Supporting Information

Energy Efficient Ultrahigh Flux Separation of Oily Pollutants from Water with Superhydrophilic Nanoscale Metal–Organic Framework Architectures

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**Materials and methods**

All materials were purchased from Sigma Aldrich, Across or TCI Europe in the common purities *purum, puriss* or reagent grade. The materials were used as required without further purification and handled in air unless otherwise noted. The water used in the experiments was subjected to a Merck-Milipore Mili-Q purification system prior to use.

**Au@SSM preparation**

The SSMs were cut into 18 x 6 cm large pieces and cleaned by ultrasonic treatment in acetone followed by ethanol and water. SSMs were positioned in a rotating vacuum deposition unit installed in a glovebox (M Braun Labmaster Pro SP equipped with an Inficon SQC-310C deposition controller). 10 nm titanium as adhesion layer and subsequently 40 nm of gold were thermally deposited under high vacuum on the mesh. The evaporation procedure was conducted for both sides of the SSM.

For the VAC synthesis the meshes were cut into 3 cm x 3 cm pieces and cleaned under nitrogen flow.

**Scanning electron microscopy (SEM)**

SEM micrographs were collected with an FEI Helios Nanolab G3 UC electron microscope with an acceleration voltage of 2 kV from a field emission gun. For the analysis, the respective samples were cut into sizes of 1 cm x 1 cm and mounted on carbon pad-modified stainless steel sample holders. No carbon layer was evaporated in high vacuum prior to analysis.

**Transmission electron microscope (TEM)**

TEM imaging and electron diffraction was conducted on an FEI Titan Themis 60-300 microscope at an acceleration voltage of 300 keV. Samples were prepared by carefully removing film material from the mesh with a sharp razor blade and mounting it onto conducting copper grids.

**Static contact angle measurements**

Contact-angle measurements were collected using an attension from Biolin Scientific. A small amount of the respective liquid was placed on the substrate by a precision syringe, while recording images with a camera speed of 1 frame per second (fps) for 10 s. The high-speed images for recording the superhydrophilic properties and water spreading were performed using 40 fps for 1 s. The image analysis was carried out with the software ImageJ using the manual mode and fitting the contour of the droplets manually.

**Inductively coupled plasma atomic emission spectrometer (ICP-AES)**

ICP-AES was conducted using water aliquots of 10 mL after each filtration cycle with 50 cycles in total. The Co ion content was determined using a Varian Vista RL ICP-AES instrument with a limit of detection (LOD) of 10 ng mL\(^{-1}\).

**Cost estimation for the gold deposition process**

We use gold for physical vapor deposition (PVD) in the common purity 99.99%. One evaporation cycle employs one gold pellet (0.3 g). According to the gold prize at the global market (1 g = 51 €) one evaporation cycle cost ca. 16 €. In our evaporation chamber, we were
able to deposit gold from one pellet on 4 meshes (392 cm$^2$) at once. Covering both sides of the mesh via two cycle we calculate a total cost of 0.04 Euro cm$^{-2}$ or 400 € m$^{-2}$.

**Water sorption**

Water vapor sorption measurements were performed at 298 K with a Quantachrome Instruments Autosorb iQ MP with a vapor option. Samples of 20 mg were preheated in vacuo at 120 °C for 12 h and degassed for five minutes in vacuo before use. Millipore® quality water was used for the vapor sorption. The temperature level was controlled by a thermostat using water as coolant.
Vapor-assisted conversion

A 3 x 3 cm Au@SSM sample was placed into glass supported petri dishes with 3 cm in diameter. A MOF precursor solution was prepared by mixing HHTP precursor (10.8 x 10^{-3} mmol; 3.5 mg) and cobalt acetate (22.0 x 10^{-3} mmol; 6 mg) in a defined ratio (1:2 n:n) in a solvent mixture of water and 1-propanol (1.5 mL : 1.5 mL). To the precursor solution, 100 μL were added from a fresh prepared solution comprising a salicylic acid modulator (0.89 mmol; 125 mg) in a water, 1-propanol (1 mL : 1 mL). 1 mL of the respective precursor solution (HHTP: 3.6 mmol L⁻¹; Co(OAc)₂: 7.33 mmol L⁻¹; salicylic acid: 0.29 mmol L⁻¹) were filled into the petri dishes, evenly covering the mesh. The setup was transferred to a polypropylene autoclave with a cap equipped with a Teflon seal. At the bottom, the autoclave was filled with 14 Raschig rings (10 mm x 10 mm, soda lime glass) to create an elevated flat platform for the petri dish. A liquid mixture of 1-propanol and water; 1:1 ; v/v) was placed as a solvent bath at the bottom of the autoclave. The autoclave was sealed and subsequently transferred to a preheated oven (85 °C) for 12 h. After the synthesis, the set-up was removed from the oven and cooled down to room temperature. The Co-CAT-1@Au@SSM meshes were rinsed with acetone and dried under nitrogen flow prior to use.

Figure S1. An illustration scheme of the vapor-assisted conversion setup for the fabrication of MOF@Au@SSM. The as-prepared Au@SSM substrates are placed in a teflon vessel, which is located on top of glass spacers in an autoclave. On the bottom of the autoclave a solvent bath is filled. Subsequently, a precursor solution is added to the substrate containing a teflon vessel. The autoclave is sealed and placed in a preheated oven for adjusted time. After the course of the synthesis, the solvent mixture dried and in the end of the reaction, the MOF@Au@SMM can be retrieved and subjected to various work-up routines.
Analysis of SSM, Au@SSM and MOF@Au@SSM meshes

EDX analysis of the respective meshes

**Figure S2.** EDX analysis of the fabricated meshes. **A** SEM micrograph of the SSM substrate and the corresponding EDX spectrum of the selected area showing the elemental composition of the alloy. **B** SEM micrograph of the Au@SSM substrate and the corresponding EDX spectrum of the selected area, confirming the presence of the deposited metals Ti and Au. **C** SEM micrograph of the MOF@Au@SSM substrate and the corresponding EDX spectrum obtained at the highlighted area (center of the mesh backbone) in the SEM image. **D** SEM of the MOF@Au@SSM substrate and the corresponding EDX spectrum recorded at the highlighted area (area close to the mesh node) in the SEM image.
EDX mapping of the respective meshes

Figure S3. A, B and C SEM micrographs of SSM, Au@SSM and Co-CAT-1@Au@SSM samples with cut-outs containing color-coded EDX mapping of the elements iron (turquoise), gold (yellow), and cobalt (dark blue), respectively. D), E) and F) display the corresponding back-scattered electron (BSE) micrographs. The respective element EDX maps of the above-depicted cut-outs of the respective elements: manganese (violet), chromium (dark green), nickel (light green), titanium (grey) are shown as insets.

SEM analysis of MOF@Au@SSM

Figure S4. Additional SEM analysis of the MOF@Au@SSM. A BSE image of the mesh showing the MOF patches in darker contrast and the uncovered metal parts in bright contrast. B Magnified SEM micrograph of a mesh node and C the corresponding BSE image. Here, the transition between MOF film, blank gold parts and stainless steel alloy are clearly visible. D Image of the pillar-like crystallite orientation on the mesh surface growing orthogonally to the curvature of the surface. E Corresponding magnified SEM image on a film crack highlighting the orientation of the MOF crystallites on the surface. F A representative SEM image of a dense array of MOF pillar-like crystallites on the mesh surface.
Macroscopic photographs of the respective meshes

![Macroscopic photographs of the respective meshes](image)

**Figure S5.** Macroscopic photographs of the stainless-steel mesh, gold coated mesh and the cut MOF membrane (from left to right).

TEM analysis

**Table S1.** Observed and calculated indices of the TEM analysis.

| Index | Observed (nm) | Calculated (nm) |
|-------|---------------|-----------------|
| (100) | 1.72          | 1.75            |
| (110) | 1.01          | 1.01            |
| (200) | 0.84          | 0.88            |
| (210) | 0.66          | 0.66            |
| (300) | 0.56          | 0.58            |
| (220) | 0.48          | 0.51            |
| (004) | 0.29          | 0.32            |

Impact of the synthesis conditions on the Co-CAT-1 growth

![SEM images of Co-CAT@Au@SSM samples](image)

**Figure S6.** SEM images of Co-CAT@Au@SSM samples. A-B the mesh was synthesized using higher and C-D lower concentrations of precursor material compared to the optimal concentration described in the experimental part.
Characterization of surface wetting properties

Reference contact angle measurements

![Figure S7. Reference contact angle measurements of the SSM and Au@SSM substrates and the averaged WCAs and OCAs. A Representative WCA of SSM and B of Au@SSM. Representative OCAs in water for C SSM and D of Au@SSM.](image)

Measured WCAs and OCAs

Table S2. Measured WCAs and underwater OCAs using DCM as a probe of Au@SSM and SSM substrates.

| Repeat | Au@SSM | SSM |
|--------|--------|-----|
|        | OCA (°) | WCA (°) | OCA (°) | WCA (°) |
| 1      | 134     | 115   | 138     | 90      |
| 2      | 128     | 116   | 140     | 95      |
| 3      | 137     | 104   | 129     | 97      |
| 4      | 135     | 109   | 140     | 89      |
| 5      | 133     | 111   | 126     | 93      |
Table S3. Measured underwater OCAs using DCM as a probe for MOF@Au@SSM substrates.

| MOF@Au@SSM | OCA (°) | Repeat | OCA (°) | Repeat |
|------------|---------|--------|---------|--------|
| 1          | 177     | 13     | 167     | 15     |
| 2          | 173     | 14     | 174     | 16     |
| 3          | 170     | 15     | 167     | 17     |
| 4          | 175     | 16     | 168     | 18     |
| 5          | 180     | 17     | 180     | 19     |
| 6          | 180     | 18     | 180     | 20     |
| 7          | 171     | 19     | 180     | 21     |
| 8          | 176     | 20     | 172     | 22     |
| 9          | 176     | 21     | 176     | 23     |
| 10         | 180     | 22     | 177     | 24     |
| 11         | 175     | 23     | 176     |        |
| 12         | 172     | 24     | 173     |        |

Crystal structure of Co-CAT-1

Figure S8. Crystal structure of Co-CAT-1 (for better illustration, the loosely bound crystal water was omitted). A View along the c-axis. B View along the b-axis. C Layered structure comprised of HHTP(H₂O)₁₂ complexes. D Continuous layer of HHTP in-plane coordinated by Co ions.
Crystal shape and pore alignment of Co-CAT-1@Au@SSM

Figure S9. Arrangement of Co-CAT-1 crystallites on the mesh backbone. MOF crystallites feature a needle-like crystallite shape. These crystallites show a honeycomb array of pore channels built up from hexagonal HHTP subunits coordinated in-plane by Co-ions.

Characterization of oil-water separation

Chemical oxygen demand determination

After filtration, an aliquot of 2 mL was taken from the filtrated water phase and subjected to a Merck Spectroquant COD cell test (Hg-free). The reaction cell contained sulfuric acid, potassium dichromate and silver sulfate catalyst. After the addition, the solution was mixed vigorously using a vortexer and the reaction cell was transferred to a preheated oven (148 °C) for 2 h. Afterwards, the vials were cooled down to room temperature, homogenized by a vortexer, and transferred to 10 mm quartz cuvettes for analysis by UV-vis spectroscopy. The same routine was performed with a COD standard test solution (100 mg L\(^{-1}\)) from VWR in water and a blank water sample.

The spectroscopic investigation was carried out using a Perkin Elmer UV/VIS/NIR Lambda 1050 spectrometer equipped with a 150 nm integrating sphere. After recording the blank measurement, the UV-vis spectrum of the standard solution was collected to determine the absorbance at 445 nm. After that, a formula was set up to calculate the COD for the following samples by measuring the absorbance at 445 nm:

\[
Abs_{445\text{nm}} \cdot 297.7 = \text{COD (mg L}^{-1}\text{)}
\]

Abs 445nm represents the absorbance of the tested water sample at 445 nm, the factor 297.7 was determined by measuring the absorbance of a COD standard solution (100 mg/L).
COD value of the filtrated water samples

Table S4. COD values and the related absorbance values at 445 nm for the filtrated water samples. The values were recorded for five filtration cycles.

|       | n-hexane | Paraffin Oil |                  |                  |                  |
|-------|----------|--------------|------------------|------------------|------------------|
|       | Absorbance at 445 nm | COD (mg/L) | Absorbance at 445 nm | COD (mg/L) |
| 1 Cycle | 0.005 | 1.48 | 1 Cycle | 0 | 0 |
| 2 Cycle | 0.043 | 12.80 | 2 Cycle | 0 | 0 |
| 3 Cycle | 0.0045 | 1.339 | 3 Cycle | 0.009 | 2.67 |
| 4 Cycle | 0.055 | 16.37 | 4 Cycle | 0.21 | 62.51 |
| 5 Cycle | 0.077 | 22.92 | 5 Cycle | 0.11 | 32.74 |

|       | n-pentane | Cyclohexane |                  |                  |                  |
|-------|-----------|-------------|------------------|------------------|------------------|
|       | Absorbance at 445 nm | COD (mg/L) | Absorbance at 445 nm | COD (mg/L) |
| 1 Cycle | 0.057 | 16.96 | 1 Cycle | 0.041 | 12.20 |
| 2 Cycle | 0.051 | 15.18 | 2 Cycle | 0.048 | 14.28 |
| 3 Cycle | 0.017 | 5.06 | 3 Cycle | 0.029 | 8.63 |
| 4 Cycle | 0.049 | 14.58 | 4 Cycle | 0.023 | 6.84 |
| 5 Cycle | 0.05 | 14.88 | 5 Cycle | 0.049 | 14.53 |

|       | 1-Dodecene | Crude oil |                  |                  |                  |
|-------|------------|-----------|------------------|------------------|------------------|
|       | Absorbance at 445 nm | COD (mg/L) | Absorbance at 445 nm | COD (mg/L) |
| 1 Cycle | 0.004 | 1.19 | 1 Cycle | 0.055 | 16.37 |
| 2 Cycle | 0.003 | 0.89 | 2 Cycle | 0.087 | 25.89 |
| 3 Cycle | 0.001 | 0.29 | 3 Cycle | 0.1 | 29.77 |
| 4 Cycle | 0.0026 | 0.77 | 4 Cycle | 0.057 | 16.96 |
| 5 Cycle | 0.0003 | 0.08 | 5 Cycle | 0.11 | 32.74 |

|       | Xylene |                  |                  |                  |                  |
|-------|--------|------------------|------------------|------------------|------------------|
|       | Absorbance at 445 nm | COD (mg/L) |                  |                  |                  |
| 1 Cycle | 0.62 | 184.57 |                  |                  |                  |
| 2 Cycle | 0.32 | 95.26 |                  |                  |                  |
| 3 Cycle | 0.37 | 110.14 |                  |                  |                  |
| 4 Cycle | 0.48 | 142.89 |                  |                  |                  |
| 5 Cycle | 0.82 | 244.11 |                  |                  |                  |
Separation efficiency results

\[ aC_xH_y + bO_2 \rightarrow cH_2O + dCO_2 \]  

(1)

The stochiometric ratio \( r(O_2) \) between the organic pollutant \( aC_xH_y \) and oxygen \( bO_2 \) (measured oxygen demand) was set according to equation (1). With the following equations the concentration of the respective pollutants was calculated:

\[
\frac{COD}{1000} \times \frac{32 \text{ g mol}^{-1}}{x \text{ mol } [O_2]} = x \text{ mol } [O_2]
\]

(2)

\[ x \text{ mol } [O_2] \times r(O_2) = y \text{ mol [pollutant]} \]

(3)

\[ y \text{ mol [pollutant]} \times M \text{ [pollutant]} = m \text{ [pollutant]} \]

(4)

The obtained \( m \text{ [pollutant]} \) was converted with the respective density of the tested pollutants to \( V_{\text{after filtration [pollutant]}} \). The \( V_{\text{after filtration [pollutant]}} \) was finally set in relation to the \( V_{\text{before filtration [pollutant]}} \) being 333 mL [pollutant] per liter filtered. The results for the respective pollutants are summarized in table S5.

**Table S5.** Separation efficiencies for the respective tested oil contaminated water samples.

| Tested Pollutant | Concentration [mg L\(^{-1}\)] |
|------------------|-------------------------------|
| n-Hexane         | 3.08                          |
| n-Pentane        | 3.52                          |
| PDMS             | 8.2                           |
| 1-Dodecene       | 0.18                          |
| Crude Oil        | 6.92                          |
| Xylene           | 48.9                          |
| Cyclohexane      | 3.3                           |
Separation efficiency – control experiments

Figure S10. Separation efficiency control experiments shown for the A Au@SSM, B SSM, respectively. For the tested pollutant $n$-hexane was chosen and colored with Sudan red dye. The water was colored by a methylene blue dye.

Figure S11. The ability of A Au@SSM, B SSM, C Co-CAT-1@Au@SSM to hold back incoming oil. For the tested oil $n$-hexane was chosen and colored with Sudan red dye.
Figure S12. Separation experiment of a mixture of oil (n-hexane) and water. For better visualization, the water and oil components were colored with methylene blue and Sudan red, respectively.

**Flux analysis**

**Table S6.** Flux of the respective mesh types for 10 runs with dd water.

| Run     | MOF/Au/SSM Flux (L m⁻² h⁻¹) | Au/SSM Flux (L m⁻² h⁻¹) | SSM Flux (L m⁻² h⁻¹) |
|---------|-----------------------------|--------------------------|-----------------------|
| 1 Run   | 995,026                     | 362,426                  | 634,920               |
| 2 Run   | 982,835                     | 565,280                  | 529,100               |
| 3 Run   | 825,805                     | 480,536                  | 634,920               |
| 4 Run   | 841,763                     | 510,924                  | 587,889               |
| 5 Run   | 770,631                     | 471,517                  | 529,100               |
| 6 Run   | 824,558                     | 528,067                  | 566,893               |
| 7 Run   | 746,005                     | 456,517                  | 566,893               |
| 8 Run   | 836,415                     | 456,517                  | 529,100               |
| 9 Run   | 781,355                     | 480,536                  | 690,131               |
| 10 Run  | 836,673                     | 484,874                  | 529,100               |

The water flux of the respective meshes was calculated by the given formula:

\[
\frac{V}{A \cdot t} = flux
\]

Where \( V \) represents the filtrated water volume, \( A \) - the area of the filter and \( t \) - the testing time. It should be noted that the height of the water column was not constant. We measured the flow of 50 mL (0.05 L) of water passing the filter. The diameters of the circular filters were in the range of 1.5 mm to 4 mm. The flux was only driven by gravity. For demonstration we added an example calculation of the MOF-based membrane flux:

\[
A = \pi \cdot r^2
\]

\[
A = \pi \cdot (1.5 \text{ mm})^2 = 7.065 \text{ mm}^2 = 7.065 \times 10^{-6} \text{ m}^2
\]

We measured 50 mL (0.05 L) passing the filter in 21 s (5.8 x 10⁻³ h)

\[
Flux = \frac{V}{A \cdot t} = \frac{0.05 \text{ L}}{7.065 \times 10^{-6} \text{ m}^2 \cdot 5.8 \times 10^{-3} \text{ h}}
\]

Yielding a flux of 1.025672 L m⁻² h⁻¹.
Table S7. Flux of four MOF/Au/SSM filters with 10 cycles respectively.

| MOF/Au/SSM | Area (ø 3 mm / 7x10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-------------|----------------------------|------------------|
| Cycle       | Time (s)                   |                  |
| 1           | 23                         | 1,127,373        |
| 2           | 26                         | 997,292          |
| 3           | 26                         | 997,292          |
| 4           | 26                         | 997,292          |
| 5           | 28                         | 926,056          |
| 6           | 24                         | 1,080,399        |
| 7           | 24                         | 1,080,399        |
| 8           | 25                         | 1,037,183        |
| 9           | 25                         | 1,037,183        |
| 10          | 20                         | 1,296,479        |

| MOF/Au/SSM | Area (ø 4 mm / 1 x 10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-------------|----------------------------|------------------|
| Cycle       | Time (s)                   |                  |
| 1           | 14                         | 1,057,143        |
| 2           | 17                         | 870,588          |
| 3           | 19                         | 778,947          |
| 4           | 21                         | 704,762          |
| 5           | 21                         | 704,762          |
| 6           | 24                         | 616,667          |
| 7           | 24                         | 616,667          |
| 8           | 20                         | 740,000          |
| 9           | 21                         | 704,762          |
| 10          | 21                         | 704,762          |

Table S8. Flux analysis of four SSM filters with 10 cycles respectively.

| SSM | Area (ø 3.8 mm / 1 x 10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-----|-------------------------------|------------------|
| Cycle | Time (s)                     |                  |
| 1     | 23                            | 690,131          |
| 2     | 28                            | 566,893          |
| 3     | 25                            | 634,921          |
| 4     | 28                            | 566,893          |
| 5     | 32                            | 496,032          |
| 6     | 27                            | 587,889          |
| 7     | 34                            | 466,853          |
| 8     | 34                            | 466,853          |
| 9     | 35                            | 453,515          |
| 10    | 29                            | 544,529          |

| SSM | Area (ø 4 mm / 1 x 10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-----|-------------------------------|------------------|
| Cycle | Time (s)                     |                  |
| 1     | 16                            | 925,000          |
| 2     | 13                            | 1,138,462        |
| 3     | 21                            | 704,762          |
| 4     | 20                            | 740,000          |
| 5     | 21                            | 704,762          |
| 6     | 19                            | 778,947          |
| 7     | 23                            | 643,478          |
| 8     | 16                            | 925,000          |
| 9     | 20                            | 740,000          |
| 10    | 22                            | 672,727          |

| SSM | Area (ø 4 mm / 1 x 10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-----|-------------------------------|------------------|
| Cycle | Time (s)                     |                  |
| 1     | 14                            | 870,588          |
| 2     | 16                            | 925,000          |
| 3     | 18                            | 822,222          |
| 4     | 16                            | 925,000          |
| 5     | 19                            | 778,947          |
| 6     | 18                            | 822,222          |
| 7     | 23                            | 643,478          |
| 8     | 23                            | 643,478          |
| 9     | 23                            | 643,478          |
| 10    | 22                            | 672,727          |

| SSM | Area (ø 4 mm / 1 x 10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-----|-------------------------------|------------------|
| Cycle | Time (s)                     |                  |
| 1     | 20                            | 587,889          |
| 2     | 28                            | 566,893          |
| 3     | 31                            | 512,033          |
| 4     | 29                            | 547,345          |
| 5     | 32                            | 496,032          |
| 6     | 33                            | 481,000          |
| 7     | 33                            | 481,000          |
| 8     | 34                            | 466,853          |
| 9     | 34                            | 473,821          |
| 10    | 34                            | 473,821          |

| SSM | Area (ø 3.8 mm / 1 x 10⁻⁴ m²) | Flux (L m⁻² h⁻¹) |
|-----|-------------------------------|------------------|
| Cycle | Time (s)                     |                  |
| 1     | 37                            | 432,507          |
| 2     | 37                            | 424,412          |
| 3     | 36                            | 437,273          |
| 4     | 39                            | 404,408          |
| 5     | 29                            | 544,529          |
| 6     | 37                            | 429,000          |
| 7     | 35                            | 453,515          |
| 8     | 40                            | 396,825          |
| 9     | 35                            | 453,515          |
| 10    | 27                            | 593,162          |
Table S9. Flux analysis of four Au/SSM filters with 10 cycles respectively.

| Au/SSM | Area (ø 3 mm / \(7 \times 10^{-6}\) m\(^2\)) | Flux (L m\(^2\) h\(^{-1}\)) |
|--------|---------------------------------|-----------------|
| Cycle  | Time (s)                        |                 |
| 1      | 55                              | 463,034         |
| 2      | 48                              | 530,560         |
| 3      | 57                              | 446,788         |
| 4      | 47                              | 541,849         |
| 5      | 55                              | 463,034         |
| 6      | 47                              | 541,849         |
| 7      | 55                              | 463,034         |
| 8      | 55                              | 463,034         |
| 9      | 57                              | 446,788         |
| 10     | 52                              | 489,748         |

| Au/SSM | Area (ø 4 mm / \(1 \times 10^{-5}\) m\(^2\)) | Flux (L m\(^2\) h\(^{-1}\)) |
|--------|---------------------------------|-----------------|
| Cycle  | Time (s)                        |                 |
| 1      | 38                              | 378,947         |
| 2      | 34                              | 423,529         |
| 3      | 37                              | 389,189         |
| 4      | 30                              | 480,000         |
| 5      | 36                              | 400,000         |
| 6      | 33                              | 436,364         |
| 7      | 43                              | 334,884         |
| 8      | 46                              | 313,043         |
| 9      | 49                              | 293,878         |
| 10     | 48                              | 300,000         |

Statistics

Figure S13. Flux of MOF@Au@SSM, SSM, and Au@SSM. For each sample type 40 data points were collected and plotted for the respective mesh.
Figure S14. Separation efficiency for each tested pollutant plotted in chart diagrams. For each calculation 5 data points were collected and plotted as box-chart diagrams for the respective tested pollutant.

Figure S15. COD value for each tested pollutant plotted in chart diagrams. For each calculation 5 data points were collected and plotted as box-chart diagrams for the respective tested pollutant.
Stability tests of the MOF@Au@SSM

WCAs and OCAs of the stability tests

Table S10. Measured WCAs and OCAs for the MOF@Au@SSM after every 5th filtration cycle. The WCAs and OCAs were measured using dd water, while the filtration was conducted under the respective aqueous medium.

|       | Cycle | 0   | 5   | 10  | 15  | 20  | 25  |
|-------|-------|-----|-----|-----|-----|-----|-----|
| dd. Water | OCA (°) | 180 | 172 | 180 | 170 | 169 | 169 |
|       | WCA (°) | 0   | 0   | 0   | 0   | 0   | 0   |
| NaCl solution | OCA (°) | 172 | 180 | 176 | 178 | 180 | 170 |
|       | WCA (°) | 0   | 0   | 0   | 0   | 0   | 0   |
| HCl solution | OCA (°) | 176 | 172 | 180 | 164 | 160 | 163 |
|       | WCA (°) | 0   | 0   | 0   | 0   | 0   | 0   |
| NaOH solution | OCA (°) | 173 | 172 | 170 | 169 | 180 | 177 |
|       | WCA (°) | 0   | 0   | 0   | 0   | 0   | 0   |

Figure S16. A Stability test of the Co-CAT-1@Au@SSM filter. The figure depicts the development of the WCA and underwater OCA measured after every 5th cycle with 25 filtration cycles in total. For the stability test, n-hexane was mixed with the saltwater (3.5 wt% NaCl; blue), water of pH 6 (green), water of pH 8 (red) and water (black) as reference prior to filtration, respectively. B Durability of water activated filter measured using the breakthrough times of 150 mL of the respective oily liquids. C Exemplary depiction of a MOF filter resisting the gravimetric pressure of 150 mL colored (Sudan red) n-hexane.
ICP analysis for cobalt detection

Table S11. The ICP analysis of the filtrated water. ICP tests for the presence of cobalt ions were conducted after the filtering of every 5th filtration cycle. 500 mL dd water were filtered by each cycle.

| Sample No. | Conc (µg/ml) |
|------------|--------------|
| 1 cycle    | <LOD         |
| 5 cycle    | <LOD         |
| 10 cycle   | <LOD         |
| 15 cycle   | <LOD         |
| 20 cycle   | <LOD         |
| 25 cycle   | <LOD         |
| 30 cycle   | <LOD         |
| 35 cycle   | <LOD         |
| 40 cycle   | <LOD         |
| 45 cycle   | <LOD         |
| 50 cycle   | <LOD         |
| LOD(µg/ml) | 0.01         |
OCA and OCA records of the stability tests

Figure S17. Contact angle measurements of the MOF-modified mesh under different conditions. The OCAs and WCAs were measured after each filtration with the respective aqueous media. A. OCA measured during 25 filtration cycles in dd water as reference. B. OCA measured during 25 filtration cycles in NaCl solution. C. OCA measured during 25 filtration cycles in water of pH 6. D. OCA measured during 25 filtration cycles in water of pH 8. E. WCA measured during 25 filtration cycles in dd water as reference. F. WCA measured during 25 filtration cycles in NaCl solution. G. WCA measured during 25 filtration cycles in water of pH 6. H. WCA measured during 25 filtration cycles in water of pH 8. Dichloromethane was used as an organic solvent for testing the OCAs.
Water sorption

Electrostatic hydration stabilization calculation

Three-dimensional periodic AM1* semiempirical molecular-orbital (MO) geometry optimizations using the in-house version of EMPIRE and starting from the experimentally suggested unit cell without the crystal water were performed within the unrestricted Hartree-Fock(UHF) formalism. The screening radius for the periodic calculations was 40 Å. The formal high-spin multiplicity of 59 (18×3 unpaired electrons on Co plus 4 unpaired electrons on the HHTTP[-3] ligands of the covalently extended layers) for a C144H168O108Co18 lattice cell gave a -168 kcal mol⁻¹ more stable structure (Structure 1) than the formal low spin multiplicity of 23 (18+4+1; Structure 2). Details of the optimized structure are given below. Subsequently, the hydration of the pore in the optimized periodic structure was investigated using an extension of the reported self-consistent reaction field (SCRF) polarizable continuum model for periodic systems. These calculations gave an electrostatic stabilization energy of -50 kcal mol⁻¹ per lattice cell for the high spin structure. The hydration of the outer surface of the crystals was investigated using two-dimensional periodic calculations on a C144H164O104Co16 repeat unit that was constructed by cutting the three-dimensional periodic structure at the catechol ligands. A formal high spin multiplicity of 53 (16×3+4+1) resulted in a -73 kcal mol⁻¹ more stable structure (Structure 3) than a low spin multiplicity of 21 (16+4+1; Structure 4) and gave an electrostatic stabilization energy of -67 kcal mol⁻¹ for the repeat unit.

EMPIRE optimized geometries.

Structure 1:

*** Summary of AM1* Calculation ***

EMPIRE'20 (Revision 2815) ***

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Co-CAT-1-dry
Molecular Formula = C144H168O108Co18
Charge = 0

Figure S18. Water vapor adsorption isotherm of Co-CAT-1 bulk material at 25 °C.
### Final geometry obtained

| 438 Co-CAT-1-dry |  |  |
|------------------|------------------|------------------|
| Co               | 0.033844         | 11.347418        | 3.299212         | 0.103292 |
| Co               | 9.704528         | 5.817352         | 3.411283         | 0.450966 |
| Co               | 9.903823         | -5.291617        | 3.301178         | 0.435777 |
| Co               | -0.181467        | 11.183405        | 10.023389        | 0.390060 |
| Co               | 9.194404         | 5.285690         | 9.932990         | 0.450520 |
| Co               | 9.602225         | -5.782302        | 10.075956        | 0.275342 |
| C                | 14.081408        | -0.485580        | 3.299330         | -0.002385 |
| C                | 12.834827        | -1.204220        | 3.228129         | 0.039387 |
| O                | 19.553273        | 0.526984         | 5.214124         | -0.278963 |
| C                | 12.786779        | -2.630207        | 3.139584         | -0.159213 |
| H                | 11.728395        | -3.188514        | 3.036125         | 0.145026 |
| C                | 15.341239        | -1.154086        | 3.427093         | -0.159044 |
| C                | 15.366521        | -2.241076        | 3.576222         | 0.012027 |
| C                | 16.551420        | -0.457424        | 3.700048         | 0.015038 |
| O                | 17.806287        | -0.977697        | 3.464917         | -0.345756 |
| Co               | 12.992560        | -6.356737        | 6.102456         | 0.029585 |
| O                | 12.714485        | -6.774202        | 7.993165         | -0.253117 |
| C                | 13.623568        | -1.392422        | 6.585854         | -0.003548 |
| C                | 12.195917        | -1.409726        | 6.554031         | -0.030098 |
| O                | 13.447391        | -6.127897        | 4.204883         | -0.259216 |
| Co               | 11.667809        | -5.085934        | 6.569763         | -0.422401 |
| C                | 11.516938        | -2.655056        | 6.576466         | -0.195420 |
| H                | 10.417668        | -2.698139        | 6.607294         | 0.093409 |
| C                | 12.229981        | -3.846004        | 6.573356         | 0.013086 |
| O                | 14.247632        | -5.056513        | 6.500336         | -0.288082 |
| C                | 14.341134        | -2.617910        | 6.579520         | -0.161204 |
| H                | 15.438451        | -2.638440        | 6.571266         | 0.124515 |
| C                | 13.669822        | -3.833281        | 6.561555         | 0.256088 |
| O                | 11.986306        | -7.890891        | 5.273319         | -0.293729 |
| O                | 14.452795        | -7.712792        | 5.915071         | -0.252597 |
| H                | 0.561912         | 9.799979         | 8.129708         | 0.248904 |
| H                | -0.702607        | 10.606689        | 7.755004         | 0.216859 |
| H                | 0.250050         | 8.810745         | 6.404075         | 0.256088 |
| H                | 1.705451         | 8.316927         | 4.570107         | 0.255680 |
| H                | 7.714691         | 3.210044         | 3.882090         | 0.291227 |
| H                | 6.254029         | 2.675641         | 4.069685         | 0.248645 |
| H                | 1.140690         | 5.893028         | 6.038100         | 0.253215 |
| H                | -0.361422        | 5.943050         | 6.362733         | 0.219328 |
| H                | -1.211429        | 8.464389         | 7.829285         | 0.217485 |
| H                | -1.310829        | 8.518655         | 6.291823         | 0.220127 |
| O                | 1.599179         | 12.620901        | 3.372624         | -0.345081 |
| C                | 2.735634         | 12.010050        | 3.369848         | 0.195871 |
| C                | 12.826414        | 1.688812         | 3.290454         | -0.06602 |
| O                | 7.918566         | 6.408025         | 3.786616         | -0.489201 |
| O                | 14.076993        | 0.954061         | 3.234483         | 0.006379 |
| O                | 9.607212         | 5.392683         | 5.333185         | -0.269857 |
| C                | 15.31244         | 1.639194         | 3.082466         | -0.174925 |
| H                | 15.32640         | 2.723260         | 2.906722         | 0.126843 |
| H                | 12.813892        | 3.105616         | 3.438262         | -0.149909 |
| C                | 13.753051        | 3.653187         | 3.592327         | 0.138148 |
| C                | 11.614097        | 3.819209         | 3.387685         | 0.029726 |
| C                | 7.732638         | 7.740899         | 3.606449         | 0.035403 |
| C                | 11.445972        | 5.159871         | 3.536122         | -0.352146 |
| Co               | 18.264084        | 2.969773         | 6.567536         | 0.046507 |
| O                | 18.302192        | 3.047258         | 8.512775         | -0.279200 |
| C                | 13.606383        | 1.099476         | 6.618125         | -0.020201 |
| C                | 14.327607        | -0.136261        | 6.618479         | 0.001872 |
### Summary of AM1 Calculation

### EMPIRE'20 (Revision 2814)

**Single-point calculation**

- **Heat of formation**: \(-5933.812313\) kcal/mol
- **SCRF electrostatic energy**: \(-2.090059\) eV
- **Electronic energy**: \(-161420861.970292\) eV
- **Core-core repulsion**: \(161335218.119127\) eV
- **Electron affinity**: \(14.406861\) eV
- **Ionization potential**: \(19.287054\) eV
- **No. of filled alpha levels**: 788
- **No. of filled beta levels**: 766
- **Core Electronic energy**: \(-161335218.119127\) eV
- **SCRF electrostatic energy**: \(-5933.812313\) kcal/mol
- **SCF cycles**: 67
- **Computation time**: 1333.866 seconds

**Final geometry obtained**

| Co-CAT-1-dry | Co  | 0.066220  | 11.589711 | 3.596183 | 0.372665 |
| Co         | 9.431434 | 5.727526  | 3.263170 | 0.409654 |
| Co         | 9.590614 | -5.228556 | 3.282753 | 0.592919 |
| Co         | -0.255893 | 10.685520 | 9.934837 | 0.386281 |
| Co         | 9.463146 | 5.415351 | 3.910077 | 0.305314 |
| Co         | 9.266003 | -5.639052 | 9.976987 | 0.591562 |
| C          | 14.104213 | -0.344290 | 3.445775 | -0.009613 |
| C          | 12.864096 | -1.093382 | 3.777319 | 0.038958 |
| O          | 19.407756 | 0.560726 | 5.552721 | -0.259552 |
| C          | 12.816936 | -2.518979 | 3.427719 | -0.161855 |
| H          | 13.753397 | -3.090765 | 3.473910 | 0.133795 |
| C          | 15.361122 | -1.006915 | 3.621291 | -0.141570 |
| C          | 15.386428 | -2.088458 | 3.804337 | 0.126102 |
| C          | 16.568348 | -0.302869 | 3.553027 | -0.009296 |
| O          | 17.857512 | -0.754811 | 3.645117 | -0.361238 |
| Co         | 13.054145 | -6.237376 | 6.242489 | 0.193034 |
| O          | 12.700731 | -6.617743 | 8.190086 | -0.261566 |
| C          | 13.543100 | -1.302090 | 6.697423 | -0.037274 |
| C          | 12.119360 | -1.339132 | 6.592000 | -0.010645 |
| C          | 13.467744 | -6.073258 | 4.290572 | -0.255106 |
| O          | 11.698071 | -5.022550 | 6.688675 | -0.355568 |
| C          | 11.473926 | -2.600256 | 6.565877 | -0.170454 |
| C          | 10.384008 | -2.685139 | 6.465147 | 0.111066 |
| O          | 14.209975 | -3.771791 | 6.663149 | 0.015466 |
| O          | 14.209975 | -4.943568 | 7.004505 | -0.389966 |
| C          | 14.283358 | -2.505310 | 6.850721 | -0.200990 |
| C          | 15.367660 | -2.489037 | 7.014279 | 0.107246 |
| C          | 13.642084 | -3.730761 | 6.831539 | 0.027101 |
| O          | 12.079473 | -7.803665 | 5.310280 | -0.287118 |
| O          | 14.524341 | -7.689040 | 5.914767 | -0.304342 |
| H          | 0.157359 | 9.456472 | 8.000998 | 0.230377 |
| H          | -1.113941 | 10.310244 | 7.786192 | 0.208034 |
| H          | 0.421110 | 8.425462 | 4.256081 | 0.240256 |
| H          | 1.947410 | 8.290810 | 4.184241 | 0.241006 |
| H          | 7.898432 | 3.222191 | 3.815874 | 0.239530 |
| H          | 6.380154 | 2.870602 | 3.872907 | 0.228414 |
| H          | 1.345129 | 5.552902 | 5.556663 | 0.237759 |
| H          | -0.145024 | 5.776219 | 5.816720 | 0.225002 |
| H          | -1.081535 | 7.851786 | 7.439676 | 0.235198 |
| H          | -1.091589 | 8.557322 | 6.073166 | 0.208083 |
| O          | 1.529360 | 12.673900 | 4.047496 | -0.420260 |
| C          | 2.750092 | 12.130741 | 3.772163 | -0.003334 |
| C          | 12.827880 | 1.828657 | 3.340188 | -0.004074 |
| O          | 7.810410 | 6.434838 | 3.858504 | -0.007889 |
| C          | 14.086263 | 1.096172 | 3.328963 | 0.003223 |
| O          | 9.411578 | 5.425488 | 5.189910 | -0.260066 |
| C          | 15.323324 | 1.779573 | 3.142203 | -0.150556 |
| H          | 15.315623 | 2.851421 | 2.901213 | 0.137441 |
| C          | 12.746093 | 3.248260 | 3.513570 | -0.191110 |
*** Summary of AM1* Calculation ***
*** EMPIRE’20 (Revision 2815) ***

Co-CAT-1-2D-periodic
Molecular Formula = C144H164O104Co16
Charge = 0
Multiplicity = 53

<> Single-point calculation
<> SCF was achieved

Heat of formation = -5656.800850 kcal/mol
SCRF electrostatic energy = -2.935163 eV
Electronic energy = -26305817.209421 eV
Core-core repulsion = 26239947.191063 eV
No. of filled alpha levels = 780
No. of filled beta levels = 728
Ionization potential = 7.238188 eV
Electron affinity = 2.658942 eV
SCF calculations = 1
SCF cycles = 10
Computation time = 54.289 seconds

<> Final geometry obtained

428
Co-CAT-1-2D-periodic

Co  5.470944  3.375789  9.443178  0.327766  0.327766
Co  -5.486425  3.385161  9.353674  0.457625
Co   5.087495 10.011190  8.731059  0.356472
C    0.757413  3.347186 13.680624 -0.066452
C    1.441722  3.238758 12.415154 -0.169996
C   -2.855670  2.943420 13.351054 -0.130104
C    1.488990  3.601643 14.865421 -0.104428
H    3.408706  2.943420 13.351054  0.130104
C   -1.488990  3.601643 14.865421 -0.104428
C   -2.548227  3.890273 14.825679  0.124103
C    0.854260  3.542690 16.090660 -0.089790
Co  -1.576793  3.842701 17.242451 -0.328789
C    6.277909  6.179620 12.916069  0.029396
O   -6.754970  8.129720 12.552095 -0.254196
C    1.304420  6.674027 13.604575 -0.003668
C   -1.318075  6.574476 12.176752 -0.019999
O   -5.964429  4.161588 13.497782 -0.252742
O   -4.981333  6.705053 11.599696 -0.408345
C   -2.553435  6.601410 11.482441 -0.169736
H   -2.581913  6.560424 10.385918  0.099195
C   -3.750092  6.687170 12.176995  0.019858
C   -4.976663  6.769137 14.180111 -0.293904
C   -2.536203  6.756202 14.305081 -0.164979
H   -2.558470  6.798720 15.401176  0.132828
C   -3.744882  6.755276 13.613275 -0.006872
C   -7.774285  5.323853 12.022112 -0.291695
O   -7.601273  6.088978 14.600320 -0.247020
H   -8.725062  4.908916 16.634172  0.243436
H   -7.728733  4.631924  1.767419  0.253841
H    3.974387  4.071835  7.799472  0.295598
H    2.953048  3.995218  6.600842  0.244353
H    5.775994  6.292378  2.744563  0.251327
O    6.029318  7.110045 -0.539634  0.226983
H    8.639097  8.144884 -0.934642  0.227573
H    8.978850  6.654881 -0.845759  0.237890
O   12.178990  3.679661  1.687446 -0.392498
O   11.615826  3.616816  2.811309  0.257525
O    1.424731  3.243996  12.516635 -0.006474
O    6.183657  4.206591  7.952785 -0.400506
C    0.664316  3.235252 13.751802  0.020471
O    5.226376  5.340245  9.692322 -0.305180
C    1.257005  3.097842 15.014661 -0.235633
H    2.349605  2.916022 15.097360  0.120163
Structure 4:

*** Summary of AM1* Calculation ***
*** EMPIRE'20 (Revision 2815) ***

<><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><><>

Co-CAT-1-2D-periodic
Molecular Formula = C144H164O104Co16
Charge            = 0
Multiplicity      = 21

<>< Single-point calculation
<> SCF was achieved

Heat of formation           = -5595.049355 kcal/mol
SCRF electrostatic energy   = -3.483230 eV
Electronic energy           = -26303009.039759 eV
Core-core repulsion         = 26231864.742162 eV
No. of filled alpha levels  = 764
No. of filled beta  levels  = 744
Ionization potential        = 10.617502 eV
Electron affinity           = 5.924837 eV
SCF calculations            = 1
SCF cycles                  = 13
Computation time            = 80.393 seconds
<>

Final geometry obtained

428
Co-CAT-1-2D-periodic
Co  6.061471  3.376574  10.415304  0.564231
Co  17.097735  3.239354  9.061666  0.580207
Co  5.553090  10.000150  12.627631  0.356996
C  20.858944  3.162246  12.492315  0.185919
C  21.270613 -0.053403  14.967529  0.065225
O  20.470269 -0.335524  17.498503  0.355242
C  15.719400  6.367848  12.752478  0.16499
C  15.456816  8.356826  12.655480  0.284211
C  20.667643  3.272866  15.120481  0.131455
H  15.976825  3.83618  15.063533  0.118984
C  20.668920  6.614188  13.586021  0.020377
C  20.717511  6.578219  12.158111  0.002894
O  15.866644  4.369466  12.853177  0.266581
C  19.086965  6.773594  11.496950  0.358911
C  19.505857  6.588478  11.430332  0.157003
C  18.289885  6.683676  12.099391  0.004265
O  16.998551  6.923848  14.046965  0.360109
C  19.422791  6.689791  14.257391  0.176937
H  18.627111  6.735738  13.534441  0.004774
C  14.270048  5.856569  11.383301  0.306503
O  14.137502  5.920613  14.017851  0.310727
H  8.747102  4.825972  0.641772  0.261070
H  8.056284  4.780625  2.023146  0.277177
H  3.108035  3.862488  8.219450  0.288913
H  7.745758  3.681960  6.707060  0.258325
H  5.895573  6.014760  1.345862  0.250265
H  6.290464  5.842347  0.129159  0.238198
H  8.327233  7.330338  1.292252  0.241446
H  9.634356  6.815048  0.671415  0.233042
O  11.944916  3.365250  1.681061  0.669629
O  11.503989  3.382321  2.897531  0.168489
C  1.570820  3.291961  12.907525  0.298488
O  6.464855  3.586656  8.523542  0.456839
C  7.745758  3.189288  14.083904  0.003607
O  5.788482  5.408392  10.441119  0.323447
C  1.326628  3.090627  15.362644  0.257872
H  2.410288  2.962649  15.475949  0.113782
C  3.956967  3.541289  13.066280  0.141830
C  3.381127  3.773407  14.052787  0.055985
C  3.783904  3.533308  11.953825  0.055985
C  7.796026  3.619129  8.269027  0.005104
