Controlling the Alignment of 1D Nanochannel Arrays in Oriented Metal-Organic Framework Films for Host-Guest Materials Design

Kenji Okada, Miharu Nakanishi, Ken Ikigaki, Yasuaki Tokudome, paolo falcaro, Christian Doonan, masahide takahashi

Submitted date: 27/05/2020 • Posted date: 28/05/2020
Licence: CC BY-NC-ND 4.0
Citation information: Okada, Kenji; Nakanishi, Miharu; Ikigaki, Ken; Tokudome, Yasuaki; falcaro, paolo; Doonan, Christian; et al. (2020): Controlling the Alignment of 1D Nanochannel Arrays in Oriented Metal-Organic Framework Films for Host-Guest Materials Design. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.12369353.v1

Here, we successfully prepared macroscopically oriented films of Cu-based pillar-layered MOFs (Cu$_2$(Linker)$_2$DABCO) having regularly ordered 1D nanochannels. The direction of 1D nanochannels was controllable by optimizing the crystal growth process; 1D nanochannels either perpendicular or parallel to substrates, which offer molecular-scale pore arrays for a macroscopic alignment of functional guest molecules in the desired direction. We also showed the fabrication of oriented Cu$_2$(Linker)$_2$DABCO MOF patterns, where the direction of 1D nanochannels is controllable on individual locations on the same substrate. These Cu$_2$(Linker)$_2$DABCO MOF films and patterns with controlled orientation are importante steps towards the development of MOF film-based applications such as sensors and electrical/optical devices because functionalities derived from the accommodated guest species in their 1D nanochannels are optimized for the rational direction on the desired substrate for the device fabrication.

File list (2)

| File name | Size   | Download | View |
|-----------|--------|----------|------|
| 3D_MOF_ChemRxiv_manuscript.pdf | 1.09 MiB | download | view on ChemRxiv |
| 3D_MOF_ChemRxiv_SI.pdf | 1.91 MiB | download | view on ChemRxiv |
Controlling the alignment of 1D nanochannel arrays in oriented metal-organic framework films for host-guest materials design

Kenji Okada,a,b,c Miharu Nakanishi,d Ken Ikigaki,a Yasuaki Tokudome,a Paolo Falcaro,c Christian J. Doonand and Masahide Takahashi**

Controlling the direction of molecular-scale pores enables the accommodation of guest molecular-scale species with alignment in the desired direction, allowing for the development of high-performance mechanical, thermal, electronic, photonic and biomedical organic devices (host-guest approach). Regularly ordered 1D nanochannels of metal organic framework (MOF) have been demonstrated as superior hosts for aligning functional molecules and polymers. However, controlling orientation of MOF films with 1D nanochannels over commercially relevant scales remains a significant challenge. Here, we report the fabrication of macroscopically oriented films of Cu-based pillar-layered MOFs having regularly ordered 1D nanochannels. The direction of 1D nanochannels is controllable by optimizing the crystal growth process; 1D nanochannels either perpendicular or parallel to substrates, which offer molecular-scale pore arrays for a macroscopic alignment of functional guest molecules in the desired direction. Due to the fundamental interest and widespread technological importance of controlling alignment of functional molecules and polymers in a particular direction, the orientation-controllable Cu2(Linkert)2DABCO films will open up the possibility of realising the potential of MOFs in advanced technologies.

Introduction

The ability to precisely align functional small molecules and polymers on macroscopic scales is a key step in the development of high-performance mechanical, thermal, electronic, photonic and biomedical organic devices.1–5 Typically, a uniform external field along one direction, such as mechanical stress, surface rubbing treatment, and electromagnetic radiation is employed to achieve alignment.6 Although these existing methodologies have realised alignment over large areas, new approaches that use molecular-scale pores to confine guests with a precise spatial orientation is gathering interest as the regularly separated pore walls engender materials that show novel functionality.7–10

Metal–organic frameworks (MOFs), also called porous coordination polymers, are crystalline materials synthesized via a node-and-linker approach.11 The pore sizes and chemistry of MOFs can be tuned to enhance host-guest interactions that lead to precise orientation of molecules adsorbed within their pore network. A salient example is the so-called ‘crystalline sponge’ approach that facilitates the structural elucidation of guests by single-crystal X-ray.12 MOFs composed of 1D pore structures (nanochannels) are excellent candidates for aligning guest molecules, indeed incorporating molecules within their pore networks has been shown to enhance mechanical, electrical and optical properties of the frameworks.13–24 Examples of MOFs that possess 1D nanochannels, crystallographically along the c axis, include pillar-layered M2(Linkert)2DABCO MOFs (Linker: 1,4-benzenedicarboxylate (BDC), 1,4-naphthalenedicarboxylate (1,4-NDC), 2,6-naphthalenedicarboxylate (2,6-NDC), and 4,4’-biphenyldicarboxylate (BPDC), DABCO: 1,4-diazabicyclo[2.2.2]octane, M = Cu, Zn)) (Fig. 1a). The dimensions of the square shaped pores can be tuned by judicious selection

---

**a Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka, 599–8531, Japan. E-mail: okada@photomater.com (K.O.), masa@photomater.com (M.T.)

b JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332–0012, Japan.

c Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, Graz 8010, Austria.

d Department of Chemistry, The University of Adelaide, Adelaide, South Australia 5005, Australia.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x
of the organic linker, from 0.57 × 0.57 nm² (1,4-NDC) to 1.08 × 1.08 nm² (BPDC), facilitating the encapsulation of specific guest molecules and polymers. For instance, Distefano et al. reported that Cu₂(BDC)₂DABCO partially substituted with 2,5-divinyl-terephthalate could be employed to align vinyl polymers with mechanical and thermal properties, that cannot be achieved by conventional polymer synthesis. Furthermore, Smoukov and co-workers showed that aligned conductive polymers can be fabricated within the nanochannels of Zn₂(1,4-NDC)₂DABCO. Though these examples show potential for orienting guests within MOF pores, they were limited to discrete crystallites which typically range from the nanometres up to millimetres in size. Recently, we expanded the scope of this area by developing a novel heteroepitaxial growth method for fabricating MOF films with crystallographic orientation, along all three axes, at the centimetre-scale. In this case, Cu(OH)₂ nanobelts were used as a sacrificial template for the epitaxial growth of 2D Cu₂(BDC)₂ and 3D Cu₂(BDC)₂DABCO MOFs. Metal hydroxides are a versatile sacrificial support for the growth of aligned MOFs as they can be deposited on a variety of substrates such as silicon wafers, SiO₂ glasses, and flexible polymeric surfaces. Given that Cu(OH)₂ plays two roles as Cu⁺ ion source and a support for MOF growth, the MOF crystal growth process should be examined by considering both the dissolution of the Cu(OH)₂ nanobelts and their role in controlling the porous crystal orientation (heteroepitaxy). Detailed investigations of these synthetic conditions, in particular the solution acidity that plays a substantial role in the Cu(OH)₂ dissolution, would enable to fabricate MOF films with different orientation. Furthermore, this would help to expand the MOF crystal growth processes from Cu(OH)₂ to other sacrificial inorganic supports. In the present study, for the first time, we successfully prepared orientation-controlled films of Cu₂(1,4-NDC)₂DABCO MOFs by investigating the synthetic conditions on the MOF crystal growth processes. Notably, the orientation of crystallographic c axis of the Cu₂(1,4-NDC)₂DABCO, corresponding to the direction of 1D nanochannels, can be set to either aligned perpendicular or parallel to the substrate controlled via facile modification of the ratio of MOF precursor concentrations i.e. linker:DABCO(Fig. 1b). We also show the fabrication of oriented Cu₂(1,4-NDC)₂DABCO MOF patterns, where the direction of 1D nanochannels is controllable on individual locations on the same substrate. These Cu₂(1,4-NDC)₂DABCO MOF films and patterns with controlled orientation are important steps towards the development of MOF film-based applications such as sensors and electrical/optical devices because functionalities derived from the accommodated guest species in their 1D nanochannels are optimized for the rational direction on the desired substrate for the device fabrication.

Methods

Materials

H₂(1,4-NDC) (1,4-naphthalenedicarboxylic acid), H₂BPDC (4,4’-biphenylidicarboxylic acid), 1,4-diazabicyclo[2.2.2]octane (DABCO), and azobenzene were purchased from Tokyo Chemical Industry Co., LTD. H₂BDC (1,4-benzenedicarboxylic acid), H₂(2,6-NDC) (2,6-naphthalenedicarboxylic acid), methanol, DMF (N,N-dimethylformamide) (99.5%), and acetic acid (99.7%) were purchased from FUJIFILM Wako Pure Chemical Corporation. All reactants were used without any further purification.

Synthesis of Cu₂(1,4-NDC)₂DABCO oriented film under dissolution and precipitation favoured condition

Oriented Cu(OH)₂ nanobelt films on substrates were prepared according to the previously reported method. The conversation from Cu(OH)₂ nanobelt to Cu₂(1,4-NDC)₂DABCO was performed at 70 °C by immersing the copper hydroxide nanobelt in 10 mL of methanol solution containing 1,4-H₂NDC (16 mM) and DABCO (4 mM). After 1 hours, the product was removed from the solution and washed with ethanol, and then dried under air. The Cu₂(BDC)₂DABCO and Cu₂(2,6-NDC)₂DABCO oriented films were synthesized in a mixed solvent (5 mL of methanol and 5 mL of DMF) containing the corresponding organic linkers (32 mM) and DABCO (8 mM) at 70 °C for 30 min. The Cu₂(BPDC)₂DABCO oriented film was prepared in a mixed solvent (5 mL of methanol and 5 mL of DMF) containing the H₂BPDC (16 mM) and DABCO (8 mM) at 70 °C for 72 hours.

Synthesis of Cu₂(1,4-NDC)₂DABCO oriented film under epitaxial growth condition

The conversation from Cu(OH)₂ nanobelt to Cu₂(1,4-NDC)₂DABCO was performed at 70 °C by immersing the copper hydroxide nanobelt film in 10 mL of methanol solution containing 1,4-H₂NDC (16 mM) and DABCO (1024 mM). After 3 hours, the product was removed from the solution and washed with ethanol, and then dried under air. The synthesis of Cu₂(BDC)₂DABCO and Cu₂(2,6-NDC)₂DABCO were conducted at the different organic linkers and pillar concentrations; 4 mM of H₂BDC and 256 mM of DABCO for Cu₂(BDC)₂DABCO and 1 mM of 2,6-H₂NDC and 64 mM of DABCO for Cu₂(2,6-NDC)₂DABCO. The Cu₂(BPDC)₂DABCO oriented film was prepared in 10 mL of methanol solution containing H₂BPDC (4 mM), DABCO (256 mM), and acetic acid (35 mM) at 60 °C for 3 hours.

Introduction of azobenzene into the Cu₂(BPDC)₂DABCO oriented film

The pores of Cu₂(BPDC)₂DABCO oriented film was activated under high vacuum (~20 Pa) at 140 °C overnight. Then, the
activated film was filled with azobenzene into borosilicate glass tubes. The glass tube was then evacuated (~10 Pa) and flame sealed to give a closed system for a vacuum vapor-phase infiltration process. The sealed ampules were placed inside a convection oven at 140 °C overnight. Excess azobenzene on the film was then removed under vacuum (~10 Pa) at 140 °C for 30 min for obtaining the AZB-loaded Cu(OH)2 nanobelts. This infiltration process was performed according to the reported method.20

**Characterization**

Morphologies of samples were observed by a field-emission scanning electron microscope (FE-SEM: S-4800, Hitachi High-Tech Corporation, Japan) (with electrically conducting metal coating). The conversion kinetics were investigated by Fourier transform infrared spectroscopy (FT-IR: ALPHA FT-IR spectrometer, Bruker Optik GmbH, Germany). Crystal phases of the obtained samples were identified by X-ray diffraction (Smart Lab, Rigaku Corporation, Japan) using CuKα radiation (λ = 0.154 nm). The degree of orientation was investigated by azimuthal angle dependence of intensity profiles (φ scan). N2 adsorption–desorption isotherms at −196 °C were obtained on a volumetric gas adsorption apparatus (BELSORP-mini II, Bel Japan Inc., Japan). Prior to the measurements, sample powders were pre-treated at 140 °C under a vacuum condition overnight. Specific surface area was estimated by the Brunauer–Emmett–Teller (BET) method. Polarization dependence of absorbance for a Cu2(BPDC)2:DABCO oriented film before and after azobenzene infiltration was performed by UV-Vis spectrophotometer (V-670, JASCO Corporation, Japan) with an integrated sphere in a reflection mode by rotating the polarization of the excitation light every 15° (rotation intervals). The excitation light was perpendicularly irradiated to the film surface.

**Results and discussion**

Cu2(1,4-NDC):DABCO films were fabricated on aligned Cu(OH)2 nanobelts via an one-pot method in which Cu(OH)2 nanobelts oriented on Si substrates were reacted with a selected organic linker and DABCO in methanol at 70 °C. In this reaction Cu(OH)2 serves as a sacrificial substrate for MOF growth. We hypothesized that the MOF growth process could be controlled by simply changing the linker:DABCO molar ratio in the reaction solution where linker and DABCO act as acid and base, respectively (Fig. 1b). At high linker:DABCO ratios, continuous Cu(OH)2 dissolution and MOF precipitation were favoured as the excess carboxylic acid-functionalised linker lowers the solution pH; Cu(OH)2 is known to dissolve in acidic conditions. Conversely, at low linker:DABCO ratios epitaxial growth of Cu2(1,4-NDC):DABCO on Cu(OH)2 is favoured as, under basic conditions, Cu(OH)2 is stable allowing the organic linkers to interact with the ‘Cu–OH’ moieties on the nanobelt surface.27,32 Close matching between the Cu2(1,4-NDC):DABCO and Cu(OH)2 lattices is required for the epitaxial growth to occur. Indeed, the family of Cu2(1,4-NDC):DABCO MOFs where Linker = BDC, 1,4-NDC, 2,6-NDC, and BPDC possess lattice parameters (a and c axes) that closely match those (or a whole number multiple) of Cu(OH)2 (Fig. S1); BDC and 1,4-NDC: 2.85%, 2,6-NDC: 2.74%, BPDC: 4.56%.15,33 Thus, under low linker/DABCO ratios this series of MOFs should grow epitaxially on a Cu(OH)2 surface.

To further investigate the effect of linker:DABCO molar ratio on crystal growth processes, we synthesized Cu2(1,4-NDC):DABCO employing varied concentrations of 1,4-H2NDC and DABCO from oriented Cu(OH)2 nanobelt films (Fig. 2a,b). We examined the morphologies of the resulting films using Scanning electron microscopy (SEM). Close inspection of the images (Fig. 2 and see Fig. S2) clearly shows that the linker:DABCO molar ratio has a significant effect on the morphologies of the resultant MOF films. Under the linker-rich, dissolution and precipitation favoured, conditions the elongated brick shape MOF crystals were aligned perpendicularly to the substrate (Fig. 2c,d). However, when the concentration of DABCO is increased (to 1024 mM from 32 mM) the elongated brick shape MOFs tend to align parallel to the substrate (parallel to the long axis of original Cu(OH)2 nanobelts) affording a highly oriented film (Fig. 2e,f and see Fig. S2). The crystallographic structure and orientation of the Cu2(1,4-NDC):DABCO were confirmed by X-ray diffraction (XRD) experiments using previously reported protocols that allow crystallographic orientation along all three axes to be examined (Fig. 3).25,34,35 For the film synthesized under linker-rich conditions, the intense (00l) diffraction signal of Cu2(1,4-NDC):DABCO in out-of-plane XRD pattern indicates that the (00l) face of the MOF is parallel to the substrate (Fig. 3a and Fig. S3). Intense (h00) and (0k0) diffraction signals are similarly high. This indicates that the Cu2(1,4-NDC):DABCO crystallographically grows primarily along the (00l) plane.
detected in the two types of in-plane XRD measurements, suggesting a random crystal orientation in in-plane direction. The interpretation of these results is that there is no epitaxial relationship between Cu(OH)$_2$ and Cu$_2$(1,4-NDC)$_2$DABCO MOF under linker-rich conditions. Furthermore, these data confirm that the 1D nanochannels (corresponding to c axis of the MOF) of the film align perpendicularly to the substrate (Fig. 3c). For the film synthesized under conditions that favour epitaxial growth (higher concentrations of DABCO) (Fig. 3b), an intense (0k0) diffraction signal is observed at 2θ≈8.2° in the out-of-plane XRD measurement. In addition, the (h00) and (00l) diffraction signals detected in both of the in-plane XRD measurements, show a distinct angular dependence. These data indicate that the (h00) and (00l) faces of the MOF crystals are aligned, over the entire surface, orthogonally to each other and perpendicularly to the substrate. This alignment is further confirmed by azimuthal angle dependence of intensity profiles (φ scan) (Fig. S4). Collectively, the comprehensive XRD experiments confirm that the 1D nanochannels in the film synthesized under the epitaxial growth conditions are oriented parallel to the substrate (Fig. 3d). The direction of the 1D nanochannels (c axis of the MOF) is determined by the a axis of the original Cu(OH)$_2$, which is consistent with the lattice matching between Cu(OH)$_2$ and Cu$_2$(1,4-NDC)$_2$DABCO MOF. We note that all the XRD experiments were performed on MOF films grown on substrates exceeding 15 × 15 mm$^2$. This shows that the MOF crystals are oriented over the entire surface and that the direction of the 1D nanochannels is controllable, by simple optimization of the synthetic conditions. It should be mentioned that homogeneous films on macroscopic scales were obtained under the dissolution and precipitation favoured (16 mM of 1,4-H$_2$NDC and 4 mM of DABCO) and epitaxial growth (16 mM of 1,4-H$_2$NDC and 1024 mM of DABCO) conditions. Lastly the 1D nanochannels were examined by 77K N$_2$ gas adsorption analysis (Fig. S5). The isotherm is type I indicating the MOF is microporous. BET analysis of the data afforded a specific surface area of 984.29 m$^2$/g.

To gain insight into the evolution of the crystal growth processes we examined both MOF synthesis conditions via SEM; high linker concentration (dissolution and precipitation regime) and high DABCO concentration (epitaxial growth regime). Figure 4 shows that MOF synthesis under high linker concentrations shows that nanosheets are formed on the Cu(OH)$_2$ nanobelts after only of 3 min. These nanosheets are considered as two-dimensional square lattices composed of Cu paddle-wheel units linked by 1,4-NDC linkers (Fig. 4a and see the XRD experiments in Fig. S6). These 2D MOF sheets show no morphological correlation to the nanobelt, suggesting that there is no epitaxial interface between Cu(OH)$_2$ and the 2D MOF, further confirming the XRD results (Fig. 3). At longer reaction times, MOF growth perpendicular to the surface of substrate is observed. Presumably, at this stage DABCO is being accommodated in the structure as a pillaring agent (Fig. 4b,c) because the peak ascribed to (00l) diffraction signal in the out-of-plane XRD pattern got increase at increased reaction time.

**Fig. 3** XRD patterns and the corresponding schematics of the Cu$_2$(1,4-NDC)$_2$DABCO film synthesized at 16 mM of 1,4-H$_2$NDC and 4 mM of DABCO (a,c), and 16 mM of 1,4-H$_2$NDC and 1024 mM of DABCO (b,d). Three setups for the XRD investigations were used; out-of-plane (blue line), in-plane (red and black line, X-ray incident angle is parallel and perpendicular to longitudinal direction of nanobelts at φ = 0°).  

**Fig. 4** Evolution of the MOF growth under each condition. SEM images of Cu$_2$(1,4-NDC)$_2$DABCO films synthesized under the dissolution and precipitation favoured condition with varied reaction time (left); 3, 5, and 10 min. SEM images of Cu$_2$(1,4-NDC)$_2$DABCO films synthesized under the epitaxial growth condition with varied reaction time (right); 10, 15, and 30 min.
In contrast, under reaction conditions that favour the epitaxial growth, no MOF growth can be detected at the surface of Cu(OH)$_2$ nanobelts after a reaction time of 10 min (Fig. 4d). At 15 min, the growth of cubic Cu$_2$(1,4-NDC)$_2$DABCO crystals, parallel (or perpendicular) to the longitudinal axis of Cu(OH)$_2$ nanobelts are observed (Fig. 4e). This result shows that the MOF crystallites grow epitaxially on Cu(OH)$_2$ at the initial growth phase and continue to grow along the longitudinal axis of the Cu(OH)$_2$ nanobelt until they connect with neighbouring crystals (Fig. 4f). A time-course SEM investigation indicates that the MOF crystals form more rapidly under high linker concentrations that yield fast dissolution of the Cu(OH)$_2$ substrate (see Fig. S8).

Based on these XRD and SEM results, we propose the following MOF growth models under conditions of high linker and high DABCO concentrations (Fig. 5). Under the linker-rich, dissolution and precipitation favoured, conditions, rapid dissolution of Cu(OH)$_2$ occurs. The liberated Cu$^{2+}$ ions react with the organic linker at the surface of the Cu(OH)$_2$ nanobelts to form two dimensional MOFs, Cu$_2$(1,4-NDC)$_2$, with the basal face of the crystal parallel to the nanobelts. Indeed, rapid dissolution of Cu(OH)$_2$ was observed only under acidic conditions (see Fig. S9). This growth mechanism does not afford an epitaxial relationship between the Cu(OH)$_2$ and the 2D MOF. The nascent 2D MOF sheets then grow perpendicular to the surface of the nanobelts via the pillaring agent, DABCO. We note that the oriented growth along perpendicular to the substrate is often observed for the one-dimensional elongated inorganic nanomaterials synthesized under the similar crystal growth process. Under basic conditions, high DABCO concentration, the deprotonated organic linkers directly interact with the surface Cu-OH moieties of the Cu(OH)$_2$ nanobelts through hydrogen bonding interactions, facilitating the epitaxial MOF growth oriented along the in-plane direction. These proposed growth mechanisms are supported by the experiments where linker:DABCO molar ratio was fixed and the solution acidity was modified (see Figs. S10 and S11).

As anticipated acidifying the reaction solution induced the dissolution of Cu(OH)$_2$, resulting in the growth of MOF crystals perpendicular to the surface of the Cu(OH)$_2$ substrate. While, the addition of base suppressed the dissolution of Cu(OH)$_2$, leading to the epitaxial MOF growth. Furthermore, the MOF growth mechanism is independent of the carboxylate linker. Orientation-controlled Cu$_2$(Linker)$_2$DABCO films were successfully synthesized using a variety of linkers including BDC, 2,6-NDC, and BPDC (Fig. 6 and see XRD patterns in Fig. S12).
Although fabrication methods have been reported that offer control of the out-of-plane orientation of MOF films, those approaches require specific organic molecules as a buffer layer on a substrate to control the orientation, which limits the substrates that can be employed. Owing to the use of Cu(OH)$_2$ nanobelts for MOF growth, the precisely aligned MOF films can be achieved on any substrate including conductive indium tin oxide (ITO) coated glass substrates and polymeric curved or flexible surfaces (see Fig. S13). In addition to substrate versatility here we show that this approach allows for the fabrication of oriented MOF patterns, in which the direction of 1D nanochannels can be controlled for the desired directions on desired locations, because the direction of 1D nanochannels is determined by the $a$ axis of the pre-deposited Cu(OH)$_2$ (Fig. 7a-d). The oriented Cu$_2$(1,4-NDC)$_2$DABCO MOF patterns were fabricated from an oriented Cu(OH)$_2$ nanobelt film with patterns, in which $a$ axis of the pre-deposited Cu(OH)$_2$ nanobelt on the outside of a large triangle aligns in a diagonal line from upper left to lower right and that on the inside of a small triangle aligns in a vertical line (b). The white parts between large and small triangles indicate the bare silicon substrate. Polarization optical microscope images of the oriented MOF patterns at the same position of the optical microscope image (c) and that at the sample 135° rotating in a clockwise fashion (d). The white arrows indicate crossed-polarizer orientation. (e) 3D intensity plot of polarization-dependent UV/Vis difference absorption spectra before and after AZB inclusion into the Cu$_2$(BPDC)$_2$DABCO oriented film where 0° indicates a parallel light polarization to the direction of 1D nanochannels and 90° perpendicular light polarization to the direction of 1D nanochannels. (f) Repeated trans–cis isomerization of the accommodated AZB by UV and visible light irradiation, monitoring the absorbance at 450 nm.

![Image of SEM images of Cu$_2$(Linker)$_2$DABCO (Linker=BDC, 1,4-NDC, 2,6-NDC, and BPDC) oriented films under the dissolution and precipitation favoured condition and the epitaxial growth condition.](image)

![Image of optical microscope images of oriented MOF patterns (b) fabricated from an oriented Cu(OH)$_2$ nanobelt film with patterns (a), in which $a$ axis of the pre-deposited Cu(OH)$_2$ on the outside of large triangle aligns in a diagonal line from upper left to lower right and that in the inside of small triangle aligns in a vertical line (b). The white parts between large and small triangles indicate the bare silicon substrate. Polarization optical microscope images of the oriented MOF patterns at the same position of the optical microscope image (c) and that at the sample 135° rotating in a clockwise fashion (d). The white arrows indicate crossed-polarizer orientation. (e) 3D intensity plot of polarization-dependent UV/Vis difference absorption spectra before and after AZB inclusion into the Cu$_2$(BPDC)$_2$DABCO oriented film where 0° indicates a parallel light polarization to the direction of 1D nanochannels and 90° perpendicular light polarization to the direction of 1D nanochannels. (f) Repeated trans–cis isomerization of the accommodated AZB by UV and visible light irradiation, monitoring the absorbance at 450 nm.](image)
parallel to the 1D nanochannels in the Cu$_2$(BPDC)$_2$DABCO oriented film (at 0, 180 and 360°). Such a unique polarization-dependent absorption was not observed in the randomly oriented film (see Fig. S14). This result clearly confirms that the accommodated A2B2 aligns along the 1D nanochannels. It should be noted that the investigated area on the oriented film for the UV/Vis measurement exceeded 30 mm$^2$, proving macroscopic alignment of the guest molecules in the oriented MOF film. Moreover, it was found that A2B2 dyes in the Cu$_2$(BPDC)$_2$DABCO oriented film were capable of photo-induced isomerization from trans to cis form by UV light irradiation and vice versa by visible light irradiation (Fig. 7f), and interestingly the alignment of the accommodated A2B2 dyes maintained after repeated trans–cis isomerization (see Fig. S15). In summary these results demonstrated that the 1D nanochannel arrays in the Cu$_2$(BPDC)$_2$DABCO oriented film allow for macroscopic alignment of guest molecules.

Conclusions

In conclusion, we have investigated an effect of carboxylic acid-functionalised linker:DABCO ratio, that is related to the solution acidity, on the MOF crystal growth process in the synthesis system of pillar-layered Cu$_2$(Linker)$_2$:DABCO MOF from Cu(OH)$_2$. Under carboxylic acid-functionalised linker rich condition, the acidic reaction solution induced the dissolution of Cu(OH)$_2$, resulting in the growth of MOF crystals perpendicular to the surface of the Cu(OH)$_2$ substrate where the 1D nanochannels (corresponding to c axis of the MOF) align perpendicularly to the substrate. Conversely, at low linker:DABCO ratios epitaxial growth of Cu$_2$(Linker)$_2$:DABCO on Cu(OH)$_2$ was favoured, which resulted in the growth of elongated brick shape MOF crystals parallel to the substrate. Since the direction of the 1D nanochannels (c axis of the MOF) is determined by the a axis of the original Cu(OH)$_2$ at the epitaxial growth condition, precisely aligned MOF patterns where the direction of 1D nanochannels can be controlled for the desired directions on individual locations were also fabricated from an Cu(OH)$_2$ nanobelt films with patterns. We also showed how the 1D nanochannels can orient guest molecules over commercially relevant scales in the 1D nanochannel arrays. These Cu$_2$(Linker)$_2$:DABCO MOF films and patterns with controlled orientation will make a significant contribution to the development of MOF film-based applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The present work is partially supported by Grand-in-Aids from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), administrated by Japan Society for the Promotion of Science (JSPS), and also by JST, PRESTO Grant Number JPMJPR19I3, Japan. K.O. acknowledges financial support from Izumi Science and Technology Foundation. P.F. acknowledges the European Union’s Horizon 2020 Programme (FP/2014-2020)/ERC Grant Agreement no. 771834 – POPCRYSTAL.

Notes and references

1. J. Xu, H. C. Wu, C. Zhu, A. Ehrlich, L. Shaw, M. Nikolka, S. Wang, F. Molina-Lopez, X. Gu, S. Luo, D. Zhou, Y. H. Kim, G. J. N. Wang, K. Gu, V. R. Feig, S. Chen, Y. Kim, T. Katsumata, Y. Q. Zheng, H. Yan, J. W. Chung, J. Lopez, B. Murmann and Z. Bao, Nat. Mater., 2019, 18, 594–601.
2. J. Xu, S. Wang, G. J. N. Wang, C. Zhu, S. Luo, J. Lin, X. Gu, S. Chen, V. R. Feig, J. W. F. To, S. Rondeau-Gagné, J. Park, B. C. Schroeder, C. Lu, J. Y. Oh, Y. Wang, Y. H. Kim, H. Yan, R. Sinclair, D. Zhou, G. Xue, B. Murmann, C. Linder, W. Cai, J. B. H. Tok, J. W. Chung and Z. Bao, Science, 2017, 355, 59–64.
3. T. Yokota, T. Kajitani, R. Shidachi, T. Tokuhara, M. Kaltenbrunner, Y. Shoji, F. Ishiwari, T. Sekitani, T. Fukushima and T. Someya, Nat. Nanotechnol., 2018, 13, 139–144.
4. K. Hisano, M. Aizawa, M. Ishizu, Y. Kurata, W. Nakano, N. Akamatsu, J. C. Barrett and A. Shishido, Sci. Adv., 2017, 3, e1701610.
5. T. J. White and D. J. Broer, Nat. Mater., 2015, 14, 1087–1098.
6. S. Liu, W. M. Wang, A. L. Briseno, S. C. B. Mannsfeld and Z. Bao, Adv. Mater., 2009, 21, 1217–1232.
7. T. Wang, L. Gao, J. Hou, S. J. A. Herou, J. T. Griffiths, W. Li, J. Dong, S. Gao, M. M. Titirici, R. V. Kumar, A. K. Che etham, X. Bao, Q. Fu and S. K. Smoukov, Nat. Commun., 2019, 10, 1–9.
8. L. Salvati Manni, S. Assenza, M. Duss, J. J. V. Vallaorao, F. Juranyi, S. Jurt, O. Zerbe, E. M. Landau and R. Mezzenga, Nat. Nanotechnol., 2019, 14, 609–615.
9. B. Le Ouay and T. Uemura, Isr. J. Chem., 2018, 58, 995–1009.
10. Y. Wu, G. Cheng, K. Katsov, S. W. Sid, J. Wang, J. Tang, G. H. Fredrickson, M. Moskovits and G. D. Stucky, Nat. Mater., 2004, 3, 816–822.
11. H. Furukawa, K. E. Cordova, O. ’O’Keefe and O. M. Yaghi, Science, 2013, 341, 1230444–1230444.
12. Y. Inokuma, S. Yoshiohashi, A. Akiyoshi, T. Arai, Y. Hitota, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, Nature, 2013, 495, 461–466.
13. S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, Nat. Mater., 2009, 8, 831–836.
14. J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen and Q. G. Gyan, Nat. Commun., 2013, 4, 2719.
15. T. Uemura, N. Yanai, S. Watanabe, H. Tanaka, R. Numaguchi, M. T. Miyahara, Y. Ohta, M. Nagaoka and S. Kitagawa, Nat. Commun., 2010, 1, 83.
16. T. Wang, M. Farajollahi, S. Henke, T. Zhu, S. R. Bajpe, S. Sun, J. S. Barnard, J. S. Lee, J. D. W. Madden, A. K. Cheetham and S. K. Smoukov, Mater. Horizons, 2017, 4, 64–71.
17. T. Iizuka, K. Honjo and T. Uemura, Chem. Commun., 2019, 55, 691–694.
18. S. Henke, A. Schneemann and R. A. Fischer, Adv. Funct. Mater., 2013, 23, 5990–5996.
19. S. Henke, W. Li and A. K. Cheetham, Chem. Sci., 2014, 5, 2392–2397.
20. N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda and S. Kitagawa, J. Am. Chem. Soc., 2012, 134, 4501–4504.
21. G. Distefano, H. Suzuki, M. Tsujimoto, S. Isoda, S. Bracco, A. Comotti, P. Sozzani, T. Uemura and S. Kitagawa, Nat. Chem., 2013, 5, 335–41.
22. H. He, E. Ma, J. Yu, Y. Cui, Y. Lin, Y. Yang, X. Chen, B. Chen and G. Qian, Adv. Opt. Mater., 2017, 5, 1601040.
N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, Nat. Mater., 2011, 10, 787–793.

N. Yanai, T. Uemura, S. Horike, S. Shimomura and S. Kitagawa, Chem. Commun., 2011, 47, 1722–1724.

P. Falcaro, K. Okada, T. Haru, K. Ikigaki, Y. Tokudome, A. W. Thornton, A. J. Hill, T. Williams, C. Doonan and M. Takahashi, Nat. Mater., 2017, 16, 342–348.

K. Ikigaki, K. Okada, Y. Tokudome, T. Toyao, P. Falcaro, C. J. Doonan and M. Takahashi, Angew. Chem. Int. Ed., 2019, 58, 6886–6890.

K. Okada, R. Ricco, Y. Tokudome, M. J. Styles, A. J. Hill, M. Takahashi and P. Falcaro, Adv. Funct. Mater., 2014, 24, 1969–1977.

K. Okada, S. Sawai, K. Ikigaki, Y. Tokudome, P. Falcaro and M. Takahashi, CrystEngComm, 2017, 19, 4194–4200.

K. Ikigaki, K. Okada, Y. Tokudome and M. Takahashi, J. Sol-Gel Sci. Technol., 2019, 89, 128–134.

P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill and M. J. Styles, Chem. Soc. Rev., 2014, 43, 5513–5560.

J. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorf and R. Ameloot, Chem. Soc. Rev., 2017, 46, 3185–3241.

G. Majano and J. Pérez-Ramírez, Adv. Mater., 2013, 25, 1052–1057.

H. R. Oswald, A. Reller, H. W. Schmalle and E. Dubler, ActaCrystallogr. Sect. C Cryst. Struct. Commun., 1990, 46, 2279–2284.

T. Tsuruoka, S. Furukawa, Y. Takashima, K. Yoshida, S. Isoda and S. Kitagawa, Angew. Chem. Int. Ed., 2009, 48, 4739–4743.

S. Furukawa, K. Hirai, K. Nakagawa, Y. Takashima, R. Matsuda, T. Tsuruoka, M. Kondo, R. Haruki, D. Tanaka, H. Sakamoto, S. Shimomura, O. Sakata and S. Kitagawa, Angew. Chem. Int. Ed., 2009, 48, 1766–1770.

T. Tsuruoka, K. Mantani, A. Miyanaga, T. Matsuyama, T. Ohhashi, Y. Takashima and K. Akamatsu, Langmuir, 2016, 32, 6068–6073.

D. Liu and E. S. Aydil, J. Am. Chem. Soc., 2009, 131, 3985–3990.

J. Wang, P. Ma and L. Xiang, Mater. Lett., 2015, 131, 118–121.

T. Ohhashi, T. Tsuruoka, S. Fujimoto, Y. Takashima and K. Akamatsu, Cryst. Growth Des., 2018, 18, 402–408.

J. L. Zhuang, M. Kind, C. M. Grytz, F. Farr, M. Diefenbach, S. Tussupbayev, M. C. Holtthauser and A. Terfort, J. Am. Chem. Soc., 2015, 137, 8237–8243.

B. Liu, M. Tu and R. A. Fischer, Angew. Chem. Int. Ed., 2013, 52, 3402–3405.
Supplementary Information

Controlling the alignment of 1D nanochannel arrays in oriented metal-organic framework films for host-guest materials design

Kenji Okada, a, b∗ Miharu Nakanishi, a Ken Ikigaki, a Yasuaki Tokudome, a Paolo Falcaro, c Christian Doonan d and Masahide Takahashi a ∗

1 Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka, 599–8531, Japan. 2 JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan. 3 Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, Graz 8010, Austria. 4 Department of Chemistry, The University of Adelaide, Adelaide, South Australia 5005, Australia
Figure S1. Schematic illustration showing crystal lattices of Cu(OH)$_2$ and Cu$_2$(Linker)$_2$DABCO from $a$-$c$ and $c$-$a$ projections, respectively. This illustration corresponds to crystal structure on the surface of Cu(OH)$_2$ nanobelts. Cu positions are highlighted by different colors for both crystals (green for Cu(OH)$_2$ and blue for Cu$_2$(Linker)$_2$DABCO). These values indicate that Cu(OH)$_2$ and Cu$_2$(Linker)$_2$DABCO MOFs provide lattice matching conditions for heteroepitaxial growth; lattice mismatches of the Cu(OH)$_2$-Cu$_2$(BDC)$_2$DABCO (Cu$_2$(1,4-NDC)$_2$DABCO), Cu(OH)$_2$-Cu$_2$(2,6-NDC)$_2$DABCO, and Cu(OH)$_2$-Cu$_2$(BPDC)$_2$DABCO systems are 2.85%, 2.74%, and 4.56%, respectively, which were calculated between the lattice constant along the $a$ axis of Cu$_2$(Linker)$_2$DABCO and the lattice constant multiplied by 2 or 3 along the $c$ axis of Cu(OH)$_2$. 
**Figure S2.** SEM images of Cu$_2$(1,4-NDC)$_2$DABCO films synthesized at varied concentrations of 1,4-H$_2$NDC and DABCO; x-y indicate concentration of 1,4-H$_2$NDC and DABCO (mM), respectively.
Figure S3. XRD pattern of powdery Cu$_2$(1,4-NDC)$_2$DABCO. The powdery Cu$_2$(1,4-NDC)$_2$DABCO was synthesized by a homogeneous reaction of Cu(OH)$_2$ nanobelt dispersion with 1,4-H$_2$NDC and DABCO in methanol at 70 °C for 3 days. The morphology and XRD pattern of the Cu$_2$(1,4-NDC)$_2$DABCO are consistent with those reported so far (e.g., Angew. Chem. Int. Ed. 48, 4739–4743 (2009) and Angew. Chem. Int. Ed. 48, 1766–70 (2009)).

Figure S4. Azimuthal angle dependence of intensity profiles of the (100) and (001) reflection of Cu$_2$(1,4-NDC)$_2$DABCO synthesized at the epitaxial growth condition. X-ray incident angle is parallel to longitudinal direction (a axis) of Cu(OH)$_2$ nanobelts at φ = 0°.
Figure S5. N\textsubscript{2} gas isotherms of Cu\textsubscript{2}(1,4-NDC)\textsubscript{2}(DABCO) synthesized with epitaxial growth condition. The BET surface area is estimated as 984.29 m\textsuperscript{2}/g. The sample weight was corrected with the TG-DTA result, which indicates the weight fraction of Cu\textsubscript{2}(1,4-NDC)\textsubscript{2}(DABCO) in the MOF/Cu(OH)\textsubscript{2} composite as 88.9%.

Figure S6. Out-of-plane and in-plane XRD patterns of the Cu\textsubscript{2}(1,4-NDC)\textsubscript{2}DABCO film synthesized at 16 mM of 1,4-H\textsubscript{2}NDC and 4 mM of DABCO for 3 min. An intense diffraction signal is only observed at 2\theta \approx 8.2^\circ in the in-plane XRD measurement, suggesting the formation of two-dimensional square lattices composed of Cu paddle-wheel unites linked by 1,4-NDC linkers with the basal face of the crystal parallel to the substrate.
Figure S7. Out-of-plane XRD patterns of the Cu$_2$(1,4-NDC)$_2$DABCO film synthesized at 16 mM of 1,4-H$_2$NDC and 4 mM of DABCO for 3, 5, and 10 min.

Figure S8. FT-IR spectra of Cu$_2$(1,4-NDC)$_2$DABCO synthesized at the dissolution and precipitation favoured condition and epitaxial growth condition with varied reaction time. Under the dissolution and precipitation favoured condition, the formation of the MOF was detected at the reaction time of 10 min. While, under the epitaxial growth condition, the formation of the MOF was detected at the reaction time of 20 min.
Figure S9. Dissolution test of Cu(OH)$_2$ nanobelts (10 mg) in 10 mL of pure methanol and methanol containing acetic acid (50 mM, 28.6 μL of 99.7% acetic acid) or NH$_4$OH (50 mM, 30.4 μL of 28% NH$_3$ aq.). The appearance of blue color indicates the presence of Cu$^{2+}$ by the dissolution of Cu(OH)$_2$ nanobelts.
Figure S10. SEM images of Cu$_2$(1,4-NDC)$_2$DABCO films synthesized at fixed concentration of 1,4-H$_2$NDC and DABCO with an addition of acid (acetic acid) or base (NH$_4$OH). The reaction solution for the addition of acid was prepared by adding 5.7 μL (10 mM) or 28.6 μL (50 mM) of 99.7% acetic acid to 10 mL methanol containing 1,4-H$_2$NDC (4 mM) and DABCO (32 mM). The reaction solution for the addition of base was prepared by adding 9.1 μL (15 mM) or 15.2 μL (25 mM) of 28% NH$_3$ aqueous solution to 10 mL methanol containing 1,4-H$_2$NDC (16 mM) and DABCO (4 mM).
Figure S11. SEM images of Cu$_2$(1,4-NDC)$_2$DABCO films synthesized at fixed concentration of 1,4-H$_2$NDC (16 mM) and DABCO (32 mM) with addition of acid (acetic acid) or base (NH$_4$OH). The reaction solution for the addition of acid was prepared by adding 5.7 μL (10 mM) or 14.3 μL (25 mM) of 99.7% acetic acid to 10 mL methanol containing 1,4-H$_2$NDC and DABCO. The reaction solution for the addition of base was prepared by adding 6.1 μL (10 mM) or 15.2 μL (25 mM) of 28% NH$_3$ aqueous solution to 10 mL methanol containing 1,4-H$_2$NDC and DABCO. Elongated brick shape Cu$_2$(1,4-NDC)$_2$DABCO crystals both perpendicular and parallel to the substrate were observed without addition of acid and base. The MOF crystals perpendicular to the substrate dominated with the addition of acid. In contract, the addition of base resulted in the MOF crystals parallel to the substrate. This result clearly shows that the orientation of the MOF films is controllable by simply changing the solution acidity and basicity.
| Linker | Dissolution and precipitation favoured condition | Epitaxial growth condition |
|--------|-----------------------------------------------|----------------------------|
| ![BDC](image) | ![XRD](image) | ![XRD](image) |
| ![2,6-NDC](image) | ![XRD](image) | ![XRD](image) |
| ![BPDC](image) | ![XRD](image) | ![XRD](image) |

**Figure S12.** Summary of XRD patterns and azimuthal angle dependence of intensity profiles of Cu₂(Linker)₂DABCO (Linker=BDC, 2,6-NDC, and BPDC) film synthesized under dissolution and precipitation favoured condition and epitaxial growth condition. Three setups for the XRD investigations were used; out-of-plane (blue line), in-plane (red and black line, X-ray incident angle is parallel and perpendicular to longitudinal direction of nanobelts at $\phi = 0^\circ$). Azimuthal angle dependences of intensity profiles were collected for the (100) and (001) reflection of Cu₂(Linker)₂DABCO synthesized at epitaxial growth condition. X-ray incident angle is parallel to longitudinal direction ($a$ axis) of Cu(OH)₂ nanobelts at $\phi = 0^\circ$. The XRD investigations and azimuthal angle dependence of intensity profiles clearly show that dissolution and precipitation favoured condition resulted in the fabrication of Cu₂(Linker)₂DABCO films with the 1D nanochannels ($c$ axis) perpendicular to substrates, and Cu₂(Linker)₂DABCO films with the 1D nanochannels ($c$ axis) parallel to substrates in the same direction are fabricated under the epitaxial growth condition.
Figure S13. Large-scale fabrication (15 × 15 mm²) of aligned Cu₂(1,4-NDC)₂DABCO films on a conductive ITO substrate (a) and a poly ethylene terephthalate (PET) film (b).

Figure S14. Angular dependence of a polarizer in integrated absorption from 330 to 380 nm for a randomly oriented Cu₂(BPDC)₂DABCO film including AZB. The randomly oriented Cu₂(BPDC)₂DABCO film was synthesized from randomly oriented Cu(OH)₂ nanobelts film at the same condition for the Cu₂(BPDC)₂DABCO oriented film.
Figure S15. Angular dependence of a polarizer in integrated absorption from 330 to 380 nm for the AZB-included Cu$_2$(BPDC)$_2$DABCO oriented film after repeated trans–cis isomerization.
