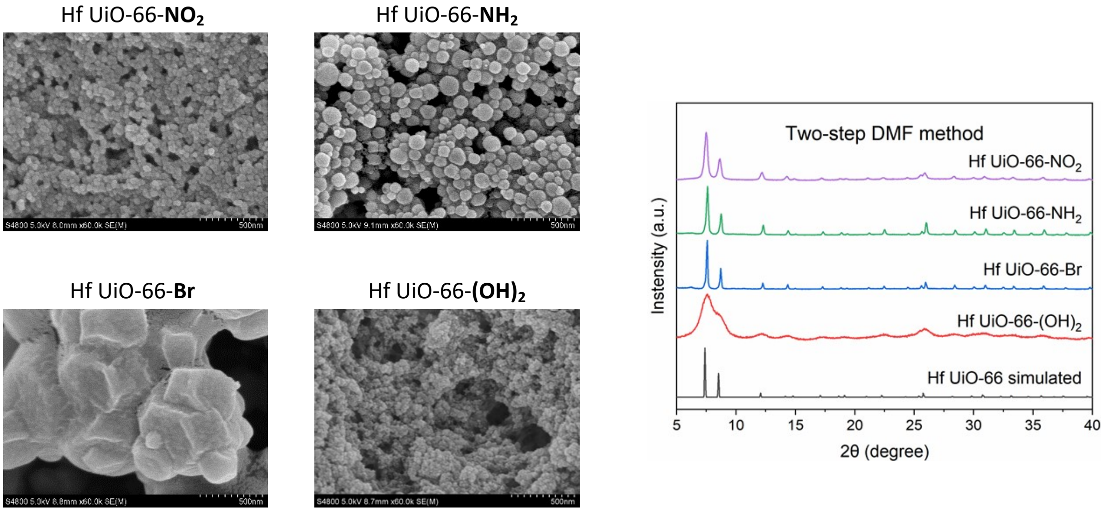
Synthesis of Hf UiO-66-NO_2: Formic acid (4 mL) and DMF (8 mL) were added sequentially to hafnium (IV) chloride (108 mg, 0.334 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-nitroterephthalic acid (218 mg, 1 mmol) was added. The resulting white suspension was stirred for 24 h at 300 rpm. The white solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 97% based on the Hf salt.

Synthesis of Hf UiO-66-NH_2: Formic acid (4 mL) and DMF (8 mL) were added sequentially to hafnium (IV) chloride (108 mg, 0.334 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-aminoterephthalic acid (183 mg, 1 mmol) was added. The resulting yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 95% based on the Hf salt.

Synthesis of Hf UiO-66-Br: Formic acid (4 mL) and DMF (8 mL) were added sequentially to hafnium (IV) chloride (108 mg, 0.334 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2-bromoterephthalic acid (247 mg, 1 mmol) was added. The resulting white suspension was stirred for 24 h at 300 rpm. The white solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 51% based on the Hf salt.

Synthesis of Hf UiO-66-$(OH)_2$: Formic acid (4 mL) and DMF (8 mL) were added sequentially to hafnium (IV) chloride (108 mg, 0.334 mmol) in a 16 ml vial. The mixture was heated at 120 °C and stirred at 600 rpm for 2 h in a silica oil bath. The colourless solution was cooled to RT and 2,5-dihydroxyterephthalic acid (209 mg, 1 mmol) was added. The resulting dark green suspension was stirred for 24 h at 300 rpm. The grey solid was recovered by centrifugation (15 000 rpm, 15 min), washed 2 times with DMF and 2 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 91% based on the Hf salt.

Synthesis of Hf UiO-66-COOH: Unsuccessful by this method.



Hf UiO-66-**NO_2**

Hf UiO-66-**NH_2**

Hf UiO-66-**Br**

Hf UiO-66-**$(OH)_2$**

Figure S4. SEM and PXRD of Hf UiO-66-X (X= -NO_2, -NH_2, -Br, -$(OH)_2$) synthesized by the two-step DMF method with pre-heating at 120 °C using a 3-fold excess of the linker.

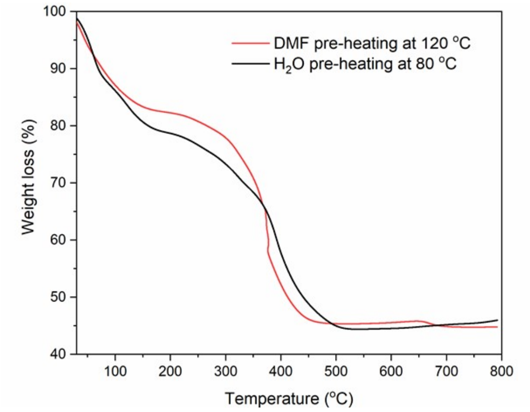


Figure S5. TGA curve of Hf UiO-66-NO_2 synthesized by the two-step H_2O method with pre-heating at 80 °C or two-step DMF method with pre-heating at 120 °C .

3.5 Ce UiO-66-NO_2 time-dependent synthesis with formic acid modulator

Synthesis of Ce UiO-66-NO_2_15 min: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 2 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 15 min at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 93% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2_30 min: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 2 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 30 min at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 94% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2_1 h: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 2 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 1 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2_24 h: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 99% based on the Ce salt.

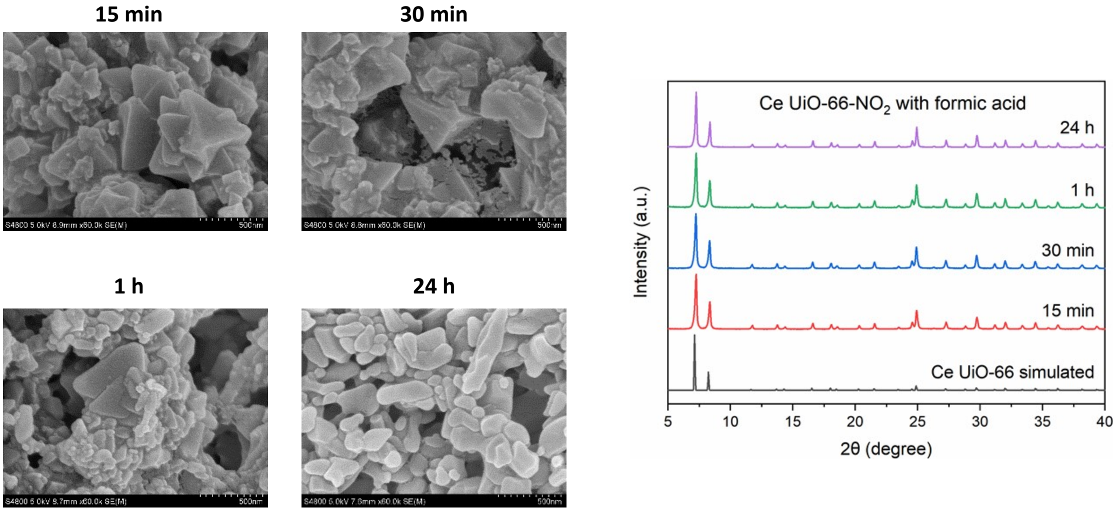


Figure S6. SEM and PXRD of Ce UiO-66-NO_2 synthesized by the one-step H_2O method with formic acid after 15 min, 30 min, 1 h, or 24 h.

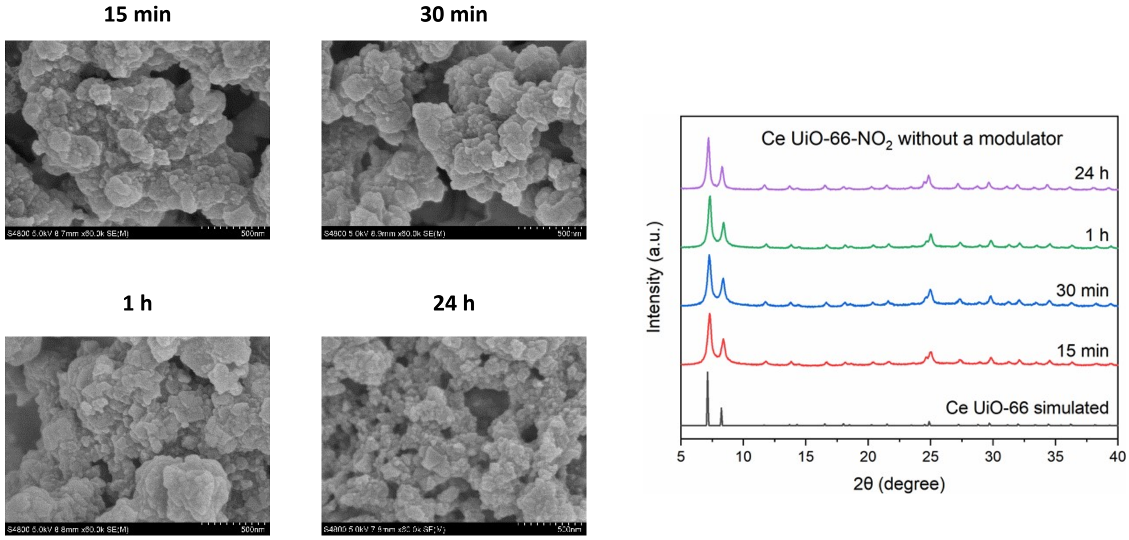
3.6 Ce UiO-66-NO_2 time-dependent synthesis without a modulator

Synthesis of Ce UiO-66-NO_2_15 min: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 2 min. Then, 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 15 min at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 95% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2_30 min: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 2 min. Then, 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 30 min at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 96% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2_1 h: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 2 min. Then, 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 1 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2_24 h: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 30 min. Then, 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.



15 min **30 min** **1 h** **24 h**

Figure S7. SEM and PXRD of Ce UiO-66-NO_2 synthesized by the one-step H_2O method without a modulator after 15 min, 30 min, 1 h, or 24 h.

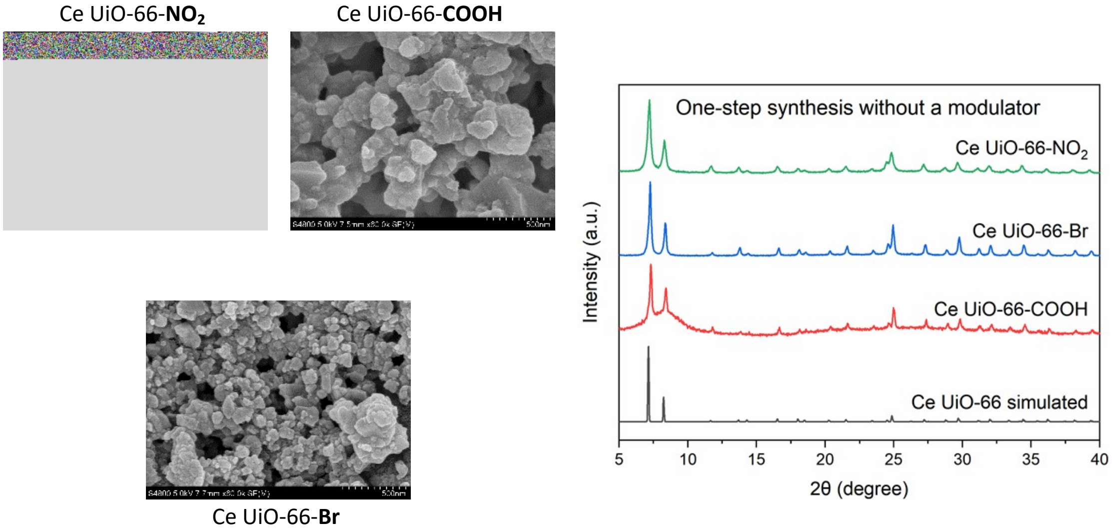
3.7 One-step H_2O synthesis of Ce UiO-66 derivatives without a modulator

Synthesis of Ce UiO-66-NO_2: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 30 min. Then, 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.

Synthesis of Ce UiO-66-COOH: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 30 min. Then, 1,2,4-benzenetricarboxylic acid (161 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 95% based on the Ce salt.

Synthesis of Ce UiO-66-Br: Ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) was dissolved in deionized water (4 ml) in a 16 ml vial with stirring at 300 rpm for 30 min. Then, 2-bromoterephthalic acid (188 mg, 0.75 mmol) was added to the yellow solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.

Synthesis of Ce UiO-66-NH_2, Ce UiO-66-$(OH)_2$: Unsuccessful by this method.


Ce UiO-66-**NO_2**

Ce UiO-66-**COOH**

Ce UiO-66-**Br**

Figure S8. SEM and PXRD of Ce UiO-66-X (X – NO_2, -COOH, -Br) synthesized by the one-step H_2O method without a modulator.

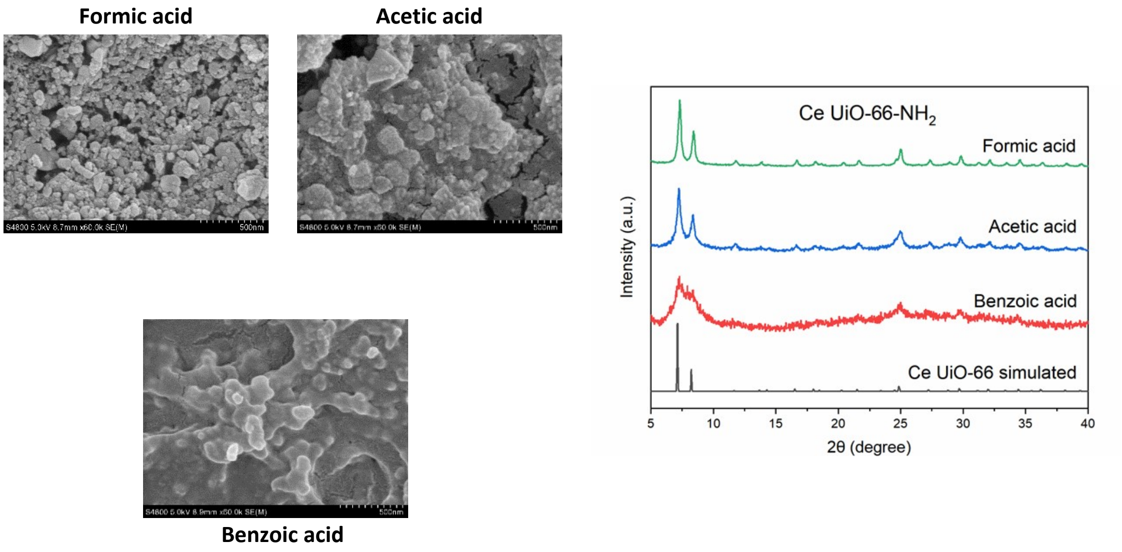
3.8 Influence of a modulator Ce UiO-66-NH_2

Synthesis of Ce UiO-66-NH_2 with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-aminoterephthalic acid (137 mg, 0.75 mmol) was added to the orange solution. The resulting brown suspension was stirred for 24 h at 300 rpm. The brown solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 21% based on the Ce salt.

Synthesis of Ce UiO-66-NH_2 with acetic acid: 98% Acetic acid (2.2 mL) and deionized water (3.3 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-aminoterephthalic acid (137 mg, 0.75 mmol) was added to the orange solution. The resulting brown suspension was stirred for 24 h at 300 rpm. The brown solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 19% based on the Ce salt.

Synthesis of Ce UiO-66-NH_2 with benzoic acid: Benzoic acid (192 mg, 1.5 mmol) and deionized water (5.5 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-aminoterephthalic acid (137 mg, 0.75 mmol) was added to the yellow suspension. The resulting brown suspension was stirred for 24 h at 300 rpm. The brown solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 18% based on the Ce salt.

Synthesis of Ce UiO-66-NH_2 with hydrochloric acid was unsuccessful.


Formic acid

Acetic acid

Benzoic acid

Figure S9. SEM and PXRD of Ce UiO-66-NH_2 synthesized by the one-step H_2O method with different modulators: formic acid, acetic acid, or benzoic acid.

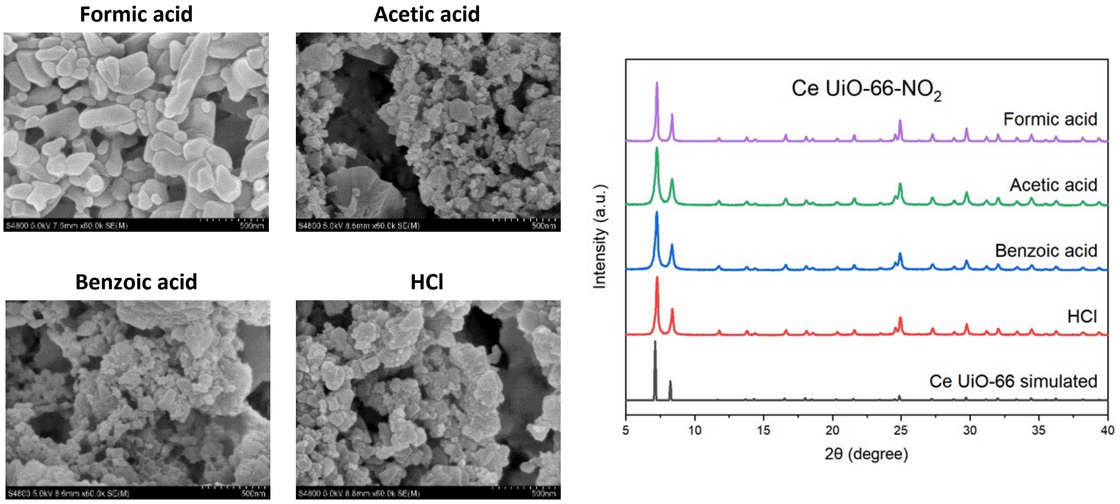
3.9 Influence of a modulator Ce UiO-66-NO_2

Synthesis of Ce UiO-66-NO_2 with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 600 rpm for 30 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 99% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2 with acetic acid: 98% Acetic acid (2.2 mL) and deionized water (3.3 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2 with benzoic acid: Benzoic acid (192 mg, 1.5 mmol) and deionized water (5.5 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the yellow suspension. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 97% based on the Ce salt.

Synthesis of Ce UiO-66-NO_2 with hydrochloric acid: 2M HCl (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-nitroterephthalic acid (163 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 87% based on the Ce salt.


Formic acid

Acetic acid

Benzoic acid

HCl

Figure S10. SEM and PXRD of Ce UiO-66-NO_2 synthesized by the one-step H_2O method with different modulators: formic acid, acetic acid, benzoic acid or HCl.

3.10 Influence of a modulator Ce UiO-66-COOH

Synthesis of Ce UiO-66-COOH with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 600 rpm for 30 min, then 1,2,4-benzenetricarboxylic acid (161 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 97% based on the Ce salt.

Synthesis of Ce UiO-66-COOH with acetic acid: 98% Acetic acid (2.2 mL) and deionized water (3.3 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 1,2,4-benzenetricarboxylic acid (161 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 98% based on the Ce salt.

Synthesis of Ce UiO-66-COOH with benzoic acid: Benzoic acid (192 mg, 1.5 mmol) and deionized water (5.5 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 1,2,4-benzenetricarboxylic acid (161 mg, 0.75 mmol) was added to the yellow suspension. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 95% based on the Ce salt.

Synthesis of Ce UiO-66-COOH with hydrochloric acid: 2M hydrochloric acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 1,2,4-benzenetricarboxylic acid (161 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 77% based on the Ce salt.

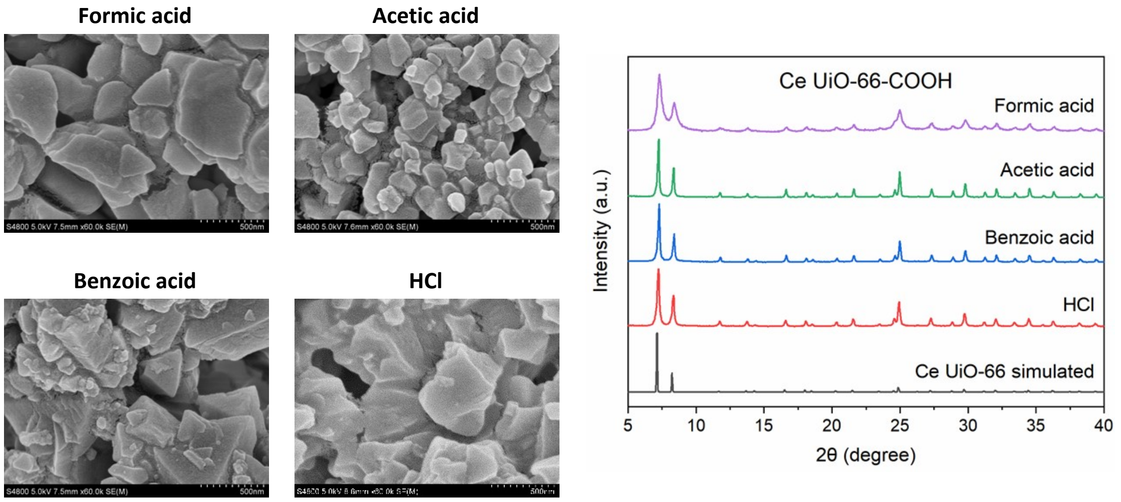


Figure S11. SEM and PXRD of Ce UiO-66-COOH synthesized by the one-step H_2O method with different modulators: formic acid, acetic acid, benzoic acid or HCl.

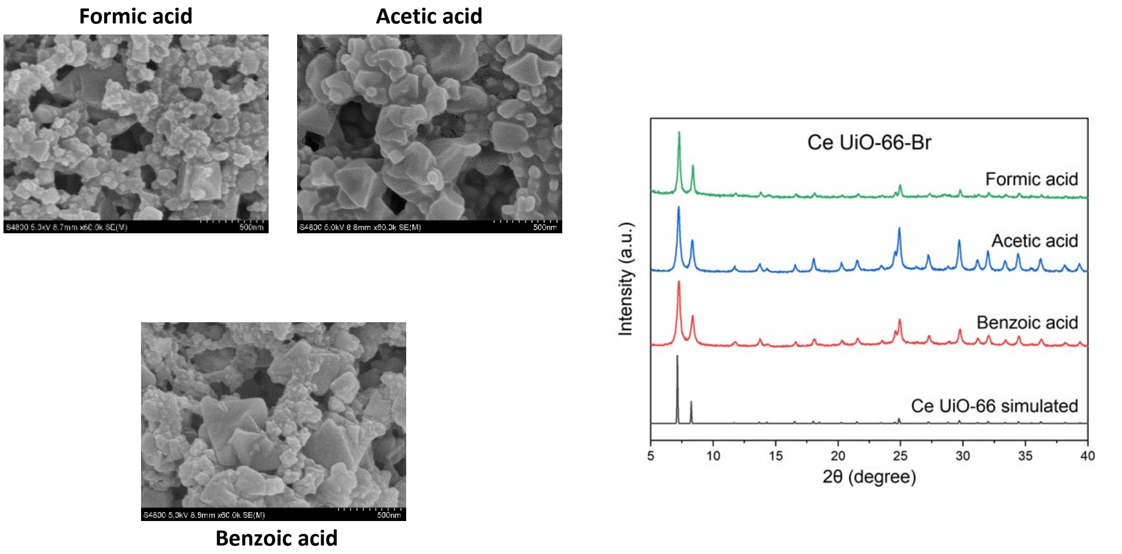
3.11 Influence of a modulator Ce UiO-66-Br

Synthesis of Ce UiO-66-Br with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 600 rpm for 30 min, then 2-bromoterephthalic acid (188 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 8% based on the Ce salt.

Synthesis of Ce UiO-66-Br with acetic acid: 98% Acetic acid (2.2 mL) and deionized water (3.3 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-bromoterephthalic acid (188 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 95% based on the Ce salt.

Synthesis of Ce UiO-66-Br with benzoic acid: Benzoic acid (192 mg, 1.5 mmol) and deionized water (5.5 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was stirred at 300 rpm for 30 min, then 2-bromoterephthalic acid (188 mg, 0.75 mmol) was added to the orange solution. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 83% based on the Ce salt.

Synthesis of Ce UiO-66-Br with hydrochloric acid was unsuccessful.



Formic acid

Acetic acid

Benzoic acid

Figure S12. SEM and PXRD of Ce UiO-66-NH_2 synthesized by the one-step H_2O method with different modulators: formic acid, acetic acid, or benzoic acid.

3.12 Two-step H_2O synthesis of Ce UiO-66 derivatives

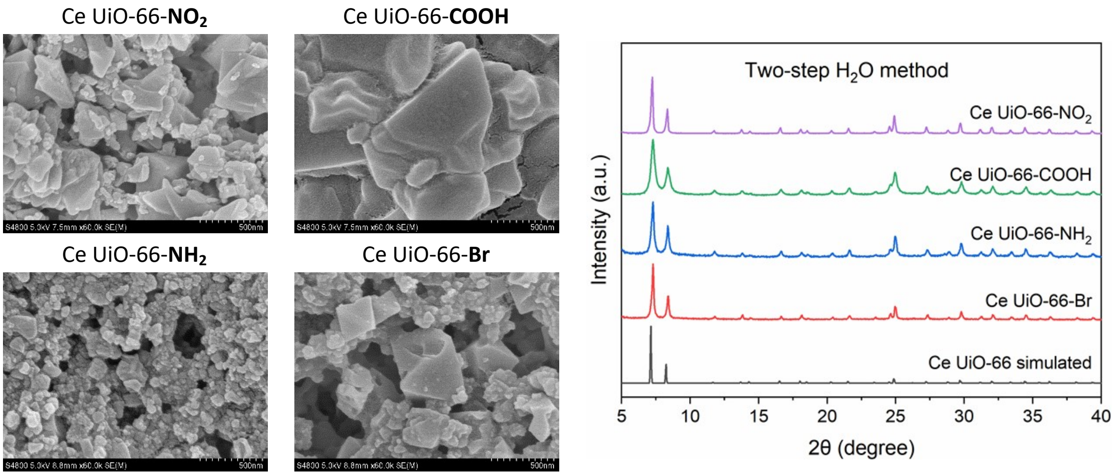
Synthesis of Ce UiO-66-NO_2 with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 80 °C and stirred at 600 rpm for 2 h in a silica oil bath. The orange solution was cooled to RT and 2-nitroterephthalic acid (163 mg, 0,75 mmol) was added. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 86% based on the Ce salt.

Synthesis of Ce UiO-66-COOH with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 80 °C and stirred at 600 rpm for 2 h in a silica oil bath. The orange solution was cooled to RT and 1,2,4-benzenetricarboxylic acid (161 mg, 0,75 mmol) was added. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 81% based on the Ce salt.

Synthesis of Ce UiO-66-NH_2 with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 80 °C and stirred at 600 rpm for 2 h in a silica oil bath. The orange solution was cooled to RT and 2-amino-terephthalic acid (137 mg, 0,75 mmol) was added. The resulting brown suspension was stirred for 24 h at 300 rpm. The brown solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 20% based on the Ce salt.

Synthesis of Ce UiO-66-Br with formic acid: Formic acid (1.5 mL) and deionized water (4 mL) were added sequentially to ammonium cerium (IV) nitrate (420 mg, 0.75 mmol) in a 16 ml vial. The mixture was heated at 80 °C and stirred at 600 rpm for 2 h in a silica oil bath. The orange solution was cooled to RT and 2-bromoterephthalic acid (188 mg, 0,75 mmol) was added. The resulting ivory yellow suspension was stirred for 24 h at 300 rpm. The ivory solid was recovered by centrifugation (15 000 rpm, 15 min), washed 4 times with ethanol (15 000 rpm, 15 min) and suspended in ethanol. The product yield was 8% based on the Ce salt.

Synthesis of Ce UiO-66-$(OH)_2$: Unsuccessful by this method.


Ce UiO-66-**NO_2**

Ce UiO-66-**COOH**

Ce UiO-66-**NH_2**

Ce UiO-66-**Br**

Figure S13. SEM and PXRD of Ce UiO-66-X (X= -NO_2, -COOH, -NH_2, -Br) synthesized by the two-step H_2O method with pre-heating at 80 °C.