

Metal-organic frameworks vs. buffers: Case study of UiO-66 stability

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Table S1. List of used materials.

| Compound | Quality | Producer |
|--|--|---------------------------|
| Acetic acid | 99.8 % | Penta – Czech Republic |
| Acetone | p. a. | Lach-Ner – Czech Republic |
| Acetonitrile | For HPLC, Gradient Grade | Sigma Aldrich |
| Disodium hydrogen phosphate dihydrate | >99 % | Penta – Czech Republic |
| Formic acid | 98 % | Penta – Czech Republic |
| HEPES (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid | ≥99.5 %, | Sigma Aldrich |
| HEPES sodium salt 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid sodium salt | ≥99.5 %, | Sigma Aldrich |
| Indium reference standard | 1 ± 0.002 g L ⁻¹ in 2% HNO ₃ | Astasol |
| <i>N</i> -Ethylmorpholine (NEM) | 97 % | Sigma Aldrich |
| <i>N,N</i> -Dimethylformamide (DMF) | p. a. | Penta – Czech Republic |
| Sodium chloride | p. a. | Penta – Czech Republic |
| Sodium dihydrogen phosphate dihydrate | >99 % | Penta – Czech Republic |
| Terephthalic acid | 98 % | Sigma Aldrich |
| Trizma®base (2-Amino-2-(hydroxymethyl)-1,3-propanediol) | 99.9% | Sigma Aldrich |
| Trizma®hydrochloride (2-Amino-2-(hydroxymethyl)-1,3-propanediol hydrochloride) | 99.9% | Sigma Aldrich |
| Zirconium (IV) chloride | 99.99 % anhydrous | Sigma Aldrich |
| Zirconium standard for ICP | 1000 mg L ⁻¹ in Zr in 2% HNO ₃ and 0.2% HF | Sigma Aldrich |

Preparation of buffer solutions

The buffers were prepared by mixing their acidic and basic components in order to avoid any addition of NaOH or acid for the pH adjustment and from this following variability in an ionic strength. The stock solutions of TRIS and NaCl were prepared in two-times greater concentrations than concentrations needed for stability tests because the buffers were diluted with the suspension of UiO-66 in a volume ratio of 1:1 (excluding 1.0 M HEPES and 0.2 M PB due to their limited solubility).

Table S2. Preparation of buffers (excluding NEM buffer).^a

| Buffers | pH | C / mol L ⁻¹ | Volume / mL | Amount / g (mol) |
|---------|-----|-------------------------|-------------|--|
| TRIS | 7.5 | 2.0 | 100 | 25.4 (0.161) Trizma [®] hydrochloride 4.62 (0.039) Trizma [®] base |
| TRIS | 9.0 | 2.0 | 100 | 3.04 (0.019) Trizma [®] hydrochloride 21.9 (0.181) Trizma [®] base |
| HEPES | 7.5 | 1.0 | 200 | 23.83 (0.1) HEPES 26.03 (0.1) HEPES sodium salt |
| PB | 7.5 | 0.2 | 100 | 0.71 (0.0045) NaH ₂ PO ₄ ·6H ₂ O 2.75 (0.0155) Na ₂ HPO ₄ ·6H ₂ O |
| NaCl | 5.6 | 2.0 | 100 | 11.7 (0.2) NaCl |

^a Column pH shows pH values of prepared solutions; C and Volume represent concentration and volume of the stock solutions, respectively; Amount represents amount (in grams, in mols in brackets) of the compounds used for the preparation of stock solutions.

N-ethylmorpholine (NEM) buffers were prepared directly from liquid NEM. For preparation of 100 mL stock solutions, 25 mL (0.2 mol), 12.7 mL (0.1 mol), 2.53 mL (0.02 mol), 1.26 mL (0.01 mol) and 0.253 mL (0.002 mol) of NEM were pipetted to 100 mL volumetric flasks followed by the addition of distilled water giving 2.0 M, 1.0 M, 0.2 M, 0.1 M and 0.02 M NEM solutions, respectively.

Preparation of saline buffers. The stability experiments were also performed in 0.01 M TRIS saline, HEPES saline and phosphate-buffered saline (PBS). The stock solutions of 0.02 M saline buffers were prepared by mixing corresponding acidic and basic forms to get pH 7.5 as described above, followed by the addition of NaCl to the final concentration of 0.3 M. After the mixing stock solutions with the UiO-66 suspension in a volume ration of 1:1 volume, the working concentrations were 0.01 M buffer and 0.15 M NaCl.

Table S3. Dissolved zirconium from 50 mg of UiO-66 in buffers after a 4 h of treatment.^a

- Total amount of zirconium in 50 mg of parent UiO-66 corresponds to a concentration of 335 mg L⁻¹ as obtained by ICP-MS of decomposed UiO-66 in a mixture of acids (nitric, hydrochloric and hydrofluoric acids, for details see experimental section in main text).

- Zirconium content was also calculated from the TGA data (Figure S2) using the equation:

$$C_{Zr} = \frac{m_{UiO-66} W_{ZrO_2} M_{Zr}}{V_{buffer} M_{ZrO_2}} = 333 \text{ mg L}^{-1}$$

, where C_{Zr} is the maximum amount of zirconium (mg L⁻¹) which can be leached from 50 mg of parent UiO-66 (m_{UiO-66}); V_{buffer} is the used buffer volume (0.05 L); W_{ZrO_2} is the mass fraction of ZrO_2 formed in the TGA measurement (45 %, i.e., 0.45 used in the formula), M_{Zr} and M_{ZrO_2} stand for the molar mass of zirconium (91.22 g mol⁻¹) and zirconium oxide (123.22 g mol⁻¹), respectively.

- Both concentrations obtained are in very good agreement.

| Solution | C/mol L ⁻¹ | Dissolved zirconium / mg L ⁻¹ | Dissolved zirconium / % |
|------------------|-----------------------|--|-------------------------|
| H ₂ O | n. a. | <LOD | <LOD |
| TRIS pH 7.5 | 0.01 | <LOD | <LOD |
| | 0.05 | 0.06 ± 0.01 | 0.019 ± 0.004 |
| | 0.1 | 3.7 ± 0.3 | 1.1 ± 0.1 |
| | 0.5 | 135 ± 14 | 40 ± 4 |
| | 1.0 | 171 ± 7 | 51 ± 2 |
| TRIS pH 9.0 | 0.01 | 0.009 ± 0.001 | 0.003 ± 0.0002 |
| | 0.05 | 97 ± 15 | 28 ± 4 |
| | 0.1 | 151 ± 16 | 45 ± 5 |
| | 0.5 | 195 ± 5 | 58 ± 1 |
| | 1.0 | 233 ± 17 | 69 ± 5 |
| HEPES | 0.01 | <LOD | <LOD |
| | 0.05 | <LOD | <LOD |
| | 0.1 | <LOD | <LOD |
| | 0.5 | <LOD | <LOD |
| | 1.0 | <LOD | <LOD |
| PB | 0.01 | 0.08 ± 0.02 | 0.024 ± 0.006 |
| | 0.05 | 12.3 ± 0.8 | 3.7 ± 0.2 |
| | 0.1 | 3.8 ± 0.5 | 1.1 ± 0.2 |
| | 0.2 | 2.0 ± 0.2 | 0.6 ± 0.1 |
| NEM | 0.01 | <LOD | <LOD |
| | 0.05 | <LOD | <LOD |
| | 0.1 | <LOD | <LOD |
| | 0.5 | 0.03 ± 0.01 | 0.009 ± 0.002 |
| | 1.0 | 0.34 ± 0.01 | 0.102 ± 0.004 |
| NaCl | 0.01 | <LOD | <LOD |
| | 0.05 | <LOD | <LOD |
| | 0.1 | <LOD | <LOD |
| | 0.5 | <LOD | <LOD |
| | 1.0 | <LOD | <LOD |

^a C is the buffer concentration; dissolved concentration of Zr in mg L⁻¹ was measured by ICP-MS with a limit of detection: LOD = 0.001 mg L⁻¹; mass percentages of dissolved Zr are calculated with respect to the total Zr amount (335 mg L⁻¹) as obtained by ICP-MS of decomposed UiO-66 in a mixture of acids.

Solubility of terephthalic acid in buffers

The solubility of terephthalic acid was studied in sealed SIMAX glass bottles: 50 mg of terephthalic acid was mixed with 50 mL of buffer or water, and the mixture was stirred (450 rpm) in an air-conditioned laboratory with constant temperature of 25 ± 1 °C for 24 h. The resulting mixture was filtered using microfilters (Whatman, 0.1 μm PTFE) and the concentration of dissolved terephthalic acid was measured by HPLC.

Table S4. Solubility of terephthalic acid in buffer media.^a

| Solution | C / mol l⁻¹ | Dissolved terephthalic acid / mg L⁻¹ |
|------------------|-------------------------------|--|
| H ₂ O | n. a. | 19.8 |
| | 0.01 | 302 |
| TRIS pH 7.5 | 0.05 | 966 |
| | 0.1 | $\geq 1000^b$ |
| | 0.5 | $\geq 1000^b$ |
| | 1.0 | $\geq 1000^b$ |
| | 0.01 | 488 |
| HEPES | 0.05 | 849 |
| | 0.1 | 952 |
| | 0.5 | $\geq 1000^b$ |
| | 1.0 | $\geq 1000^b$ |
| | 0.01 | 677 |
| PB | 0.05 | 941 |
| | 0.1 | 971 |
| | 0.2 | $\geq 1000^b$ |
| | 0.01 | 845 |
| NEM | 0.05 | 957 |
| | 0.1 | 967 |
| | 0.5 | $\geq 1000^b$ |
| | 1.0 | $\geq 1000^b$ |
| | 0.01 | 23.1 |
| NaCl | 0.05 | 26.3 |
| | 0.1 | 27.8 |
| | 0.5 | 29.3 |
| | 1.0 | 29.3 |

^a C is the buffers concentration; Dissolved terephthalic acid represents the equilibrium concentration of terephthalic acid in various media at 25 ± 1 °C.

^b Concentrations were above 1000 mg L⁻¹. The solubility above this level is not relevant for this study because a total linker content in parent UiO-66 is 446 mg L⁻¹.

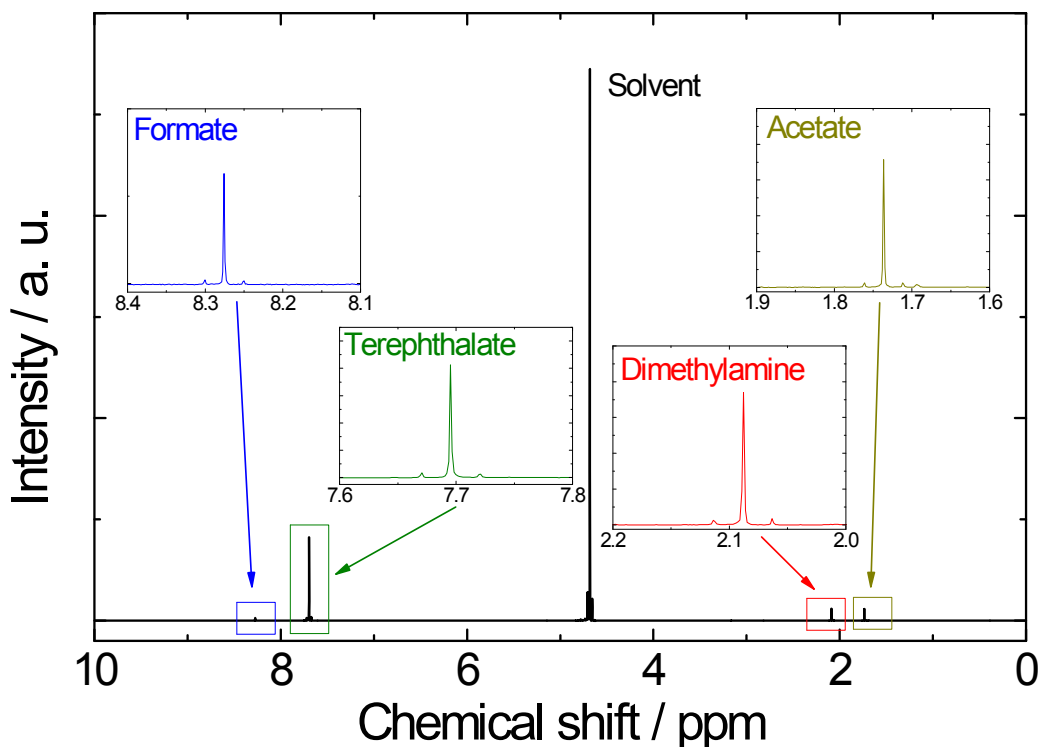


Figure S1 ^1H NMR spectrum of dissolved parent UiO-66 in 1.0 M NaOH/D₂O at room temperature.

The signals are assigned to formate (blue, 8.3 ppm), terephthalate (green, 7.7 ppm), N,N-dimethylamine (red, 2.1 ppm) and acetate (dark yellow, 1.7 ppm). The most intensive peak at 4.7 ppm belongs to H₂O. A terephthalate/acetate molar ratio of 1.00/0.18 obtained from ^1H NMR measurement is in good agreement with that of similarly prepared UiO-66.¹ A terephthalate/formate molar ratio was 1.00/0.13. The total molar ratio of terephthalate/monocarboxylates was 1.00/0.31. The detailed description can be found in previous works.^{1,2}

1. Shearer, G. C.; Chavan, S.; Bordiga, S.; Svelle, S.; Olsbye, U.; Lillerud, K. P. Defect Engineering: Tuning the Porosity and Composition of the Metal–Organic Framework UiO-66 via Modulated Synthesis. *Chem. Mater.* **2016**, *28*, 3749–3761.
2. Bůžek, D.; Demel, J.; Lang, K. Zirconium Metal–Organic Framework UiO-66: Stability in an Aqueous Environment and Its Relevance for Organophosphate Degradation. *Inorg. Chem.* **2018**, *57*, 14290-14297.

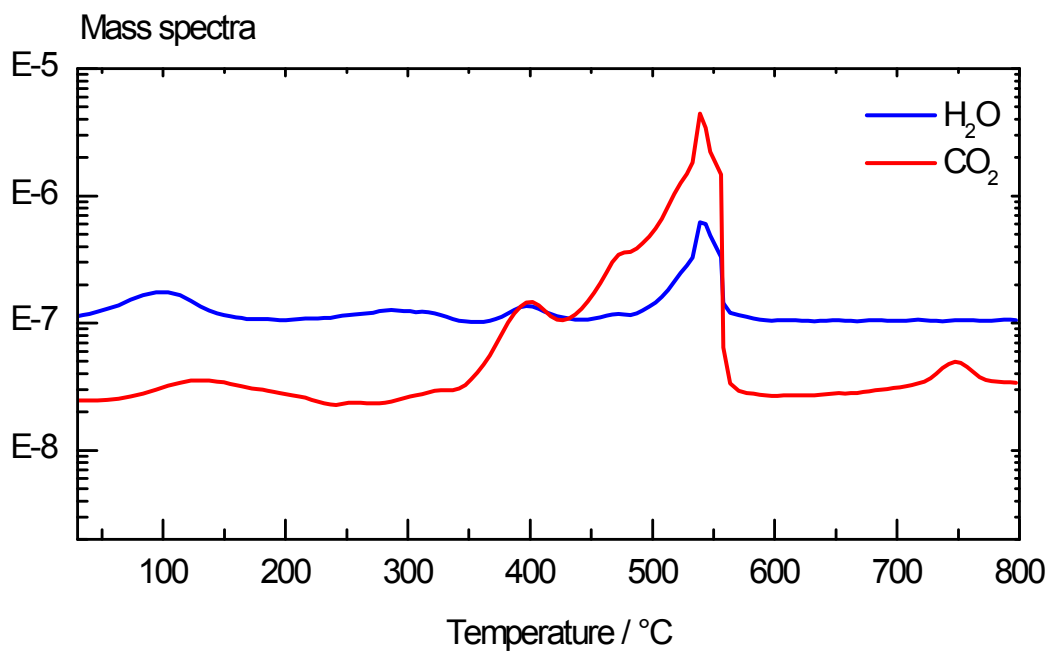
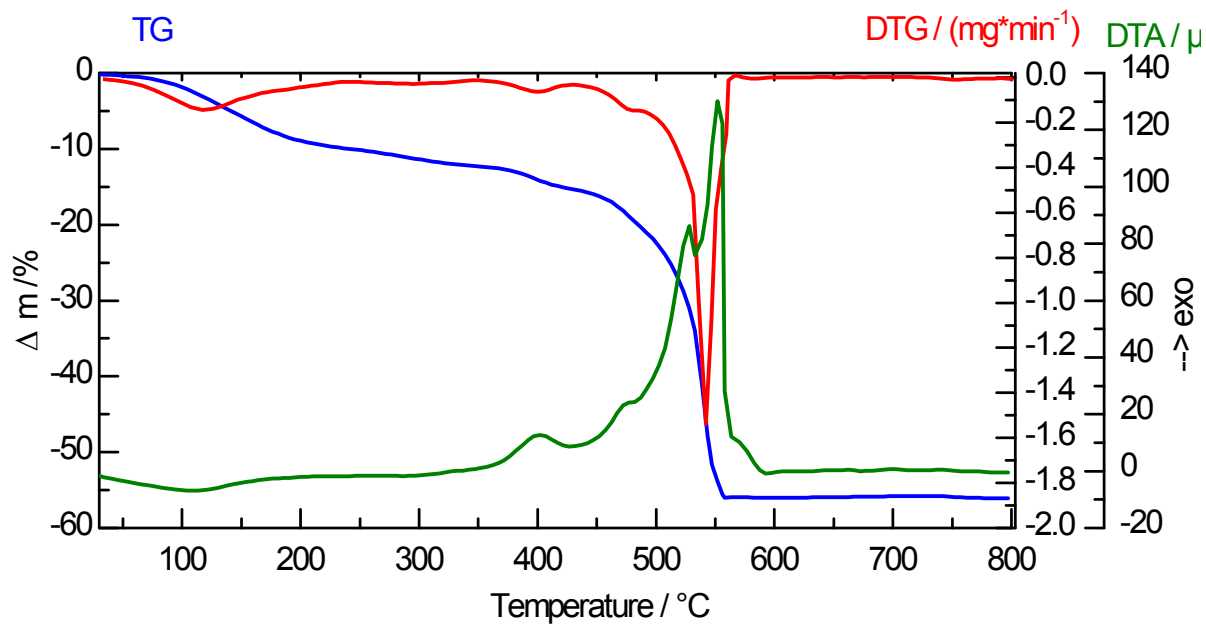


Figure S2. DTA/TGA curves (top) and the evolution of gases (bottom) for parent UiO-66. The measurements were performed in synthetic air (flow rate 30 mL min⁻¹) from room temperature to 800 °C with a heating rate of 5 °C min⁻¹. The mass spectra were recorded at m/z set to H₂O and CO₂.

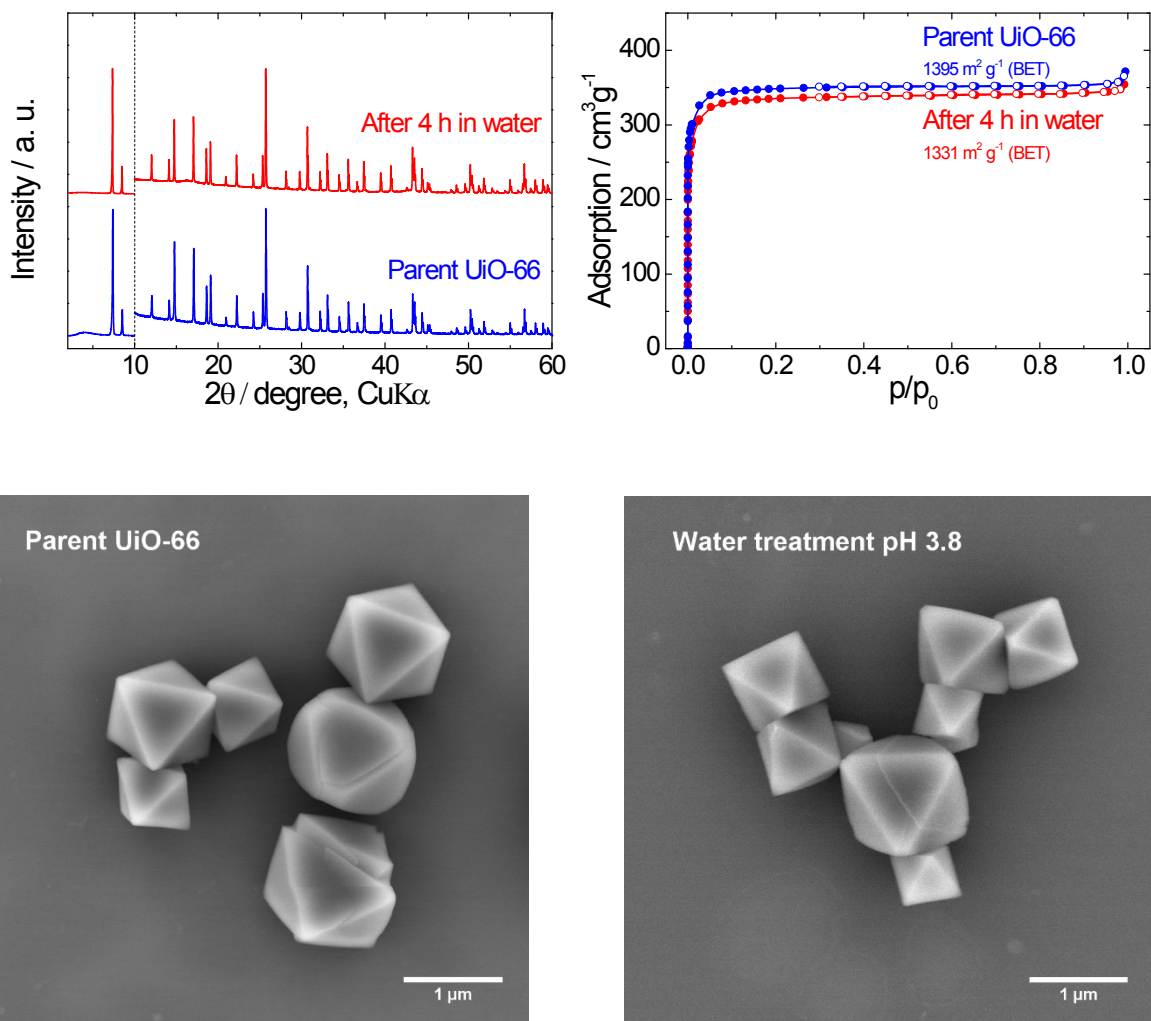


Figure S3. Stability of parent UiO-66 in neat water (natural pH 3.8).

Upper row: PXRD patterns (left) and N₂ adsorption isotherms (right) of parent UiO-66 before and after a 4 h treatment in water. The release of the terephthalate linker, if any, was below the detection limit of HPLC analysis (< 0.01 mg L⁻¹).

Bottom row: SEM images of parent UiO-66 before (left) and after (right) a 4 h treatment in water.

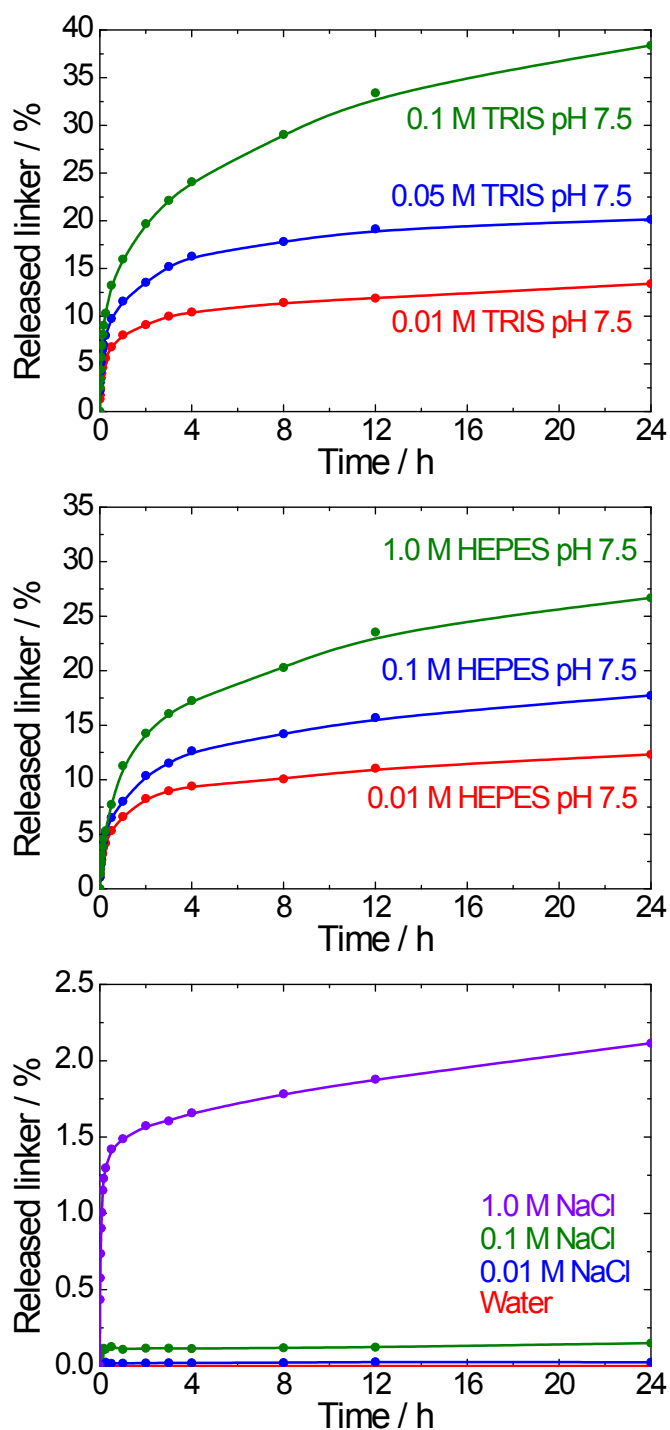


Figure S4. The stability of UiO-66 in TRIS, HEPES, and NaCl solutions, a 24 h treatment at 25 °C.

A blank experiment in water showed no terephthalate release during a 24 h treatment (concentration of terephthalic acid was below the HPLC detection limit, i.e., 0.01 mg L⁻¹).

Trials in PB buffers were not performed longer since UiO-66 completely decomposes after a 4 h treatment.