Facile Orientational Control of $M_2L_2P$ SURMOFs on ⟨100⟩ Silicon Substrates and Growth Mechanism Insights for Defective MOFs

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Supporting Information

ABSTRACT: Layer-by-layer growth of Cu$_2$(bdc)$_2$(dabco) surface-mounted metal—organic frameworks (SURMOFs) was investigated on silicon wafers treated with different surface anchoring molecules. Well-oriented growth along the [100] and [001] directions could be achieved with simple protocols: growth along the [100] direction was achieved by substrate pretreatment with 80 °C piranha, while growth along the [001] direction was enabled by only rinsing silicon with absolute ethanol. Growth along the [001] direction produced more homogeneous SURMOF films. Optimization to enhance [001]-preferred orientation growth revealed that small changes in the SURMOF growth sequence (the number of rinse steps and linker concentrations) have a noticeable impact on the final film quality and the number of misaligned crystals. This new straightforward protocol was used to successfully grow other layer pillar-type SURMOFs, including the growth of Cu$_2$(bdc)$_2$(bipy) with simultaneous suppression of framework interpenetration.

KEYWORDS: MOFs, SURMOFs, silicon, methodology, surface anchoring molecules, silatranes

INTRODUCTION

Metal—organic frameworks (MOFs) have long been investigated for their potential to combine the best aspects of molecular chemistry with the practical advantages of materials science, especially when considering industrial applications. Driven by the accelerating climate crisis, our laboratory and others have strong interest in constructing MOFs that can facilitate the renewable conversion of energy-poor feedstocks into energy-rich fuels, such as by the hydrogen evolution reaction.

One promising route is installation of well-understood discrete molecular catalysts with high turnover frequencies into solid-state MOF lattices in an effort to improve turnover numbers. A current hypothesis is that common deactivation pathways—especially bimolecular ones—can be inhibited by site-isolating molecular active sites. This approach is slightly analogous to how enzymatic active sites are protected by virtue of being located inside a protein pocket with a carefully tuned environment of specific residues. In recent years, we and others have taken the approach of incorporating fuel-forming molecular catalysts into MOFs and driving catalysis either photochemically or electrochemically. Both approaches have long-term merit (e.g., photochemically driven hydrogen evolution using solid-state particle suspensions may be scalable), so we are currently working on the concept of using renewable produced electricity to power electrolytic fuel synthesis. Toward this end, we and others have developed redox-active MOF electrodes, which in some cases can also drive productive fuel-forming catalysis.

Despite the success of these initial efforts, fundamental questions remain, particularly with regard to the interplay between charge/counterion transport (diffusion and mass transport questions), catalyst kinetics (turnover frequency), and long-term stability. These parameters are expected to have a strong dependence on film thickness—especially regarding the relationship between catalytic turnover with the diffusion of charge, counterions, and substrate. However, the standard means for producing electrocatalytically active MOFs remains direct solvothermal growth onto electrode surfaces or electrophoretic deposition. These methods usually yield relatively thick (>1 μm) films and can result in uncontrolled crystal orientations. More concerning is the possibility that for thick, randomly oriented MOF crystals interfaced with electrodes, good redox connection with all parts of the MOF may be poor and much of the MOF may not be electrochemically addressable and ultimately not catalytically active. To understand the interplay between electrochemical activity and film thickness, further exploration of controlled growth at electrochemical surfaces is needed.

To this end, we are actively seeking to leverage the rich field of surface-mounted MOFs (SURMOFs) to produce well-defined, electrode-attached, redox-active MOFs. SURMOFs grown in an epitaxial fashion were first reported in 2007 by Wöll and co-workers. The fundamental SURMOF principle of alternatively exposing a substrate to dilute solutions of metal-containing secondary building units (SBUs) and then linkers to grow highly oriented MOFs essentially layer-by-layer (LbL) on substrates has had great success.

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MOFs,\textsuperscript{28} heteroepitaxial stacking of different MOFs,\textsuperscript{29} suppression of interpenetration,\textsuperscript{30} long-range energy transport,\textsuperscript{31} thin-film structural flexibility,\textsuperscript{32} and other beneficial features\textsuperscript{33–35} have been demonstrated using the SURMOF approach.

To date, however, few reports exist using SURMOFs for electrochemical, photoelectrochemical, or electrocatalytic studies,\textsuperscript{17,36,37} and the vast majority of SURMOFs prepared epitaxially are grown on gold substrates coated with organic thiol self-assembled monolayers (SAMs).\textsuperscript{38,39} Although thiol SAMs on Au provide excellent control, large-scale applications such as solar fuel production will require SURMOFs to be based on earth-abundant components. Additionally, tantalizing opportunities exist for interfacing SURMOFs with photoactive materials for light harvesting. An alternative substrate that meets these criteria is silicon, which is already widely used in solar energy applications, information technology, and microelectronics. In the solar fuel community, molecular catalysts have been successfully immobilized onto silicon to drive fuel-forming reactions using photo-generated charges.\textsuperscript{40}

As our initial effort into this field, we sought to develop the methodology for growing layer pillar-type MOFs\textsuperscript{43,44} of the general formula $M_2L_2P$ on silicon substrates ($M$ = metal ion, $L$ = layer linker, and $P$ = pillar linker). Given the demonstrated utility of using TiO$_2$ as a surface corrosion-protecting layer for silicon,\textsuperscript{45,46} as a substrate for catalyst materials,\textsuperscript{47,48} and to limit back electron transfer in devices,\textsuperscript{49} we also targeted $M_2L_2P$ SURMOFs on TiO$_2$-coated silicon. Specifically, we began our investigations with Cu$_2$(bdc)$_2$(dabco) as a model system (Figure 1, where bdc = 1,4-benzenedicarboxylate and dabco = 1,4-diazabicyclo[2.2.2]octane). Cu$_2$(bdc)$_2$(dabco) and analogous layer pillar SURMOFs have been well studied, though almost entirely using gold substrates coated with SAMs terminated with functional groups to initiate growth.\textsuperscript{29,30,50,51} SAMs terminated with pyridyl and carboxylic acid functionalities have been used to align the first layer of SURMOFs, resulting in predominantly $[100]$- or $[001]$-oriented $M_2L_2P$ SURMOFs, respectively (see Figure 1 for crystallographic axes).\textsuperscript{50,52} We anticipate that the fundamental insights learned here will enable us and others to more rationally develop functional (photo)electrochemical $M_2L_2P$ SURMOFs on silicon.

![Figure 1. Structure and principal crystallographic axes of Cu$_2$(bdc)$_2$(dabco), the M$_2$L$_2$P-type MOF investigated here. Portions of the structure and hydrogen atoms are omitted for clarity.](image)

**RESULTS AND DISCUSSION**

Multiple methods exist for growing SURMOFs in an epitaxial fashion, including manual immersions, pump systems, dipping robots, and spraying. We are interested in approaching “true” LbL programming of an SURMOF content, so we utilized an automated pump system which exposes the substrate to solutions containing either the metal salt or a linker in an alternating fashion, with the possibility for rinse steps in between. Apart from commercial automated quartz crystal microbalance flow systems,\textsuperscript{32,33,34} custom-built macroscale pump systems have been used.\textsuperscript{55–57} In this paper, we detail the construction and programming of such an automated pump system for SURMOF preparations (see the Supporting Information).

As a starting point, we attempted growth of Cu$_2$(bdc)$_2$(dabco) using the protocol reported for the structurally analogous chiral Cu$_2$(F$_4$–L–camphoric acid)$_2$(dabco) SURMOF on quartz,\textsuperscript{58} rationalizing that the SiO$_2$ oxide layer should mimic the SiO$_2$ quartz surface. Consequently, a $[100]$-sided polished silicon wafer and a quartz slide (in comparison with the prior study\textsuperscript{58}) were cleaned in 80 °C piranha (3:1 v/v concentrated H$_2$SO$_4$ to 30% aqueous H$_2$O$_2$), washed extensively with water, and air-dried. These substrates were then immediately transferred to the automated pump system substrate container (preheated to 50 °C) and soaked for 15 min in 1 mM copper acetate ethanol solution, soaked twice with ethanol (0.5 and 4.5 min, respectively), soaked for 30 min in an ethanolic solution of 0.2 mM H$_2$bd and 0.2 mM dabco, and soaked twice with ethanol again (0.5 and 4.5 min, respectively), before repeating the cycle.

After 40 cycles, examination by out-of-plane grazing incidence X-ray diffraction (GIXRD) showed that Cu$_2$(bdc)$_2$(dabco) had indeed formed on both the $[100]$ silicon wafer and the quartz slide compared to the simulated pattern for Cu$_2$(F$_4$–bd)(dabco)\textsuperscript{59} (Figure S4). On quartz, a strong preferred orientation along the $[001]$ direction was observed, as evidenced by the suppression of the $[100]$ peak. This is consistent with the prior report for Cu$_2$(F$_4$–bd)(dabco) grown on piranha-treated quartz, where growth in $[001]$ direction was observed and rationalized by the high density of $–\text{OH}$ groups induced by piranha treatment to favor the substitution at the apical position of the copper paddlewheel SBUs.\textsuperscript{58}

On piranha-treated silicon, however, out-of-plane XRD revealed a strong preferred orientation along the $[100]$ direction (Figure S4). Scanning electron microscopy (SEM) analysis revealed that this SURMOF was not a homogeneous thin film but rather isolated rods and plates with overall very poor surface coverage (Figure S10). Practical application of SURMOFs will likely require higher surface coverage, so we next sought different growth conditions. We were intrigued by the report that while $[100]$-oriented Cu$_2$(F$_4$bd)$_2$(dabco) (F$_4$bd = tetrafluorobenzene-1,4-dicarboxylate) SURMOF also grew as isolated rods/plates with poor surface coverage, the $[001]$-oriented version formed significantly smoother homogeneous films on SAM-coated gold surfaces.\textsuperscript{58} Consequently, we sought to modify the initial silicon surface treatment to achieve $[001]$-oriented Cu$_2$(bdc)$_2$(dabco) and so hopefully more homogeneous films.

Despite the rich literature for using SAMs to control SURMOF orientation, the vast majority of reports are on gold
substrates coated with thiol SAMs presenting pyridine, carboxylate, or hydroxyl headgroups to template subsequent SURMOF growth.\(^5\) Therefore, we initially turned to alternative surface anchoring molecules more appropriate for silicon in an attempt to form SAMs, which would present a nitrogen base to the solution and so hopefully template growth of Cu\(_2\)(bdc)\(_2\)(dabco) along the [001] direction. Few reports of SAM-modified silicon as substrates for SURMOF growth exist to date;\(^{31,57,60}\) perhaps the clearest example is that the growth of a porphyrin-containing SURMOF on silicon required use of a silane SAM with a carboxylic acid headgroup.\(^{31}\)

Three surface anchoring molecules were screened (Scheme 1), containing either carboxylic acid or silatrane surface anchors for binding to the silicon surface and either pyridine or amine headgroups to template [001] SURMOF growth.\(^6\) The caged structure of the silatrane is known to deprotect upon surface binding to form siloxane surface bonds, which have excellent aqueous and electrochemical stability.\(^{62,63}\) In general, after surface sensitization, all SURMOF preparation attempts were made at 50 °C as higher temperatures favor substitution at the apical position of copper paddlewheel clusters,\(^{62}\) and the same pump sequence described above was utilized. The silicon cleaning method and sensitization method varied (full details are given in the Supporting Information), and out-of-plane GIXRD utilized to determine whether growth had proceeded in the desired [001] direction.

As depicted in Figure 2, the majority of tested surface treatments resulted in either Cu\(_2\)(bdc)\(_2\)(dabco) growing in both the [100] and [001] orientations or less growth at all. For room-temperature piranha-treated silicon, both iNA and sil2 increased the fraction of [001]-oriented SURMOF relative to no treatment after cleaning, while for slides treated with 80 °C piranha, none of the surface treatments resulted in highly crystalline SURMOF of any orientation. We hypothesize that neither iNA nor sil2 gave complete [001]-preferred orientation because of the incomplete surface coverage by the anchoring group. As a simpler method for favoring growth in [001] direction was found (below), further investigation was not performed.

Within the screened conditions, the optimal surface treatment found for growing [001]-oriented Cu\(_2\)(bdc)\(_2\)(dabco) proved to be either just washing the silicon surface with ethanol or washing with ethanol followed by sensitization with 1 mM iNA—both very mild treatments. In both cases, increasing the number of growth cycles from 50 to 100 resulted in an increase of the undesired [100] orientation (Figure S5). Much to our satisfaction, analysis by SEM (Figures S11 and S12) revealed that the most homogeneous, [001]-oriented films were achieved by only washing the silicon surface with absolute ethanol. That such a simple pretreatment step—ethanol washing—can lead to highly oriented SURMOF homogeneous films of this type makes this new methodology highly desirable. Despite the lack of an intentionally added anchoring group (SAM), it is likely that the first SBU layer bonds to free oxygen lone pairs on surface Si—OH or Si—O—Si moieties per related precedent with quartz and metal oxide substrates.\(^{64−66}\)

It should be noted here that while out-of-plane (and, more rarely, in-plane) XRD is sometimes the sole evidence for assessing the degree of preferred orientation SURMOF growth, we found here that while the XRD data indicated only one preferred orientation, the corresponding SEM apparently showed a minor fraction with [100]-preferred orientation. We strongly suspect that the crystals of [100]-preferred orientation were not easily observed by XRD because (1) they were few in number and (2) any tilt of such crystals away from the XRD vector results in no signal. In these cases, confident assignment of the minor orientation required a combination of SEM of crystals grown dominantly as the other preferred orientation (here, the [100] phase observed by XRD in Figure S4 on piranha-treated silicon with accompanying SEM in Figure S10) and prior literature assignment of preferred orientation of the similar MOF Cu\(_2\)(F\(_4\)bdc)\(_2\)(dabco).\(^{52}\) We...
also attempted to probe the preferred orientation (and composition) by attenuated total reflection–IR,\textsuperscript{52} unfortunately, the signal intensity was too weak for confident signal assignment.

During the exploration of different surface treatments, we also investigated the growth of Cu\textsubscript{2}\((\text{bdc})_2\)(dabco) SURMOFs on TiO\textsubscript{2}-coated silicon. TiO\textsubscript{2} surfaces have enormous utility, both as a protecting layer for silicon\textsuperscript{51} and as a metal oxide surface for subsequent further modification. Currently, few examples of LbL epitaxial SURMOF growth on TiO\textsubscript{2} surfaces exist.\textsuperscript{50} We found that [001]-oriented Cu\textsubscript{2}\((\text{bdc})_2\)(dabco) could be grown on TiO\textsubscript{2}-coated Si surfaces without any further surface sensitization (Figure S6).

Next, we sought to further suppress the residual growth in [100] direction on bare silicon and obtain smoother, more homogeneous films. A review of reported procedures for growing M\textsubscript{L}\textsubscript{P}-type SURMOFs showed a few cases where no rinsing with neat solvent was performed between the very first metal and linker treatments,\textsuperscript{51,53} including one Cu\textsubscript{2}\((\text{bdc})_2\)(dabco) SURMOF example.\textsuperscript{54} In these reports, no explanation was given for the deviation from the typical SURMOF soaking routine of always rinsing between steps. We hypothesized that by not rinsing after the first metal soak step, better initial surface coverage of the preformed copper acetate paddlewheel could be achieved and/or provide residual unattached metal salt on the surface for subsequent self-assembly into the first MOF layer. Comparison of the SEM images after 20 cycles where either (a) soaking with neat ethanol was performed twice after each metal or linker soak, as described above, or with (b) a sequence where the substrate was not soaked in neat ethanol between only the first metal and linker soaks showed a clear reduction in the number of undesired [100]-oriented crystals for the latter case, recognizable as perpendicularly aligned thin plates in the SEM images (Figure 3A,B).

To further refine this procedure for growing [001]-oriented Cu\textsubscript{2}\((\text{bdc})_2\)(dabco), we next considered why misaligned crystals were formed. If the first SURMOF layer is templated correctly, only one orientation should result. Indeed, the early SURMOF work demonstrated that essentially flawless control over the final bulk orientation could be achieved.\textsuperscript{27,50,67} For M\textsubscript{L}\textsubscript{P}-type SURMOFs, a recent work by Terfort and co-workers probed the influence of temperature on the final orientation of Cu\textsubscript{2}\((\text{F}_{4}\text{bdc})_2\)(dabco) grown on an SAM-sensitized gold surface.\textsuperscript{52} Apart from the key takeaway that elevated temperature facilitated substitution at the apical position of copper paddlewheel SBUs, thereby favoring growth in [001] direction (an approach we utilized here), the authors also considered the mechanisms that lead to misaligned growth. In essence, the appearance of misaligned [100] crystals on top of initially [001]-aligned growth (and vice versa) points to crystal twinning arising from defect sites.

Rotation along the carbon–carbon bond of terephthalic acid bound to a copper paddlewheel SBU results in a defect site, which can allow twinning (schematically shown in Figure 4), as recently proposed by Terfort and co-workers.\textsuperscript{52} For this rotation to be possible, other linkers must be missing. We hypothesized that increasing the concentration of dabco linker might limit missing axial linker defects and thereby suppress twinning. Although the resulting SURMOF grown using 1 mM instead of 0.2 mM dabco was still primarily oriented in the [001] direction as found by GIXRD (Figure S7C), SEM revealed a rough surface with poor homogeneity and many undesired [100] crystals (Figure 3C). In contrast, a slight increase of the H\textsubscript{2}bdc linker concentration from 0.2 to 0.4 mM totally suppressed the formation of misaligned [100] crystals at 20 cycles (see Figure S7D for XRD pattern) and yielded a more homogeneous film consisting of interlocking Cu\textsubscript{2}\((\text{bdc})_2\)(dabco) crystallites (Figure 3D). That such a minor change—an increase of concentration from 0.2 to 0.4 mM of H\textsubscript{2}bdc—resulted in a noticeable change of final film homogeneity underscores the high sensitivity of SURMOF growth to the conditions employed. Reproducibility of this
method was checked by preparing multiple samples with 20 total cycles of growth; XRD analysis (Figure S9) showed only the presence of crystals with [001]-preferred orientation, while SEM showed that dense films with essentially complete surface coverage were formed for each batch, though some variability in the surface structure at higher resolution was observed from batch to batch (Figures S18 and S19). Large-area SEM (Figure S20) and macroscale photography confirmed that large areas (up to ca. 1 cm²) tested could be reliably coated (Figure S27).

With this optimized growth procedure in hand, we probed the elemental surface composition for Cu₂(bdc)₂(dabco) grown with 50 cycles by X-ray photoelectron spectroscopy (XPS). The peaks in the survey spectra corresponded to the binding energies of C, N, O, Si, and Cu (Figure S21). Because XPS probes the top ≈10 nm of a sample, the presence of Si indicates that the surface coverage over the area surveyed (100 μM) may be incomplete, consistent with the observation of occasional pinholes in the film by SEM.

Analysis of the high-resolution XPS scan of the Cu 2p region reveals peaks centered at 934.9 and 954.8 eV (Figure S22). The strong satellite features at ≈943 and 964 eV are consistent with the presence of Cu²⁺ species in the film. While the expected Cu/N ratio for this MOF is 1, the experimental ratio was ca. 1.8, suggesting missing dabco linker defects and/or trapped copper (this ratio was approximately the same even for a sample prepared with rinse steps between every metal soaks).

For some of the best-studied SURMOFs (e.g., HKUST-1 grown on SAM/Au substrates), epitaxial growth may approach the limit of one physical MOF layer per cycle. The thickness of crystalline thin films can be determined using the Scherrer equation; specifically, the average crystallite size along a crystallographic direction can be directly obtained using the full width at half-maximum (fwhm) of the XRD peak in interest. In the case of well-oriented crystals—such as a SURMOF—this analysis then provides an estimation of the SURMOF thickness.

To test how the thickness of Cu₂(bdc)₂(dabco) varies with a number of growth cycles, we obtained high-resolution out-of-plane GIXRD data of the [001] peak of Cu₂(bdc)₂(dabco) thin films grown at 10, 20, 35, 50, and 65 cycles (Figure S8). Subsequently, the [001] XRD peaks were fit to obtain the fwhm of each SURMOF, and the average crystallite size in the [001] direction estimated by the Scherrer equation. The result of this analysis was slightly confusing, as it revealed a nonlinear increase in the average crystallite size, with a plateau at approximately 28 nm after 35 cycles (Figure S23). Examination of the SEM micrographs of the same films (Figures S13–S16) revealed two key takeaways: (1) increasing the number of growth cycles from 10 to 20 cycles resulted in greatly improved surface coverage as pinholes were filled and (2) the films consisted of many discrete interlocking disc-shaped crystals.

Together with the XPS data that suggest missing linker defects (e.g., dabco), the Scherrer analysis data strongly support a growth mechanism where individual crystal domains grow in the [001] direction to a maximum of ca. 30 nm before a new domain begins. Indeed, no single-crystal structure is known for Cu₂(bdc)₂(dabco), nor were we successful in our own efforts to obtain single crystals—suggesting that this particular MOF is prone to defects which hinder larger crystal growth. Furthermore, while surveying the literature of known M₃L₃P-type SURMOFs grown in an LbL fashion, we noticed that the Zn₃L₃P-type MOF usually had known single-crystal structures, while we could only find one example of a Cu₃L₃P-type MOF with a known single-crystal structure: Cu₂(bdc)₂(bipy). Even the structure of Cu₂(bdc)₂(bipy) was originally reported based on powder XRD (PXRD) data before refined synthetic methods produced crystals of sufficient size and quality for single-crystal XRD analysis.

The hypothesis that this particular SURMOF grows as intergrown crystallites was further tested by atomic force microscopy (AFM) and cross-sectional SEM. AFM imaging of a sample grown with 20 cycles shows significant texturing and protrusions, which appear to be individual crystallites as well as aggregates (Figures S24 and S25). Cross-sectional SEM of a wafer with Cu₂(bdc)₂(dabco) SURMOF grown as 50 cycles (Figure S17) shows excellent surface coverage, a textured surface, and an average film thickness which is clearly thicker than expected if each growth cycle deposits a monolayer of MOF (ca. 1 nm per layer). The larger than expected thickness based on the number of growth cycles suggests a storage mechanism where reactants are temporarily “stored” in the growing SURMOF material, a phenomena with precedent in the SURMOF community. The attempt at estimating the thickness from the Scherrer XRD analysis (above) is contextualized by these results: while the “thickness” appears to plateau even with increasing growth cycles, the AFM and SEM data reveal that this SURMOF grows as interlocking crystallites which appear to reach a maximum size. These data provide insight into how SURMOF growth can be more complex—and less “ideal”—when using materials which are prone to defects.

With a successful protocol established for growing well-oriented Cu₂(bdc)₂(dabco) SURMOF on flat silicon substrates, we next considered other SURMOFs. In particular, M₃L₃P-type MOFs that include photo- and electroactive ligands would be attractive for building functional materials by virtue of being able to tune two separate ligands. As detailed above, Cu₂(bdc)₂(dabco) is a useful model system for developing growth methodology, and we were curious if this new methodology could be readily extended to other MOFs. Cu₂(1,4-ndc)₂(dabco), a well-known SURMOF usually grown on SAM/Au substrates (1,4-ndc = 1,4-naphthalenedicarboxylate), was a clear initial target. Indeed, using the newly developed protocols, crystalline and highly [001]-oriented Cu₂(1,4-ndc)₂(dabco) thin films on silicon could be obtained (XRD pattern shown in Figure S26).

MOFs with expanded unit cells will be critical for photo- and electroactive MOFs in order to accommodate the larger linkers typically required, so finally we sought to construct Cu₂(bdc)₂(bipy) (bipy = 4,4'-bipyridine). Larger linkers do carry the complication of increasing the likelihood of interpenetrated growth, and M₃L₃P-type MOFs are no exception. However, in a seminal demonstration of the utility of the SURMOF method by Wöll and co-workers, interpenetration was suppressed in the growth of Zn₂(bdc)₂(bipy) on SAM-coated Au substrates. The XRD pattern of an ethanol-washed silicon substrate after attempting to grow Cu₂(bdc)₂(bipy) showed two sharp peaks (Figure S5). Comparison of the experimental SURMOF pattern with the simulated patterns of the two known crystal forms clearly shows that the experimental pattern only matches that of the EtOH-solvated crystal form despite being dried under an Ar stream prior to the measurement. Furthermore, a slight enhancement (based on the simulated relative intensity)
of the [002] peak relative to the [001] peak is observed. Both of these observations nicely match with the prior report that removal of the interpenetrated lattice enhances the signal intensity of the [002] peak for the structurally related Zn₂(bdc)₃(bipy) SURMOF grown on a SAM-coated Au substrate. These results demonstrate that noninterpenetrated, highly [001]-oriented Cu₂(bdc)₂(bipy) can be successfully grown on ethanol-washed silicon.

The applicability of the prior Zn₂(bdc)₃(bipy) SURMOF report of avoiding interpenetration to the growth of Cu₂(bdc)₂(bipy) on unmodified silicon points to the versatility of the SURMOF technique and the utility of the new methods reported here. It also demonstrates that more complex SURMOFs can be built without needing precious metals (gold) during construction.

CONCLUSIONS

SURMOFs grown in an epitaxial fashion, nominally one layer at a time, have overwhelmingly been constructed on gold surfaces coated with well-behaved SAMs. To our knowledge, the present paper is the first systematic report of orientational control of M₂L₂P-type SURMOFs on silicon. Notably, and to our surprise, no sensitization with a surface anchoring molecule was required. The [100] orientation of Cu₂(bdc)₂(dabco) can be promoted by cleaning the Si surface with 80 °C piranha, while the preferred [001] orientation can be obtained by the mild procedure of simply washing the silicon surface with absolute ethanol. To our knowledge, such orientational control is rare on the more common Au substrate without surface anchoring molecules, and as such, this method represents a simpler method for controlling SURMOF orientation. There is a clear need for additional exploration with other classes of SURMOFs to see if similar orientational tuning can be achieved on silicon.

Further exploration found that subtle tuning of the initial soaking sequence and linker concentrations yielded clear improvements in the homogeneity of the final SURMOF film. We rationalize these changes from the perspective of suppressing the possibility for missing linker SBUs that then permit crystal twinning, building from prior hypotheses. This work also provides one of the very few examples of how seemingly trivial changes in pump sequence and component concentrations can have large changes in the resulting SURMOF film properties. Although unexpected, these results complement the recent study on Cu₂(F₄bdc)(dabco) wherein temperature control over a relatively small range (5–60 °C) was found to have a rather dramatic influence on the final SURMOF orientation and quality. Further unanticipated result was that there appeared to be a limiting thickness in the [001] direction for crystallite growth of Cu₂(bdc)₂(dabco) of about 30 nm; we hypothesize that Cu₂(bdc)₂(dabco) is particularly prone to defective sites. AFM and SEM analysis confirm that while excellent surface coverage of this particular SURMOF can be obtained, the actual material is composed of many small domains rather than monolithic crystals. These results provide rare insight into how MOFs, which may inherently have more defective sites, translate into SURMOF growth, and we expect that this information will help guide future studies. We specifically anticipate that many copper-based M₂L₂P SURMOFs will be more challenging to implement than their zinc analogues based on the results here.

Finally, we demonstrate that our methodology to control the orientation of M₂L₂P SURMOFs can be generally applied to isoreticular analogues, including those with expanded unit cells. In the case of Cu₂(bdc)₂(bipy), the seminal experiment of suppressing interpenetration using epitaxial SURMOF growth was replicated on silicon. Of note, this was achieved without using gold surfaces coated with well-aligned SAMs.

Looking ahead, we intend to apply these new methods for orientational control of M₂L₂P SURMOFs with redox-active linkers to investigate the effect that their orientation relative to the electrode surface has on electron transport kinetics. We expect that such fundamental studies will have important implications for MOFs containing electrocatalytic sites. Furthermore, we are optimistic that the simpler protocols presented here for growing well-oriented SURMOFs on flat silicon opens the door for electrochemical and photo-electrochemical solar-fuel generating devices while also removing the need for gold substrates.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12407.

Experimental procedures, overview of pump system construction and example code, additional SEM images, AFM data, and XRD patterns (PDF)

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