Supplementary Information

Control of Structural Flexibility of Layered-Pillared Metal-Organic Frameworks Anchored at Surfaces

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1. Supplementary Methods

Materials. All reagents and solvents were purchased from commercial suppliers (Sigma Aldrich, TCI and Alfar Aesar) and used without further purification. Cu(NO₃)₂·3H₂O and Cu(OAc)₂·H₂O were used as metal precursors for powder synthesis and thin-film fabrication of the Cu-based layered-pillared metal—organic frameworks (MOFs), respectively. The alkoxy-functionalised linker, i.e. 2,5-diethoxy-1,4-benzenedicarboxylic acid (H₂DE-bdc) and 2,5-bis(2-methoxyethoxy)-1,4-benzenedicarboxylic acid (H₂BME-bdc), were prepared via Williamson ether synthesis from dimethyl 2,5-dihydroxy-1,4-benzenedicarboxylate according to published procedure.¹ 1,4-diazabicyclo[2.2.2]octane (dabco) was used as a pillared linker (see Supplementary Figure 1).

H₂DE-bdc; ¹H-NMR (200 MHz, DMSO-d6): δ 12.90 (s, 2H), 7.26 (s, 2H), 4.04 (d, 4H), 1.29 (t, 6H).

H₂BME-bdc; ¹H NMR (250 MHz, DMSO-d6): δ 7.30 (s, 1H), 4.12 (dd, J = 5.3, 3.9 Hz, 2H), 3.64 (dd, J = 5.3, 3.9 Hz, 2H), 3.31 (s, 3H).

Bulk powder MOF synthesis. Cu₂(DE-bdc)₂(dabco) powder (¹bulk) was prepared under solvothermal reaction condition, which was slightly modified from the previously reported procedure for the Zn²⁺ containing analogue.¹ Cu(NO₃)₂·3H₂O (241.6 mg, 1 mmol), H₂DE-bdc (254.2 mg, 1 mmol) and dabco (56.0 mg, 0.5 mmol) were suspended in DMF (15 ml) and sonicated until the precursors were fully dissolved. The solution was left at room temperature for 20 min and then a precipitate formed. This precipitate was removed by filtration prior to transferring the clear filtrate into a screw jar (25 ml), which was sealed and subsequently heated to 120 °C for 48 h. After cooling down to room temperature, the mother liquor was firstly decanted and then exchanged by fresh DMF, the mixture was stirred for 30 min and left to settle for 24 h. Afterwards, the DMF was exchanged by CHCl₃, the mixture was stirred for 30 min and left to settle for 24 h.
The solvent exchange procedure with CHCl₃ was repeated for 2 times prior to collecting 1\textbf{bulk} by filtration with a frit. The collected product was washed 3 more times with 10 ml CHCl₃. 1\textbf{bulk} was subsequently transferred to a Schlenk tube and activated overnight at 130 °C. Cu₂(BME-bdc)₂(dabco) powder (2\textbf{bulk}) was prepared using the same synthetic procedure as for preparing 1\textbf{bulk}, instead of H₂DE-bdc, H₂BME-bdc (314.3 mg, 1mmol) was used as a linker.

\textbf{Characterisations of MOF powders.} Crystallinity and phase purity of the compounds 1\textbf{bulk} and 2\textbf{bulk} was identified by powder X-ray diffraction (XRD, D8 Bruker-AXS advance instrument, flat mode, Debye-Scherrer geometry, slit width of 0.05°, Cu K\textsubscript{α} radiation, 2θ range from 5° to 50°, position sensitive detector, Ni filter and step size of 0.0141°). Infrared (IR) spectra were recorded on a Bruker Alpha-P FT-IR (ATR-Mode, 48 scans) located in a glovebox. Thermogravimetric analysis (TGs) were recorded on a Netzsch STA 409 PC TG-DSC apparatus (heating rate of 5 K min\textsuperscript{-1}, in a stream of N\textsubscript{2} gas with constant flow rate of 20 ml min\textsuperscript{-1}). Roughly 10 mg of samples were placed in a pre-weighted, clean aluminium oxide crucible. The TG curves were background-corrected by subtraction of a measurement conducted with an empty crucible under the same conditions.

\textbf{MOF thin-film fabrication.} Au-coated quartz crystal microbalance sensors (QCM, commercially available by Q-Sense, AT cut type, Au electrode, diameter 14 mm, thickness 0.3 mm and fundamental frequency ca. 4.95 MHz) were used as the substrates. Prior to the fabrication of MOF thin-films, the substrates were immersed in 20 \textmu M solution of 16-mercaptophexadecanoic acid (MHDA) in ethanol mixed with 5% v/v acetic acid for 24 h to generate the COOH terminated substrate. In order to generate the pyridyl terminated surface, 20 \textmu M solution of 4-(4-pyridyl)phenylmethylthiol (PMBT) in ethanol was used instead of MHDA. These substrates were subsequently used for the fabrication of MOF films. Thin-films of 1 and 2 (coined the terms as 1\textbf{tf} and 2\textbf{tf}; x = total deposition cycles, respectively) were fabricated by a stepwise liquid-phase epitaxial process (LPE, Supplementary Figure 2) at controlled temperature of 40 °C using an automated QCM instrument (Q-Sense E4 Auto) operated in the continuous flow mode with a constant flow rate of 100 \textmu L min\textsuperscript{-1} for a total of 40, 60, 80 and 120 deposition cycles (1\textbf{tf}₄₀, 1\textbf{tf}₆₀, 1\textbf{tf}₈₀ and 1\textbf{tf}₁₂₀, respectively). In each deposition cycle, the functionalized QCM substrate was alternatingly exposed to the precursor solutions as follows: Cu(OAc)₂·H₂O (0.5 mM in
ethanol) 10 min, ethanol (rinse) 5 min, the mixed organic linkers (H₂DE-bdc + dabco for 1tfₓ and H₂BME-bdc + dabco for 2tfₓ, 0.2 mM in ethanol) 10 min and finally ethanol 5 min. Note that, the QCM frequency change was monitored in-situ during the fabrication process. In addition, 1tf was fabricated on the —pyridyl terminated QCM substrate by LPE process for 60 cycles (named as 1tfₓ₆₀-py) in order to study the influence of crystallite orientation on the structural flexibility of the MOF thin-films. For comparison, the prototypic layered-pillared Cu₂(bdc)₂(dabco) (3) thin-film was prepared by LPE for 60 cycles using commercially available 1,4-benzenedicarboxylic acid (H₂bdc) as the carboxylate linker (named as 3tfₓ₆₀).

### Characterisation of MOF thin-films.

Surface morphology and surface coverage were investigated by a field emission scanning electron microscope (FE-SEM, ZEISS Gemini Sigma 300 VP). Cross-sectional SEM images were measured by a JEOL JSM-7500F operated in Gentle Beam mode without sputtering in order to determine the film thickness. Sorption properties of the MOF thin-films fabricated on QCM substrates were carried out on an environmental-controlled QCM (BEL-QCM-4 instrument, MicrotracBEL Corp.) at controlled temperature (25 °C) using methanol as probe molecule (the schematic setup is illustrated in Supplementary Figure 3). Prior to the sorption measurements, the films were activated in-situ within the BEL-QCM instrument by purging with dry He gas with a flow rate of 100 sccm for 2 h until the change of QCM frequency was stable within the range of ±5 Hz in 20 min. The mass of the MOF film was determined by conversion of the frequency difference between the MOF-deposited QCM substrate and the fundamental frequency of the SAM-functionalised QCM substrates, according to Sauerbrey’s equation.² Afterwards, methanol sorption isotherms at 25 °C were collected by varying P/P₀ of saturated methanol vapour in He gas flow from 0.0 to 95.0%. The adsorption amounts were calculated according to the Sauerbrey’s equation:

\[
\Delta F = -\frac{2F_0^2}{A\sqrt{\mu \cdot \rho}} \cdot \Delta M
\]  
\( F_0 \) : fundamental frequency, \( A \) : surface area of electrode, \( \mu \) : shear stress of quartz \((2.947 \times 10^{10} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2})\) and \( \rho \) : density of quartz \((2648 \text{ kg} \cdot \text{m}^{-3})\).

The adsorption amount at each P/P₀ \((\Delta M)\) on the MOF thin-films \((M_0)\) was derived as:

\[
\text{Adsorption amount (g/g): } \frac{\Delta M}{M_0} = \frac{F - F_s}{F_s - F_0}
\]  

² Sauerbrey’s equation.
**M₀**: initial weight of the MOF film sample, \( F \): measuring frequency at each relative vapour pressure and \( F_s \): frequency after final activation of the MOF film sample.

**In-situ synchrotron X-ray diffraction during methanol adsorption.** Crystalline phase and structural flexibility during methanol adsorption of the MOF bulk powders and thin-films were identified by grazing incidence XRD (GIXRD, Beamline BL9 of the DELTA synchrotron radiation source, Dortmund, Germany). An X-Ray energy of 15.0 keV corresponding to a wavelength of 0.827 Å was used. The angle of incidence was 0.6°. The diffraction images were converted to diffraction patterns utilizing the software package Fit2D. In order to investigate structural flexibility of the MOFs upon adsorption and desorption of polar guests (herein, methanol) at room temperature (25 °C), the sample stage was connected to a temperature-controlled graphite-dome (DHS 1100, Anton Paar). This sample stage was further connected with a custom-built He gas flow system, which could semi-quantitatively control the dosed amount of methanol vapour into the sample chamber (the schematic setup is illustrated in Supplementary Figure 4). The MOF sample was placed in the sample chamber and covered with the graphite dome. The temperature of the sample chamber was kept constant at 25 °C during the whole experiment. In-situ GIXRD patterns were recorded in different stages of the methanol sorption process as follows: 1) the as-synthesised, solvated stage (mimicked by dropping methanol onto the sample); 2) the activation process (by purging the sample with He gas); 3) the methanol adsorption with 4 different relative vapour pressures (P/P₀) of 10%, 20%, 50% and 80%; and 4) the desorption (by purging with He gas). To control the P/P₀, the pressure-controlled valves at the pure He gas line and the one that passed through the methanol vaporiser were adjusted to change the mixing ratio, while keeping the total pressure at the outlet constant.
2. Supplementary Figures

Supplementary Figure 1 | Chemical structure of metal and organic precursors used for preparation of the Cu-based layered-pillared MOFs.

a

Supplementary Figure 2 | Stepwise liquid-phase epitaxial growth of Cu$_2$(DE-bdc)$_2$(dabco) (1tf$_x$) thin-films. (a) The Au-coated QCM substrate was firstly functionalised with the SAM providing a surface terminated with a suitable functionality (either COOH or pyridyl). (b) In each LPE deposition cycle, the functionalized QCM substrate was alternatingly exposed to the precursor solutions as follow: Cu(OAc)$_2$ (10 min), ethanol (5 min), a mixture of H$_2$DE-bdc and dabco (10 min), and ethanol (5 min). The fabrication was operated in the continuous flow mode at a controlled temperature of 40 °C. Note that, H$_2$BME-bdc and H$_2$bdc were used instead of H$_2$DE-bdc for the LPE growths of 2tf$_x$ and 3tf$_x$, respectively.
Supplementary Figure 3 | Schematic experimental setup of an environmentally-controlled QCM used for organic vapour adsorption in MOF thin-films.

Supplementary Figure 4 | Schematic experimental setup of the in-situ GIXRD measurements during methanol vapour adsorption.
Supplementary Figure 5 | XRD patterns of as-synthesised (black) and activated (red) of 1bulk and 2bulk. (using Cu Kα radiation as an X-ray source)

Supplementary Figure 6 | Pawley refinements of GIXRD patterns of 1bulk in (a) MeOH solvated and (b) activated form. (using synchrotron X-ray wavelength of 0.827 Å)
Supplementary Figure 7 | Pawley refinements of GIXRD patterns of 2bulk in (a) MeOH solvated and (b) activated form. (using synchrotron X-ray wavelength of 0.827 Å)

Supplementary Table 1 | Summary of refined lattice parameters of 1bulk and 2bulk samples in MeOH-solvated and activated form based on Pawley refinement of synchrotron-based GIXRD data.

| Refined lattice parameters | 1bulk MeOH solvated | 1bulk activated | 2bulk MeOH solvated | 2bulk activated |
|----------------------------|---------------------|-----------------|---------------------|-----------------|
| Space group                | C 2/m               | C 2/m           | C 2/m               | C mmm           | P 21/m          |
| a (Å)                      | 15.779760           | 18.772260       | 15.67380            | 16.06264        | 18.82834        |
| b (Å)                      | 14.816613           | 9.972752        | 15.05001            | 14.36069        | 11.37029        |
| c (Å)                      | 9.568058            | 9.626891        | 9.525823            | 9.580806        | 9.468338        |
| α (°)                      | 90                  | 90              | 90                  | 90              | 90              |
| β (°)                      | 95.0695             | 93.6579         | 95.0979             | 90              | 91.2751         |
| γ (°)                      | 90                  | 90              | 90                  | 90              | 90              |
| Volume (Å³)                | 2228.286            | 1798.589        | 2238.166            | 2210.009        | 2026.515        |
| Notation                   | 1bulk, lp phase    | 1bulk, np phase | 2bulk, lp phase #   | 2bulk, np phase |

*Note: The 1bulk, lp phase appears as a minor phase in 1bulk activated form, which may occur due to the incomplete activation process of the MOF powder sample.
Supplementary Figure 8 | FT-IR spectra of activated 1bulk and 2bulk.

Supplementary Figure 9 | TG traces of activated 1bulk and 2bulk.
Supplementary Figure 10 | GIXRD profiles of 2\textsubscript{bulk} upon methanol sorption at 25 °C. (using synchrotron X-ray wavelength of 0.827 Å). Adsorption of 10% P/P\textsubscript{0} methanol initiates the framework breathing transition from the activated, narrow-pore (np) form to the solvated, large-pore (lp) form. 2\textsubscript{bulk} is fully converted to the solvated, lp form after adsorption of methanol from 20% P/P\textsubscript{0} and higher. Purging the 2\textsubscript{bulk} sample with He gas at 25 °C desorbs methanol out of the framework and shows the reversible structural transition of 2\textsubscript{bulk} back to the activated, np phase. Note that, the representative diffraction peaks of the lp and np phase are highlighted in yellow and green, respectively.
**Supplementary Figure 11** Changes in the QCM oscillator frequency (F) as a function of time at the early stage of the LPE growth of (a) 1tf40, (b) 1tf60, (c) 1tf80, and (d) 1tf120. Generally, the LPE growth of 1tfx shows saturation during each deposition step of the metal and the organic linkers, indicating a self-terminated growth of the layered-pillared MOF thin-films by the LPE process.
Supplementary Figure 12 | Crystallite size of MeOH-solvated 1tfx samples calculated from GIXRD patterns by using Scherrer Equation. (using Cu Kα radiation as an X-ray source). Prior to the GIXRD measurement, MeOH (1 drop) is added on the 1tfx films for preparing the solvated form. GIXRD measurement was measured shortly after adding MeOH to the thin-film sample using 2θ-scan in the range of 7° to 11°, which is covered the main diffraction peaks of the MOF 1.
Supplementary Figure 13 | Schematic representation of the possibilities for structural responsiveness upon methanol sorption process of the MOF 1. (a) 1tf₄₀ exhibits a restricted framework flexibility due to strong interactions of the MOF crystallites with the substrate surface leading to a high activation barrier for the lp-to-np transformation. Hence, only the lp form is observed, regardless of the sample treatment; (b) The larger crystallite-dimension films (1tf₆₀, 1tf₈₀, or 1tf₁₂₀) exhibit framework flexibility with some restrictions. Only the crystallite domains at the top, further away from the surface can undergo the transition between np and lp forms during methanol adsorption, while the bottom part which is strongly attached to the surface still remains in the lp form. MeOH of at least 20% P/P₀ is required to initiate the framework transformation; (c) 1bulk undergoes a breathing transformation upon methanol sorption already at 10% P/P₀; (d) If the obtained materials consisting of the low crystallite-dimension thin film mixed with the bulk powder on top of it, the bulk powder should undergo the breathing phenomenon by introduction of methanol also at low P/P₀ MeOH i.e. at least 10%. Moreover, all of the “loose” bulk crystals on top of the thin film would have been easily flushed away during the washing step with ethanol in the LPE process. Note that, the schematic representation shown herein is only a suggested structure based on lattice refinements and is not a depiction of the actual structure.
Supplementary Figure 14 | In-plane GIXRD profiles of the $1\text{tf}_x$ materials during in-situ methanol sorption at 25 °C. (a) $1\text{tf}_{40}$, (b) $1\text{tf}_{60}$, (c) $1\text{tf}_{80}$ and (d) $1\text{tf}_{120}$ were fabricated on the —COOH functionalised QCM substrates. The $1\text{tf}_x$ materials exhibit a significantly different structural flexibility upon methanol sorption than $1\text{bulk}$. A marked dependence of the structural flexibility on the total number of fabrication cycles is observed. Note that, the highlighted labels in yellow and green color represent the main diffraction peak belonging only to the $\text{lp}$ and $\text{np}$ phase, respectively.
Supplementary Figure 15 | Top-view SEM images of the thin films: (a) 1tf₄₀, (b) 1tf₆₀, (c) 1tf₈₀, and (d) 1tf₁₂₀ fabricated by LPE process on the —COOH functionalised QCM substrates. Scale bar at each panel represents a length of 5 µm.

Supplementary Figure 16 | High-magnification SEM images of the thin films: (a) 1tf₄₀, (b) 1tf₆₀, (c) 1tf₈₀, and (d) 1tf₁₂₀ fabricated by LPE process on the —COOH functionalised QCM substrates. Scale bar at each panel represents a length of 1 µm.
Supplementary Figure 17 | Particle size distribution measured from the SEM images of the thin films: (a) 1tf$_{40}$, (b) 1tf$_{60}$, (c) 1tf$_{80}$, and (d) 1tf$_{120}$ fabricated by LPE process on the —COOH functionalised QCM substrates.

Supplementary Figure 18 | Film thickness of (a) 1tf$_{40}$, (b) 1tf$_{60}$, (c) 1tf$_{80}$, and (d) 1tf$_{120}$ measured from the cross-sectional SEM images. The thin films were fabricated by LPE process on the —COOH functionalised QCM substrates.
Supplementary Table 2 | Comparison of crystallite size (calculated from GIXRD based on Scherrer Equation), average particle size (top-view SEM images), and film thickness (cross-sectional SEM images) of the 1tf\(_x\) samples.

| Thin-film samples | Crystallite size (nm) | Particle size (µm) | Film thickness (µm) |
|-------------------|-----------------------|-------------------|--------------------|
| 1tf\(_{40}\)      | 37.069                | 0.206             | 0.430              |
| 1tf\(_{60}\)      | 38.055                | 0.319             | 0.742              |
| 1tf\(_{80}\)      | 40.009                | 0.526             | 0.840              |
| 1tf\(_{120}\)     | 40.384                | 0.412             | 0.996              |

Supplementary Figure 19 | Methanol adsorption isotherms at 25 ºC of (a) 1tf\(_{40}\), (b) 1tf\(_{60}\), (c) 1tf\(_{80}\), and (d) 1tf\(_{120}\) measured by environmentally-controlled QCM. Filled and empty symbols depict adsorption and desorption. 1tf\(_{40}\) exhibits a single-step methanol adsorption, whereas 1tf\(_{60}\), 1tf\(_{80}\) and 1tf\(_{120}\) show two-steps methanol adsorption. A significant change in the slope of the methanol adsorption isotherm at P/P\(_0\) of 0.15 indicates the starting point of the framework transformation from np to lp. In correspondence with the in-situ GIXRD profiles during the methanol adsorption process, these methanol adsorption data reveal the dependency of the structural flexibility of 1tf\(_x\) on the total number of LPE fabrication cycles or in other word, the MOF crystallite dimension anchored at the substrate surface.
Supplementary Figure 20 | Out-of-plane and in-plane GIXRD profiles measured during methanol sorption at 25 °C of 1tf60-Py. 1tf60-Py was fabricated by LPE process on the —pyridyl functionalised QCM substrates for 60 cycles. According to the out-of-plane GIXRD patterns, the as-synthesised (or MeOH-solvated) 1tf60-Py exhibits a preferred growth along the dabco-related orientation of the framework, which can be assigned to the (001)-orientation by referring to the previously-reported Zn-based analogous structure. Hence, most of the crystal planes containing the Cu2(DE-bdc)2 grids are fixed parallelly to the substrate surface. During all methanol adsorption measurements, 1tf60-Py remains in the lp form, indicating a restriction of the framework flexibility compared to 1tf60 prepared with an identical number of LPE cycles. This observation shows a strong dependency of the guest-induced structural flexibility of the thin-films on the orientation of the crystallites anchored to the substrate surface.
Supplementary Figure 21 | Methanol sorption isotherm at 25 °C of 1tf60-Py. 1tf60-Py was fabricated by 60 LPE cycles on a —pyridyl functionalised QCM substrates. (a) 1tf60-Py shows preferred growth orientation along the (001) direction (referring to the previously-reported Zn-based analogous structure)\(^1\) and shows a tiny step at \(P/P_0\) of 0.15 in the methanol adsorption curve. However, there is no phase transition observed in the in-situ GIXRD measurement upon methanol adsorption (see also Supplementary Figure 15); (b) Comparison of the methanol adsorption profile of 1tf60-Py with 1tf40 and 1tf60. The adsorption isotherm of 1tf60-Py shows a shape closer to 1tf40 than 1tf60, underlining the rigid nature of the film further. In contrast, 1tf60 film shows a two-steps adsorption profile with a change starting at \(P/P_0\) of 0.15 due to the np-to-lp framework transformation of the crystallite domains at the upper layers of the thin film. In other words, the flexibility is inhibited if the growth direction of 1tf is changed from along the (110) direction to the (001) direction. Note that, the total specific adsorption capacity is similar for 1tf40, 1tf60 and 1tf60-Py when reaching high relative pressures, as all MOF crystallites are in the lp form at this stage, highlighting the similar quality and porosity of the obtained 1tfx samples.

Supplementary Figure 22 | Top-view SEM micrographs of 1tf60-Py. The film was fabricated by LPE process on the —pyridyl functionalised QCM substrates for 60 cycles. Scale bar at each panel represents a length of (a) 5 \(\mu\)m and (b) 1 \(\mu\)m.
Supplementary Figure 23 | Out-of-plane GI-XRD profiles of 2tfₓ upon in-situ methanol sorption at 25 °C. (a) 2tf₆₀, (b) 2tf₈₀, and (c) 1tf₁₂₀ were fabricated by the LPE process on —COOH functionalised QCM substrates. These 2tfₓ samples exhibit preferred growth along the (010) lattice plane (referring to the literature), similar to the 1tfₓ analogues. Moreover, 2tfₓ also reveals a different structural responsiveness upon methanol sorption from the 2bulk. The structural flexibility depends on the total number of LPE fabrication cycles as in the case of 1tfₓ films. However, the change in lattice parameters during the np-to-lp breathing transition of 2tfₓ is smaller than for 1tfₓ (see also the Pawley refinements of 1bulk and 2bulk in Supplementary Figure 6 and 7), highlighting the fine tuning of the guest-induced structural flexibility by the choices of alkoxy-functionalised pendent groups within the frameworks.
Supplementary Figure 24 | In-plane GI XRD profiles of 2tfₙ upon in-situ methanol sorption at 25 °C. (a) 2tf₆₀, (b) 2tf₈₀, and (c) 1tf₁₂₀ were fabricated by the LPE process on —COOH functionalised QCM substrates. 2tfₓ reveals a different structural responsiveness upon methanol sorption from the 2bulk, and shows a dependency of the structural flexibility on the total number of LPE fabrication cycles as similar as observed in the 1tfₓ films. Note that, the structural flexibility of the thin-films is less clearly observed in the in-plane direction in comparison with the out-of-plane direction due to the preferred crystallite orientation of the LPE-fabricated 2tfₓ thin-films along the growth direction (parallel to the substrate surface).
Cu₄(bdc)₂(dabco) thin-films (3tfₓ)

Supplementary Figure 25 | Out-of-plane GIXRD profiles of the 3tf₆₀ upon in-situ methanol sorption at 25 °C. The 3tf₆₀ was fabricated by the LPE process on the —COOH functionalised QCM substrates (60 cycles). No structural transition is observed during the methanol adsorption process and hence the MOF framework structure remains unchanged. This result emphasizes that the framework flexibility of the Cu-based layered-pillared MOFs thin films is initiated by the introduction of the alkoxy-functionalised pendent sidechains at the benzene-1,4-dicarboxylate linkers.
3. Supplementary References

1. Henke S., Schneemann A., Wütscher A. & Fischer R. A. Directing the breathing behavior of pillared-layered metal-organic frameworks via a systematic library of functionalized linkers bearing flexible substituents. *J. Am. Chem. Soc.* **134**, 9464-9474 (2012).

2. Sauerbrey G. Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung. *Z. Phys.* **155**, 206-222 (1959).

3. Krywka, C. *et al.* The small-angle and wide-angle X-Ray scattering set-up at beamline BL9 of DELTA. *J. Synchrotron Radiat.* **14**, 244-251 (2007).

4. Hammersley, A. P., Svensson, S. O., Hanfland, M., Fitch, A. N. & Häusermann D. Two-dimensional detector software: from real detector to idealized image or two-theta scan. *High Pressure Research* **14**, 235-248 (1996).

5. Schneemann, A. *et al.* Different breathing mechanisms in flexible pillared-layered metal–organic frameworks: impact of the metal center. *Chem. Mater.* **30**, 1667-1676 (2018).