Infrared Crystallography for Framework and Linker Orientation in Metal-Organic Framework Films

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Materials

H$_2$(1,4-NDC) (1,4-naphthalenedicarboxylic acid), H$_2$BDC (1,4-benzenedicarboxylic acid), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Tokyo Chemical Industry Co., Ltd. Ethanol (99 %), dimethylformamide (DMF, 99.8 %) and methanol were purchased from FUJIFILM Wako Pure Chemical Corporation. All reactants were used without any further purifications.

MOF film synthesis

MOF film synthesis from Cu(OH)$_2$ nanobelts. Oriented Cu(OH)$_2$ nanobelt films were deposited on Si ATR crystals with the long axis of the nanobelts perpendicular to the long side of the crystal as reported previously. Prior to MOF conversion, the film on the surface was reduced to a circle with 10 mm diameter. This served two purposes: (i) accurate $\phi$-scan measurements, and (ii) decreasing the amount of analyzed material in ATR spectroscopy, which was necessary to stay in the linear range of the detector.

CuBDC films were obtained from the conversion of Cu(OH)$_2$ films from a saturated solutions of H$_2$BDC in 5:2 ethanol:water at room temperature. After 10 min, the films were rinsed with ethanol and dried under a N$_2$ flow.

Cu(1,4-NDC):DABCO and Cu(BDC):DABCO films were synthesized by immersing Cu(OH)$_2$ films in 3 mL solvent at 70°C with following reaction times and linker:DABCO ratios:
| Linker:DABCO | solvent | reaction time |
|--------------|---------|---------------|
| Cu₂(1,4-NDC)₂DABCO with [001] OOP orientation | 4 mM:16 mM MeOH | 1 h |
| Cu₂(1,4-NDC)₂DABCO with [010] OOP orientation | 4 mM:512 mM MeOH/DMF = 50/50 | 2 h |
| (001) Cu₂(BDC)₂DABCO with [001] OOP orientation | 4 mM:16 mM MeOH | 30 min |
| Cu₂(BDC)₂DABCO with [010] OOP orientation | 4 mM:512 mM MeOH/DMF = 50/50 | 2 h |

After reaction, the films were rinsed with ethanol and dried under ethanol-rich atmosphere. This procedure prevented the film from delaminating from the Si substrate.

FigS. 1: Photograph of MOF films in circular shape on Si ATR crystals.

**MOF films by Layer-by-Layer Synthesis.**

The synthesis of Cu₂(1,4-NDC)₂DABCO and Cu₂(BDC)₂DABCO films by LbL method and the liquid handling setup was adapted from Ref. 3. A peristaltic pump (Ismatec Reglo) with 4 channels was connected with Tygon MHLL (Ismatec) typing with I.D. 0.76 mm and 1/16 ″ PTFE tubing with I.D. 0.75 mm (GL Sciences) and stainless steel needles. The Si ATR crystal was enclosed in 5 mL microwave vials (Biotage) and needles pierced the septum for liquid supply. A vent needle without any tubing connection was added.

FigS. 2: Photograph of automated liquid handling for the layer-by-layer synthesis.
SURMOFs were prepared at 50 °C. 1 mM copper acetate and 0.1 mM organic linker+0.1 mM DABCO dissolved in ethanol was applied alternatingly. All solutions were applied with 2 mL/min. One full reaction cycle was:

1. Soak in 5 mL copper acetate for 15 min
2. Remove copper acetate solution
3. Rinse with 5 mL absolute ethanol (no holding time)
4. Remove ethanol
5. Soak in Linker+DABCO solution for 15 min
6. Remove Linker+DABCO solution
7. Rinse with 5 mL absolute ethanol (no holding time)
8. Remove ethanol

After 3 or 10 cycles, respectively, the coated ATR crystal was removed from the reaction vial and rinsed with ethanol and dried under N₂ flow. The backside and the facets of the crystal were cleaned with cotton swabs with diluted HCl and ethanol.

CuBDC films were prepared by manual LbL deposition: ATR crystals were successively placed in ethanolic 1 mM copper acetate solution and ethanolic 0.1 mM BDC solution for 1 min each at room temperature. After soaking in each solution, films were rinsed with absolute ethanol and dried with N₂ flow. After 3 and 10 cycles, respectively, the backside and the facets of the crystal were cleaned with cotton swabs with diluted HCl and ethanol.

**Instrumentation**

**IR Spectroscopy.** IR spectra were recorded on a Jasco 4600 spectrometer. IR transmission spectra were recorded using a TGS detector with an aperture of 7.1 mm to allowing for broad illumination and hence averaging of the MOF film. 32 scans were averaged and a blank Si piece served as background spectrum. The polarization of light was adjusted by automated wire-grid polarizer equipment (Jasco). ATR spectra were acquired using a N₂-cooled MTC detector.

![Sample Compartment of Jasco FTIR spectrometer](image)

![Si ATR crystal](image)

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A 3D-printed ATR unit was adapted from ref. 4 using Autodesk Inventor for the blueprints and prepared with a Forge DLP optical 3D printer (Flashforge) using FH1000 resin (Hunter). ATR crystals (20 x 10 x 0.5 mm, 45°) cut from double side polished Si wafer and a depth of penetration \(d_p = 0.49 \mu m\) (\(\lambda = 1500 \text{ cm}^{-1}\), \(n(\text{Si}) = 3.42\) \(n(\text{MOF}) = 1.05\)) and an effective pathlength of \(d_{e\parallel} = 0.48 \mu m\) \(d_{e\perp} = 0.24 \mu m\), yielding at total effective pathlength
of $\frac{d_{\parallel}+d_{\perp}}{2} \cdot N = 7.1$ µm with $N=20$ were used. Si ATR crystals were reused and prior to film deposition, Si ATR crystals were cleaned with diluted HCl and EtOH.

X-ray diffraction was performed on a Smart Lab X-ray diffractometer (Rigaku Corporation, Japan) using CuKα radiation ($\lambda = 0.154$ nm). The degree of orientation was investigated by azimuthal angle dependence of intensity profiles ($\phi$ scan). In-plane parallel and in-plane-perpendicular patterns were recorded parallel and perpendicular to the long axis of the ATR crystal, respectively.

Scanning electron microscopy: Morphologies of the samples were observed using a field-emission scanning electron microscope (FE-SEM: S-4800, Hitachi High-Tech Corporation, Japan) (with an electrically conducting metal coating).

Profilometer: Film thickness was determined using a Surfcorder ET200 (Kosaka Laboratory Ltd).

**Structures of 2D and 3D MOF films**

![Visualization of the crystal structure of the MOF films used in this study.](image)

FigS. 4: Visualization of the crystal structure of the MOF films used in this study.
Characterization of Cu(OH)$_2$ nanobelts

FigS. 5: SEM images of (left) aligned Cu(OH)$_2$ nanobelts and (right) random oriented Cu(OH)$_2$ nanobelts.

Definition of $F_{IR}$ and $F_{XRD}$

| $F_{IR}$ | 1 | 0.5 | 0 |
|----------|---|----|---|
| $F_{XRD}$ | 1 | $\infty$ | 1 |

FigS. 6: Schematic representation of the extreme cases for the degree of in-plane orientation obtained from XRD and FTIR data.

Refractive Index and Porosity

Exact refractive index determination of the sample consisting of MOF, remaining Cu(OH)$_2$ precursor and air is an intricate task. Here, $n_2$ was estimated from MOF refractive indices reported in literature,$^5$ and the porosity of the MOF film defined as the displaced volume of a given solvent. For simplicity and as the majority of Cu(OH)$_2$ is consumed, we decided to neglect its contribution to the refractive index (compare spectra before and after reaction in FigS. 5). Spectra of MOF films were soaked in ethanol and compared with the absorbance of pure ethanol on bare Si ATR crystals. The ratio of these values, defined as porosity, was found to be $81\%$ and $91\%$ for CuBDC and Cu(1,4-NDC):DABCO films, respectively.

$$\text{porosity} = \frac{A_{2972\text{cm}^{-1}}(\text{EtOH, on film})}{A_{2972\text{cm}^{-1}}(\text{Pure EtOH})}$$ (S1)
The effective refractive index of the mixture $n_{2, \text{effective}}$ of MOF and air was then retrieved using the Bruggeman effective medium approximation,\(^5,7\) and reported refractive indices of pure materials ($n(\text{CuBDC}) = 1.4$ and $n(\text{Cu}_2(1,4-\text{NDC})_2\text{DABCO}) \approx n(\text{Cu}_3(\text{BTC})_2) = 1.5$) yielding $n_{2, \text{effective}}(\text{CuBDC}) = 1.07$ and $n_{2, \text{mix}}(\text{Cu}_2(1,4-\text{NDC})_2\text{DABCO}) = 1.04$. From these estimations, the fractions of the evanescent wave intensities were derived to be $E_x^2 = 0.30$, $E_y^2 = 0.33$, $E_z^2 = 0.37$ and were highlighted in Figure 4 in the manuscript. Note that due to the low slope of the field amplitude fractions in $x$- and $z$- directions, uncertainties arising from the assumptions to derive $n_{2, \text{mix}}$ only have minor effects on the field amplitude fractions. Based on this fact, we consider these calculations to be sufficiently accurate to study the orientation of MOF films using ATR spectroscopy.
Investigations in $x,y,z$ direction using ATR Spectroscopy

FigS. 9: Polarized FTIR ATR spectra of bulk water. The isotropy of the liquid yields a dichroic ratio of 2. Note that due to detector saturation in the region of the OH stretching vibration, this ratio is not achieved.

FigS. 10: XRD patterns of Cu$_2$(BDC)$_2$DABCO (A: [001]-preferred OOP orientation, C: [010] preferred OOP orientation and no in-plane orientation, E: [010] preferred OOP orientation with in-plane orientation) and Cu$_2$(1,4-NDC)$_2$DABCO (B: [001]-preferred OOP orientation, D: [010] preferred OOP orientation and no in-plane orientation, F: [010] preferred OOP orientation with in-plane orientation) films in different crystallographic orientations. IR spectra are given in Fig. 5 in the manuscript.
Dichroic ratio of MOF films with [010]-preferred OOP orientation

MOF films without in-plane orientation (only oriented in z-axis) are a special case as the transition dipole moment of the $v_{\text{symm}}(\text{COO}^-)$ band has to be divided into a fraction interacting in the x-y plane and a fraction interacting in z-direction. The ratio of these fractions is 1:1. This case has been discussed for liquid crystal systems and the dichroic ratio was determined using a ordering factor $S$, and the angle $\alpha$ between the transition dipole moment and the z-axis:\textsuperscript{8,9}

$$R = \frac{E_x^2}{E_y^2} + \frac{E_z^2}{E_y^2} \cdot \frac{1 + S(3 \cdot \cos(\alpha)^2 - 1)}{1 - \frac{3}{2}S(3 \cdot \cos(\alpha)^2 - 1)}$$ (S2)

In the case of MOF films with [010] preferred OOP orientation without in-plane orientation, no ordering in the plane is present, thus, $S=0$ and the dichroic ratios can be determined as follows:

- Fraction in x-y plane: $\alpha=90^\circ$, $S=0$
  $$R_{x,y} = 2$$
- Fraction in z-axis: $\alpha=0^\circ$, $S=0$
  $$R_z = 2$$

As both fractions contribute to the same extent to the dichroic ratio, the average of both fractions of 2 is visible in the IR spectra. For checking purposes, we considered equation S2 also for the aligned MOF cases: Here, $S=1$:

- Fraction in x-y plane: $\alpha=90^\circ$, $S=1$
  $$R_{x,y} = 1$$
- Fraction in z-axis: $\alpha=0^\circ$, $S=1$
  $$R_z \to \infty$$

The average of $R_{x,y}$ and $R_z$ still approaches $\infty$, meaning for perfectly aligned films, no absorbance is observed in the s-polarized spectrum for the $v_{\text{symm}}(\text{COO}^-)$ band.

**Determination of framework orientation for transmission spectra**

Due to the lack of information in z-direction, spectra of films highly oriented in this direction might be misinterpreted for films with low degree of orientation in transmission measurements (compare FigS.11). For (100) oriented 3D MOFs, the transition dipole of the $v_{\text{asymm}}(\text{COO}^-)$ band aligned in z-direction and for perfectly aligned films is not visible in transmission spectra. A comparably low absorbance of $v_{\text{asymm}}(\text{COO}^-)$ band compared to the $v_{\text{symm}}(\text{COO}^-)$ band is observed with no explainable polarization dependence (compare FigS. 9 in ESI). In the case of (001) orientation in transmission spectra, solely the $v_{\text{symm}}(\text{COO}^-)$ band can be interpreted for clarifying the in-plane orientation. Keeping this in mind, IR transmission spectroscopy allows for quick assessment of the crystallographic orientation.

![FigS. 11: IR spectra of Cu$_2$(1,4-NDC)$_2$DABCO film with [001] orientation recorded in transmission and ATR configuration.](image-url)
Characterization of SURMOFs

FigS. 12: XRD patterns of CuBDC, Cu$_2$(BDC)$_2$DABCO, and Cu$_2$(1,4-NDC)$_2$DABCO obtained by Layer-by-Layer synthesis. Corresponding IR spectra are given in Figure 7 in the manuscript. XRD patterns are in accordance with literature.\textsuperscript{10,11}

As no reflection were visible in the XRD pattern of the CuBDC film with 10 layers, a film with 50 layers was deposited on an ATR crystal. The corresponding XRD pattern is given in FigS. 12 and the polarization dependent IR spectra is given in FigS.13.

FigS. 13: IR spectra recorded in ATR configuration of CuBDC with 50 layers prepared by layer-by-layer method.
DFT calculations for aromatic linker orientation

Density functional theory calculations were performed with Gaussian 09 software. For all atoms B3LYP G++(d,p) basis set was employed.\(^\text{12}\)

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**FigS. 14:** Transition dipole moments of BDC calculated with DFT in Gaussian 09. Yellow arrow: sum transition dipole moment at certain vibration; blue arrows: transition dipole moments of each atom.

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**FigS. 15:** IR transmission spectra of Cu\(_2\)(BDC)\(_2\)DABCO with [010] preferred OOP orientation prepared from randomly aligned (left) and aligned (right) Cu(OH)\(_2\). Polarization dependence of the bands associated with the aromatic linker around 800 cm\(^{-1}\) is only found for the aligned MOF film.

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**FigS. 16:** Calculated XRD pattern for Cu\(_2\)(BDC)\(_2\)DABCO with different orientation of the aromatic linker.
FigS. 17: IR transmission spectra of Cu$_2$(1,4-NDC)$_2$DABCO with (001) orientation prepared from aligned and oriented Cu(OH)$_2$ nanobelts. Polarization dependence of the bands associated with the aromatic linker around 800 cm$^{-1}$ is only found for the aligned MOF film.
Structure of CuBDC
Crystal structure for copper(II) terephthalate coordination polymer was used from Deakin et al. 13

Fig S. 18: OOP and IP XRD patterns of CuBDC films obtained in this study compared with simulated 2D MOF pattern with Cu paddle wheel connectivity.

Fig S. 19: OOP and IP XRD patterns of CuBDC films obtained in this study compared with crystal structure of a coordination polymer with all BDC linkers aligned parallel.
**Film Thickness**

**Table S1: Thickness of all films prepared from Cu(OH)$_2$.**

| Film Composition | Thickness (nm) |
|------------------|----------------|
| CuBDC on ordered Cu(OH)$_2$ | 220 nm |
| CuBDC on random Cu(OH)$_2$ | 210 nm |
| Cu$_2$(1,4-NDC)$_2$DABCO from ordered Cu(OH)$_2$ with [001] orientation | 800 nm |
| Cu$_2$(1,4-NDC)$_2$DABCO from ordered Cu(OH)$_2$ with [010] orientation | 1200 nm |
| Cu$_2$(1,4-NDC)$_2$DABCO from random Cu(OH)$_2$ with [010] orientation | 1500 nm |
| Cu$_2$(1,4-NDC)$_2$DABCO from ordered Cu(OH)$_2$ with [001] orientation | 1100 nm |
| Cu$_2$(1,4-NDC)$_2$DABCO from ordered Cu(OH)$_2$ with [010] orientation | 1500 nm |
| Cu$_2$(1,4-NDC)$_2$DABCO from random Cu(OH)$_2$ with [010] orientation | 1600 nm |

The film thickness of 3D MOFs deposited by LbL were determined to be ≈ 50 nm (which is in line with literature, e.g. Ref. 14). From single crystal data, the layer thickness corresponds to 10.8 Å. Therefore, for a film with 40 deposited layers should theoretically correspond to 43.2 nm, which is in very good agreement with the found film thickness and we can rather assume a mono-layer deposition.

**Author Contributions**

B.B.: Investigation, Methodology, Curation, Writing – original draft; K.I.: Investigation; K. O.: Validation, Writing – review & editing, Resources; M.T.: Validation, Resources, Writing – review & editing, Funding acquisition

**References**

1. Falcaro, P. et al. Centimetre-scale micropore alignment in oriented polycrystalline metal-organic framework films via heteroepitaxial growth. Nat. Mater. **16**, 342–348 (2017).
2. Okada, K. et al. Controlling the alignment of 1D nanochannel arrays in oriented metal-organic framework films for host-guest materials design. Chem. Sci. **11**, 8005–8012 (2020).
3. McCarthy, B. D. et al. Facile Orientational Control of M2L2P SURMOFs on (100) Silicon Substrates and Growth Mechanism Insights for Defective MOFs. ACS Appl. Mater. Interfaces **11**, 38294–38302 (2019).
4. Baumgartner, B. et al. 3D Printing for Low-Cost and Versatile Attenuated Total Reflection Infrared Spectroscopy. Anal. Chem. **92**, 4736–4741 (2020).
5. Redel, E. et al. On the dielectric and optical properties of surface-anchored metal-organic frameworks: A study on epitaxially grown thin films. Appl. Phys. Lett. **103**, (2013).
6. Bruggeman, D. A. G. Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen. Ann. Phys. **416**, 636–664 (1935).
7. Baumgartner, B. et al. Pore Size-Dependent Structure of Confined Water in Mesoporous Silica Films from Water Adsorption/Desorption Using ATR–FTIR Spectroscopy. Langmuir **35**, 11986–11994 (2019).
8. Mirabella, F. M. Internal Reflection Spectroscopy: Theory and Applications. (Marcel Dekker, 1993).
9. Fringeli, U. P. In Situ Infrared Attenuated Total Reflection (IR ATR) spectroscopy: A Complementary Analytical Tool for Drug Desing and Drug Delivery. Chimia (Aarau). **46**, 200–214 (1992).
10. Liu, J. et al. A novel series of isoreticular metal organic frameworks: Realizing metastable structures by liquid phase epitaxy. Sci. Rep. **2**, 1–5 (2012).
11. Wang, Z. et al. Control of Water Content for Enhancing the Quality of Copper Paddle-Wheel-Based Metal-Organic Framework Thin Films Grown by Layer-by-Layer Liquid-Phase Epitaxy. Cryst. Growth Des. **18**, 7451–7459 (2018).
12. Frisch, M. J. et al. Gaussian 09. (2013).
13. Deakin, L. et al. Observation of ferromagnetic and antiferromagnetic coupling in 1-D and 2-D extended structures of copper(II) terephthalates. Inorg. Chem. **38**, 5072–5077 (1999).
14. Delen, G. et al. Mechanistic Insights into Growth of Surface-Mounted Metal-Organic Framework Films Resolved by Infrared (Nano-) Spectroscopy. Chem. - A Eur. J. **24**, 187–195 (2018).