Homogenous Microporous Thin Films Assembled Using Discrete Metal-Organic Polyhedra

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May 23, 2024

Abstract

Homogeneous films with tailored microporous structures are crucial for several applications, yet fabricating such films presents significant challenges. This is primarily because most microporous materials have crystal sizes in the nano- and micrometer ranges, which inevitably generates intergranular spaces in the films, thereby complicating the fabrication of these thin films. We used functionalized metal-organic polyhedra (MOPs) as discrete microporous units and assembled them into homogenous microporous films. This study focused on avoiding the generation of intergranular spaces while controlling packing parameters and film thicknesses. Initially, the MOP units, influenced by van der Waals forces between the functionalized acyl carbon chains, displayed an affinity to form spindle-shaped blocks and islands. As the MOP concentration increased, these structures self-assembled into a hexagonally packed structure with an in-plane orientation and a maximum stacking of two layers of MOPs. By contrast, un-functionalized MOPs yielded a disordered film structure formed by random agglomeration. Evidently, functionalized adipoyl chloride influences the orientation of the MOP network films with uniformly distributed micropores, effectively preventing the formation of intergranular spaces. Additionally, formaldehyde adsorption and desorption experiments revealed that the MOP network films possess superior adsorption and desorption capacities. The proposed approach signifies a breakthrough in the fabrication of homogenous microporous films.

Article category: Full Paper

Subcategory: Metal Organic Polyhedra, Metal Organic Frameworks

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Homogeneous films with tailored microporous structures are crucial for several applications, yet fabricating such films presents significant challenges. This is primarily because most microporous materials have crystal sizes in the nano- and micrometer ranges, which inevitably generates intergranular spaces in the films, thereby complicating the fabrication of these thin films. We used functionalized metal-organic polyhedra (MOPs) as discrete microporous units and assembled them into homogenous microporous films. This study focused on avoiding the generation of intergranular spaces while controlling packing parameters and film thicknesses. Initially, the MOP units, influenced by van der Waals forces between the functionalized acyl carbon chains, displayed an affinity to form spindle-shaped blocks and islands. As the MOP concentration increased, these structures self-assembled into a hexagonally packed structure with an in-plane orientation and a maximum stacking of two layers of MOPs. By contrast, un-functionalized MOPs yielded a disordered film structure formed by random agglomeration. Evidently, functionalized adipoyl chloride influences the orientation of the MOP network films with uniformly distributed micropores, effectively preventing the formation of intergranular spaces. Additionally, formaldehyde adsorption and desorption experiments revealed that the MOP network films possess superior adsorption and desorption capacities. The proposed approach signifies a breakthrough in the fabrication of homogenous microporous films.

1. Introduction

Homogenous films with tailored micropores have garnered considerable interest due to the predictable and optimized performances of these films in a variety of fields, including gas storage and catalysis. The superior performances of these films can be attributed to the uniform distribution of micropores throughout the films and the consistent interactions between the micropores and target molecules. Metal-organic frameworks (MOFs) are an attractive material for preparing homogenous microporous films, as MOFs possess designable pore structures and permanent micropores. To fabricate MOF-based films, various methods, including direct growth, coating processes, printing, and the use of composites, have been successfully explored. However, producing a homogenous MOF film remains a considerable challenge due to the typical micrometer-scale crystal sizes of MOFs. This micrometer-sized material exhibits less efficient close-packing behavior than nanomaterials, leading to undesired heterogeneities owing to interparticle spaces, grain boundaries, and cracks. More specifically, even though MOFs inherently possess uniform micropores, the formation of structural intergranular spaces is inevitable when fabricating a homogenous film. A promising solution involves constraining the microporous material to a discrete micropore system. By assembling the discrete micropore system into a uniform layered film, a homogenous microporous film devoid of the inherent limitations of typical MOF films can be realized.

Metal-organic polyhedra (MOPs), commonly termed as a nano-cage, epitomize the concept of a discrete micropore system. MOPs typically possess the same pore system as that of the MOFs made of organic linkers and metal nodes; however, additional crystal growth is restricted by preventing interconnections.
This distinctive feature maintains the discrete micropore system and facilitates the high-level pore design of the films. Furthermore, the discrete MOP nanocages exhibit excellent processibility owing to high solubility, which allows for the uniform dispersion and concentration of MOPs in a solvent to be precisely controlled.[24] These properties combined with a well-defined discrete pore structure and enhanced processibility render MOPs a promising candidate for fabricating homogenous microporous films. Although MOPs have demonstrated the potential to be used for fabricating large super-frameworks,[25,26] current methods have failed to assemble discrete MOPs into homogenous films. In this study, we added carbon chains to encourage interactions between MOPs such that the MOPs can be assembled into a uniformly layered microporous film. Unlike the method using unfunctionalized MOPs, our strategy using functionalized MOPs with carbon chains uniformly distributes the discrete micropores, which have specific orientations that can be controlled via enhanced close packing, throughout the films. A homogenous microporous MOP film was deposited on the surface of a quartz crystal microbalance (QCM), and the porosity of this film was determined. The frequency variations of the QCM indicated that the homogenous microporous MOP film exhibited 11- and 2-fold higher amounts of formaldehyde uptake than the uncoated QCM and a non-homogenous MOP film, respectively, at ambient temperature.
2. Results and Discussion

Pristine Zr-based MOPs were synthesized as discrete nano-cages for fabricating homogenous microporous films. First, a Zr cluster ([Cp$_3$Zr$_3$O(OH)$_3$(COO)$_3$]$^+$) was formed via the hydrolysis of bis(Cp)ZrCl$_2$.[25, 27] The resulting Zr cluster ([Cp$_3$Zr$_3$O(OH)$_3$(COO)$_3$]$^+$) had six coordination points, three of which were capped by Cp molecules, leaving only three coordination points for connections with linkers.[28] Subsequently, BDC-NH$_2$ ligands were added to the Zr-cluster solution, coordinating with the tritopic Zr clusters to form tetrahedral Zr-based MOPs (Figure 1).

Figure 2. Characterization of the synthesized MOP crystals, discrete MOPs, and MOP-NUs. (a) Powder XRD patterns and simulated XRD patterns of a MOP crystal. (b) FESEM image and illustration (inlet) of a MOP crystal. (c) NMR spectra of the MOP-NUs, discrete MOPs, and acyl chloride. (d) FT-IR spectra of the MOP-NUs and discrete MOPs. (e) N$_2$ adsorption of the MOP-NUs and discrete MOPs.

The XRD patterns of the Zr-based MOPs display narrow peaks consistent with the simulated XRD patterns.
of MOP crystals (Figure 2a). Furthermore, the MOP crystals exhibit cubic morphologies, suggesting a periodic arrangement of the discrete MOPs, as shown in the FESEM (Figure 2b) and optical microscope images (Figure S1).\textsuperscript{[25]} Due to the periodical arrangement of discrete MOPs, the MOP crystals were highly crystalline and possessed a cubic morphology, evidencing the formation of the intended discrete MOP nanocages. The MOP crystals immersed in MeOH were easily separated into discrete MOPs because the hydrogen bonds between the discrete MOPs were replaced by the strong interactions between the MOPs and MeOH.\textsuperscript{[25]} The XRD patterns devoid of the aforementioned narrow peaks (Figure S2) and the FESEM images (Figure S3) reveal the structural changes from MOP crystals to discrete MOPs. Electrospray ionization mass spectroscopy (ESI-MS) clearly demonstrated the existence of discrete MOPs after the detachment process (Figure S4). The ESI-MS spectra of the discrete MOPs contain only two peaks, i.e., at 1607.8 and 3212.7 m/z, corresponding to [2]\textsuperscript{2+} and [1]\textsuperscript{1+}, respectively. These distinguishable peaks confirmed that the discrete MOPs did not merge into large MOP crystals or form biproducts.

To produce a MOP network film (MOP-NF), discrete MOPs were functionalized using adipoyl chloride, forming a MOP-NU via a condensation reaction between NH\textsubscript{2} and adipoyl chloride. A mixture of discrete MOPs and adipoyl chloride was heated in an oven at 90 °C for 2 days, yielding dark-orange MOP-NUs. The \textsuperscript{1}H NMR spectra of the digested discrete MOPs and acyl chloride (Figure 2c) show the characteristic peaks induced by the benzene protons in BDC-NH\textsubscript{2} and the protons of aliphatic carbon in the ranges of 8.4–7.6 and 2.4–1.0 ppm, respectively, confirming that a condensation reaction occurred. The integrated area ratio of approximately 1:4 was used to estimate the relative quantities of BDC-NH\textsubscript{2} and adipoyl chloride corresponding to the two peak regions; this is consistent with the estimation that each of the six BDC-NH\textsubscript{2} ligands anchored each acyl carbon chain. The resultant secondary amide group donates electrons to the benzene structure, which splits the three peaks, as shown by a, b, and c in Figure 2c. The protons in acyl chloride appear in two triplets, as shown by d and e in the figure; this is expected in an identical chemical structure. In the spectra of the MOP-NUs, the aforementioned peaks appear to be up-field shifted with respect to those of discrete MOPs and acyl chloride because the amide group causes all the protons of benzene and the carbon chains to be shielded by electron-rich nitrogen and oxygen. The absence of signals indicating biproducts also confirms that the condensation reaction was successful. The presence of an amide group in the MOP-NUs was confirmed via FT-IR spectroscopy. In the FT-IR spectrum of the MOP-NUs, the peaks at 1340 and 1480 cm\textsuperscript{-1} in the blue region were significantly attenuated with respect to those of the discrete MOPs. These attenuated peaks are associated with a C–N stretching mode, suggesting the restricted stretching motion of large and heavy carbon chains. Another peak appeared at 1650 cm\textsuperscript{-1} and was red-shifted with respect to the peak at 1625 cm\textsuperscript{-1} in the spectrum of the discrete MOPs (red region). The shift related to N–H bending vibration indicated that the primary amine was converted into a secondary amine. The peaks corresponding to the generated carbonyl groups and aliphatic carbon chains in the green region appeared at
1700 cm\(^{-1}\). The peaks corresponding to C–N, N–H, C=O, and C–C indicated that the primary amine group was converted into a corresponding amide group during the condensation reaction. The nitrogen physisorption isotherms of the MOP-NUs and the discrete MOPs displayed high amounts of adsorption at low relative pressures, indicating the presence of micropores (Figure 2e). At high relative pressures, the discrete MOPs exhibited high amounts of adsorption due to pore condensation, which typically corresponds to adsorption through large pores (> 50 nm), whereas the MOP-NUs exhibited negligible adsorption. This difference implies that the discrete MOPs randomly contained large interspaces between them, lacking sufficient force to yield a closely packed structure in a preferred direction. Interestingly, the isotherm obtained from the MOP-NUs exhibited a hysteresis and a rather linear uptake in the middle-relative-pressure range; this can generally be attributed to the presence of mesopores. The acyl carbon chains in the MOP-NUs generated van der Waals forces, resulting in closer proximity between the MOP-NUs than between the randomly stacked MOPs.

**Figure 3.** AFM images and profiles showing the formation of a MOP-NF. (a–e) Schematic illustration of the mechanism of MOP-NF formation following the increased concentration of MOP-NUs. (f–j) AFM images and profiles corresponding to (f) 0.5 μg/ml, (g) 1.25 μg/ml, (h) 5.00 μg/ml, (i) 20.00 μg/ml, and (j) 40.00 μg/ml of MOP-NFs. (k) AFM image of the MOP-NFs (20 μg/ml) over a large area.

The carbon chains introduced into the MOP-NUs increased the proximity between the MOP-NUs; based on this deduction, the formation mechanism of the MOP-NFs was investigated. First, a MOP-NU solution was prepared by considering that MOP-NUs reach saturation at a concentration of 0.8 mg/ml. The dispersion and concentration of the MOP-NUs were maintained below this threshold to ensure complete solvation (Figure S7). The MOP-NU solution was subsequently spread via centrifugal forces generated during a spin-coating process, and a uniform MOP-NU layer was formed on a silicon wafer. Next, heat treatment was used to convert the MOP-NUs to MOP-NFs. To investigate the film-formation process, atomic force microscopy (AFM) was conducted to quantify the roughness and textures of the MOP-NFs prepared using different concentrations of MOP-NUs and MOPs. Film formation using the MOP-NFs is schematically depicted in Figures 3a–e, elucidating five sequential steps. At the lowest concentration of the MOP-NUs, the AFM images and surface topography profiles indicated that the MOP-NUs were formed as spindle-shaped structures with a height of 1.5 nm, which is consistent with the height of an individual MOP (Figures 3f and S8). The height of the spindle-shaped structures was approximately 1.5 nm, suggesting that the MOP-NUs attracted each other and formed one-dimensional blocks. Previous studies on tetrahedral nanoparticle packing have revealed that the lowest packing density is achieved when convex spindle-shaped structures are formed.\(^{[29]}\) We hypothesized that the spindle-like structures of the MOP-NUs were formed owing to increased van der Waals forces generated by aliphatic carbon chains. As the MOP-NU concentration increases to 1.25 μg/ml (Figure 3g), the AFM images of the MOP-NUs reveal the formation of islands. As the MOP-NU concentration increases to 5.00 μg/ml, these islands join to form a double-layered island (Figure 3h). Notably, the AFM profile of the double-layered islands shows two distinct step heights: 1.5 and 3.0 nm in the lateral and central areas, respectively. The 3.0-nm height is approximately twice the height of individual MOPs, indicating that the spindle-like structures self-assembled into islands and subsequently expanded into double-layered islands without continued stacking. At a concentration of 20.00 μg/ml (Figure 3i), MOP-NFs were formed without any spindle-shaped blocks or islands. The profile of the MOP-NFs reveals low surface roughness and full coverage (Figures 3k), whereas that of the unfunctionalized MOPs shows high surface roughness with many spaces between the MOPs (Figures S9d). When the MOP-NU concentration was above 20.00 μg/ml, double-layered islands reappeared on the surface of the MOP-NFs (Figure 3j). The subsequent island formation process suggests that the thickness of the homogenous MOP-NFs can be controlled in two-layer increments of approximately 3.0 nm owing to the re-stackable nature of the films. The functionalized acyl chains in the MOP-NUs induce van der Waals interactions between the MOP-NUs, resulting in the formation of characteristic blocks such as spindle-shaped blocks and islands, which contribute to the formation of a homogenous microporous film. Overall, the film-formation process using MOP-NUs differs from that using MOPs only, as the latter do not form characteristic blocks and are randomly agglomerated (Figure S9).
To investigate the arrangement of MOP-NUs within the MOP-NFs, GISAXS was conducted, as this characterization technique can reveal periodically dispersed micropores at q positions in a reciprocal space. The GISAXS scattering profiles of the MOP-NFs and MOPs exhibit strong reflections along the qz axis (out-of-plane axis) at qy = 0 Å⁻¹, indicating that both films are layered. Interestingly, the GISAXS scattering profile of the MOP-NFs shows patterned reflections at 29.0° and 58.1°, with the ratios at the q positions of the patterns estimated to be 1:3, i.e., 0.462:0.797. These angles and q-position ratios are consistent with the theoretical values of 60° and 3 corresponding to a hexagonal lattice structure, indicating that MOP-NFs with hexagonal closed packing were formed. Additionally, the absence of peaks corresponding to the 1:4 and 1:7 ratios in the scattering pattern obtained from the MOP-NFs indicates that the films were stacked in a maximum of two layers. The inter-distance between the MOP-NUs was calculated as 0.572 nm from the q positions at 0.788 and 1.36 nm; this inter-distance corresponds to the length of an adipoyl chloride chain. The short inter-distance between the MOP-NUs suggests that they were pulled toward each other, resulting in hexagonal closed packing while being stacked in only two layers.

By contrast, the GISAXS scattering profile of the MOPs showed a ring pattern that indicates a disordered structure owing to the presence of randomly stacked MOPs. The distinctive differences between the GISAXS patterns indicate that the presence of one-dimensional spindle-like particles is crucial for preferentially orienting in-plane directions parallel to the substrate. Notably, the orientation difference can be attributed to the presence of functionalized acyl carbon chains. These results suggest that the high interaction strength between the MOPs owing to the chemical modification with the acyl carbon chains in the MOP-NUs is critical for yielding homogenous films via hermetic hexagonal packing, as interparticle spaces are eliminated owing to the MOPs being densely packed. More specifically, chemical modifications of the MOP-NUs resulted in spontaneous dense packing with hexagonal stacking in only two layers while uniformly distributed micropores occupied the interparticle spaces.

We speculated that a homogeneous film featuring uniformly spread micropores and mesopores can effectively adsorb and allow gas molecules to diffuse into it. To evaluate the efficacy of the pore structures in the MOP-NFs, we initially tested the formaldehyde adsorption capacities of powder-state MOPs and MOP-NUs in a...
closed-loop system. Formaldehyde was chosen as an adsorbate due to its high affinity toward micropores at ambient temperatures. The closed-loop system consisted of a large gas mixing chamber connected to both a sample chamber and a gas detector (1512i photoacoustic gas monitor, LumaSense Technology). When the target formaldehyde concentration was reached in the gas mixing chamber using a gas control system, the formaldehyde was subsequently directed through the sample chamber. The adsorption abilities of the MOP and MOP-NU powder samples are compared in Figure 5a. Both the MOPs and MOP-NUs were repeatedly exposed to formaldehyde concentrations in the range of 0–45 ppm. The results indicated that the MOP-NUs adsorbed 18.8 mg/g of formaldehyde, which is more than twice that absorbed by the MOPs, i.e., 7 mg/g, particularly at a formaldehyde concentration of 40 ppm. The higher amounts of adsorbed formaldehyde in the MOP-NUs than that in the MOPs implied that the mesopores formed by the close proximities between interacting MOPs are advantageous because these mesopores provide effective transport pathways for formaldehyde.

**Figure 5.** Formaldehyde gas adsorption and desorption experiments on the MOP-NFs using a quartz crystal microbalance (QCM). (a) Formaldehyde adsorption behaviors of MOP-NU and MOP powders. (b) Schematic illustration of formaldehyde gas adsorption and desorption experiments. (c) Schematic illustration of the mechanism of the formaldehyde gas adsorption and desorption experiments using the QCM. (d) Real-time sensor responses related to formaldehyde gas adsorption on the AC, MOP, and MOP-NF films coated on the QCM.

The QCM method was used to determine the formaldehyde adsorption-desorption abilities of the MOP-NFs. The QCM method, based on the piezoelectric property of a quartz crystal, can measure extremely low mass changes owing to adsorbed gas molecules within pores during real-time monitoring. Thus, the high-quality, reliable, and accurate QCM method enables adsorption and diffusion efficiencies to be comprehensively compared. Three different films: an acyl chloride (AC) film, a MOP film, and MOP-NFs were spin-coated on a QCM at 3000 rpm for 20 s, followed by vacuum drying at 50 °C (Figures 5b and S11). Subsequently,
the three films were placed in the sample chamber of the close-loop system in which they were exposed to 8.5 ppm of formaldehyde molecules. The adsorption of formaldehyde onto the MOP-NFs increases the overall mass of film coated on the QCM, thereby decreasing the frequency of the QCM, which is attributable to the piezoelectric effect of the quartz crystal, as depicted in Figure 5c. The QCM frequency increased when the adsorbed gas was gradually desorbed upon exposure to nitrogen gas. In the QCM plot (Figure 5d), the large frequency change of 45 Hz corresponding to the MOP-NFs suggests a higher adsorption capacity of the MOP-NFs compared to those of the AC and MOP films, which exhibited frequency changes of 21 and 27 Hz, respectively, in relation to formaldehyde. By contrast, the uncoated QCM displayed only a minimal frequency variation of 4 Hz (Figure S12).

This implies that the MOP-NFs exhibit an effective surface interaction with formaldehyde molecules, leading to increased mass accumulation on the film during the adsorption process. The ordered structure of the MOP-NFs facilitates the maximum utilization of the micropores and the diffusion of formaldehyde through the mesopores arising from the stationary acyl carbon chains between the MOP-NUs, minimizing hindrance to molecular diffusion without reducing pore windows due to the free acyl carbon chains. The MOP-NFs exhibited nearly double the amount of desorption than that of the MOPs, which indicated that the adsorbed formaldehyde escaped freely owing to the well-ordered micropores that were not blocked by other hindrances.

3. Conclusion

Homogenous microporous MOP-NFs were developed by meticulously controlling the concentration of MOP-NUs and employing acyl-carbon-chain functionalization. This approach facilitated the self-assembly of MOP-NUs into uniformly microporous, two-layered, hexagonally packed MOP-NFs. The MOP-NFs displayed desirable features, such as a uniform dispersion of micropores and mesopores, specific MOP orientation, and crack-free structure. Formaldehyde adsorption and desorption experiments using the QCM method revealed that the MOP-NFs possessed superior adsorption and desorption capacities in relation to formaldehyde. MOP-NFs yielded higher frequency changes of 45 Hz in comparison with 21 and 27 Hz yielded by the AC and bare MOP films, respectively. This disparity in frequency changes can be attributed to the maximum utilization of micropores, and the mesopores between the MOP-NUs guaranteed unhindered accessibility of formaldehyde to the micropores. These results confirm that the functionalized discrete MOPs satisfy the criteria for producing truly homogeneous microporous films. The results of this study indicate that the developed MOP-NFs are highly suitable for applications requiring uniformly porous films.

4. Experimental Section

Materials: Cp₂ZrCl₂ (here, Cp denotes cyclopentene), 2-aminoterephthalic acid (BDC-NH₂), N,N-diethylformamide (DEF), acetonitrile, deionized water (DI-water), methanol (MeOH), adipoyl chloride, and triethylamine (TEA) were purchased from Sigma-Aldrich, Korea. All reagents were used as received without further purification.

Synthesis of MOPs and MOP NUs: For synthesizing MOP crystals, Cp₂ZrCl₂ (17.5 mg, 0.06 mmol) and BDC-NH₂ (5.4 mg, 0.03 mmol) were dissolved in DEF (1 mL). DI water (150 μL) was added to the mixture, followed by a reaction in an oven at 60 °C for 8 h. After the reaction, a yellow powder was obtained, which was washed three times with DEF (10 mL) in a centrifuge. For synthesizing discrete MOPs, the synthesized MOP crystals were soaked in MeOH for 3 days. A yellow MOP cage was obtained via centrifugation and dried in a freeze-dryer.

For synthesizing MOP-NUs, discrete MOPs (10.7 mg) were dissolved in a mixture of acetonitrile (1.7 ml) and DI water (1.7 ml) in a 20 ml vial. TEA (6.67 μl) was added to the solution to optimize the pH of the mixture, and the color of the solution changed to pale yellow. Adipoyl chloride was added to the solution, which changed color to transparent yellow. The preparation of the mixture was followed by a reaction in an oven at 120 °C for 2 days. After the reaction, a brown powder was obtained and washed three times with MeOH in a centrifuge.

Characterization of the MOPs and MOP-NUs: Powder XRD patterns were obtained using a Bruker D8
Advanced (TRIO/TWIN) instrument at 1600 W (40 kV and 40 mA). X-rays were scanned at 4°/min in the range of 5–20° using a Si holder. The surface morphologies and sizes of the MOFs were verified using a FESEM (JEM-7600F, JEOL). The powdered sample was dispersed in ethanol and dropped onto a holder. Additionally, 1H NMR analysis of the digested MOFs was conducted using a Bruker Avance III HD 500 NMR spectrometer. To prepare the samples for measurement, 3 mg of dried MOF powder was digested and dissolved in a mixture of dimethyl sulfoxide-d6 (700 μL) and HCl (200 μL) under sonication. An FT-IR spectrometer (Nicolet IS50, Thermo Fisher Scientific) was used to investigate the structure of the synthesized MOP-NUs. Gas adsorption analysis was conducted using a BELSORP-max (MicrotracBEL Corp.) gas adsorption analyzer. Samples were prepared and measured after evacuation at 120 °C for 24 h. GISAXS measurements were conducted at the 5 A beamline of the Pohang Accelerator Laboratory, Republic of Korea. The angle of the incident X-rays was maintained at 0°, and the energy of the incident photon was 11.56 keV. The patterns formed on the substrates were imaged using an AFM (Park Systems XE-100) in the noncontact mode.

Acknowledgements

This study was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIT) (Nos. NRF-2021R1C1C2012825 No. 2022R1A2B5B01001826 and No. RS-2023-00218255). The authors thank Jikeun Seo for his valuable advice on the AFM experiments.

Conflict of Interest

The authors declare no competing financial interest.

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

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Metal-Organic Polyhedra (MOPs), referred to as nano-cages, are periodically assembled through functionalization using acyl chloride. This process results in the formation of a homogeneous microporous MOP network film. The film is distinguished by in-plane orientation and double-layered arrangement, enhancing formaldehyde adsorption capabilities. This increased efficiency is attributed to the uniform pore distribution and the absence of cracks within the film.

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Supporting Information
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