SUPPORTING INFORMATION

Post-Assembly Transformations of Porphyrin-Containing Metal-Organic Framework (MOF) Films Fabricated via Automated Layer-by-Layer Coordination

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Section S1. General materials & synthesis

Materials

meso-Tetrakis(4-carboxyphenyl)porphyrin (**TCPP**) (Frontier Scientific), 1,4-diazobicyclo[2.2.2]octane (**dabco**) (Sigma-Aldrich), magnesium bromide ethyl etherate (Sigma-Aldrich), 3-aminopropyltrimethoxysilane (Sigma-Aldrich), and 4,4'-dipyridyl (**bpy**) (Sigma-Aldrich) were obtained from commercial sources and used as received. Solvents were obtained from Sigma-Aldrich and used as received. Deionized water was provided as a part of the building facility at Northwestern University. (100) Single-sided silicon (20KΩ/cm) was obtained from University Wafers. Single-sided indium tin oxide-coated (ITO) glass was obtained from Delta Technologies, Ltd.

Fabrication of MOF thin films.

The number of cycles was controlled using an automated setup adapted from the design of Arslan *et al.*[1] First, silicon and ITO were cut into 0.75 x 1 cm^2 pieces. The ITO and silicon were cleaned in a saturated solution of Alconox, deionized water, acetone, and then isopropanol; each step was performed for 10 minutes. The hydroxyl-terminated surface was then amine-terminated by soaking a 1:100 *(v:v)* solution of (3-aminopropyl)trimethoxysilane (3-APTMS) in ethanol for 60 minutes, followed by rinsing with hexanes, rising with water, and oven drying (70 °C, 15 minutes). To facilitate consistent film preparation, a computer-controlled automated pump system[2] was built to perform the repeated immersion cycles in an oven at 40 °C. The substrates were subsequently soaked in 0.1 mM zinc(II) acetate, 2 μM **TCPP**, 2 μM **bpy** (all in ethanol) for 5, 10, and 10 minute soaks, respectively. To form pre-magnesiated films, 2 μM solution of **Mg-TCPP** was used in placed of 2 μM solutions of **TCPP**.

SALE of MOF thin films.

Films were subjected to heating at 43ºC for 13 hours in a continuously stirred, 2 mM solution of **dabco** in DMF. These samples were then rinsed in DMF before TOF-SIMS and profilometry measurements were executed.

Magnesiation of MOF thin films.

Upon formation of the MOF films containing free-base porphyrins, films were exposed to a solution of 5.2 mg of magnesium bromide diethyl etherate in 10 ml of dichloromethane at room temperature for 12 hours with stirring. These samples were then rinsed in dichloromethane before UV-Vis and XPS measurements were taken.

Zinc metalation of MOF thin films.

Upon formation of the MOF films containing free-base porphyrins, films were exposed to a solution of 4.39 mg of zinc acetate dehydrate in 10 ml of methanol at room temperature for 40 hours with stirring. These samples were then rinsed in methanol before UV-Vis and XPS measurements were taken.

Synthesis of tetrakis(4-carboxyphenyl)porphyrinatomagnesium(II)

Based on Lindsay's method[3], under a standard reaction condition, *meso*-tetrakis(4-carboxyphenyl)porphyrin (118 mg, 0.149 mmol) and anhydrous manganese iodide (1.2 g, 4.3 mmol) were dissolved separately each in 8 mL of DMF using sonication and then the solutions were combined and transferred into a 20-mL microwave vial. Then, NEt_3 (1.5 mL, 10.8 mmol) was added to the reaction mixture, and the vial containing the uniform solution was loaded with a magnetic stir bar, crimp-capped and placed in a microwave reactor at 170 °C for 40 min. Then, the basic reaction mixture was transferred into a separation funnel to which EtOAc and water were added. Next, HCl (1M) was added dropwise till the pH changed into neutral allowing the product to transfer from the aqueous phase to the organic phase. Afterwards, the reaction mixture was washed with water (5x200 mL) and the organic phase was dried using the rotary evaporator and finally the dark purple product was scratched from the flask's wall. ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.36 (d, J=8.2 Hz, 8H, Ar), δ = 8.45 (d, J=7.9 Hz, 8H, Ar), 8.86 (s, 8H, β-pyrrole-H), 11.49 (br s, 4H, CO_2H); MALDI-ToF MS: m/z = 812.665, calcd. For $C_{48}H_{29}MgN_4O_8$ $[M+H]^+$: 813.184; UV/Vis (MeOH): λ_{max} [log ε (Lmol^{-1}cm^{-1})]= 425 nm [4.64], 565 nm [3.16], 615 nm [2.94].

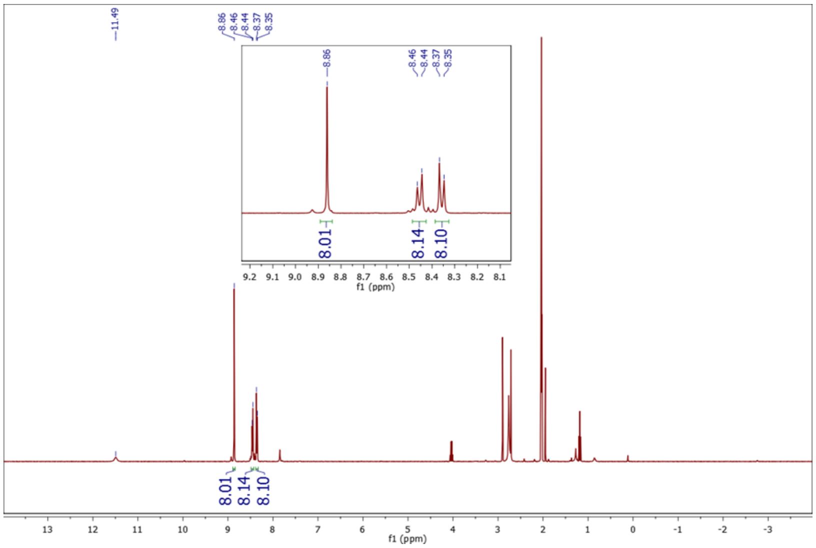

Figure S1. ^{1}H NMR (400 MHz, acetone-d_6) of *meso*-tetrakis(4-carboxyphenyl)porphyrinatomagnesium(II).

Target

Target type	0221598
Target serial number	0001767
Position	L15

Laser

Laser beam attenuation	4
Laser beam focus	3
Laser repetition rate	50 Hz
Number of shots	1000

Spectrometer

positive voltage polarity	POS
PIE delay	0 ns
Ion source voltage 1	19 kV
Ion source voltage 2	16.72 kV
Lens voltage	8.3 kV
Linear detector voltage	0.669 kV
Deflection on	
Deflection mass	

Instrument

Instrument type	autoflex
Serial instrument number	238320.00114
Name of computer	FLEX-PC
Operator ID or name	BDAL@DE
flexControl version	flexControl 3.4.127.0
flexAnalysis version	

Figure S2. MALDI-ToF MS of *meso*-tetrakis(4-carboxyphenyl) porphyrinatomagnesium(II).

Section S2. Instrumentation

1.1 Profilometry.

Dektak 150 surface profiler was used to monitor the thickness at 6.5 μm for measured range, 3.00 mg for stylus force, and scan duration of 20 s.

1.2 UV-vis Spectroscopy

UV-vis absorption measurements were performed on a Cary 5000 spectrophotometer. Single-sided ITO was blanked before each measurement.

1.3 X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed using a Thermo Scientific ESCALAB 250Xi with a monochromatic AlKα x-ray source (1486.6 eV) in an ultrahigh vacuum. Spectra were recorded at 23.5 eV pass energy, 150 W x-ray source power, and a take-off angle of 70°. XPS was used to determine the atomic concentrations of the metals inside the MOFs by identifying and quantifying the ratios of metal components in the MOF films.

1.4 Time-of-flight secondary ionization mass spectrometry (TOF-SIMS)

TOF-SIMS data were acquired using a Physical Electronics TFS-2100 (TRIFT II) instrument controlled by Cadence software. High-mass resolution positive ion spectra of $m/\Delta m > 3000$ at m/z 25 (C_2H^-) were acquired using a bunched $^{69}Ga^+$ ion pulse at an impact energy of 15 keV, an ion current of 600 pA per pulse, a pulse width of 14 ns (700 ps after bunching), and a pulse frequency of 10 kHz. Total ion doses in these measurements were approximately $< 1 \times 10^{12}$ ions/cm^2. Spectra from 100 μm × 100 μm areas on the sample surfaces were acquired using the Cadence software. In all cases, two different positions of the same surfaces were measured in order to estimate the reproducibility of the TOF-SIMS data.

1.5 Ellipsometry

Measurements were performed using the J. A. Woollam M-2000 Spectroscopic Ellipsometer. Data was collected from MOF films grown on silicon substrates. Optical constants were fitted using a model consisting of silicon substrate and B-spline layer.

Section S3. Characterization.

Sample	Zn	Mg	Mn
Zn(MgTCPP)(MnPorphyrin) MOF	180.2	1.0	42.4
Washing solution of Zn(MgTCPP)(MnPorphyrin) MOF	2.7	1.2	1.0

Table S1. ICP-OES data shows the demetalated TCPP is metalated with Zn and the excess of Zn is detected mainly due to low time of washing (1 day). Zn(MgTCPP)(MnPorphyrin) MOF was synthesized according to published procedure.[4]

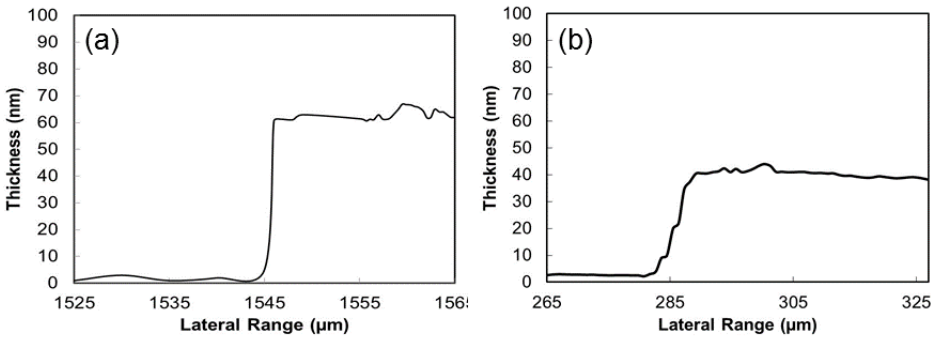

Figure S3. Profilometry of films of **L2-MOF** (a) before and (b) after SALE treatment.

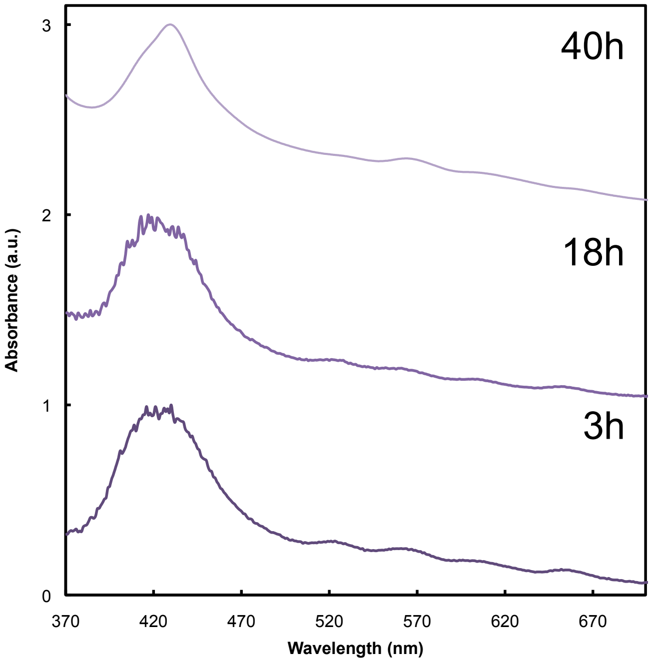

Figure S4. UV-Vis spectra of films of **L2-MOF** show collapse of four Q bands to two Q bands upon metalation by zinc after 40 h of reaction time.

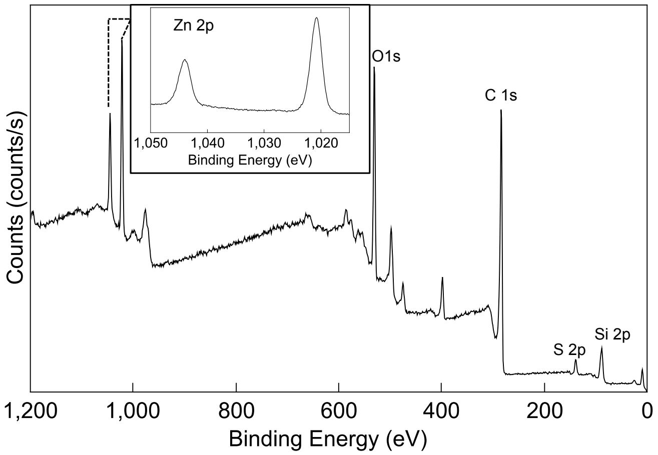

Figure S5. XPS spectrum insets show regions where peak for Zn $2p_{3/2}$ appear in **L2-MOF**.

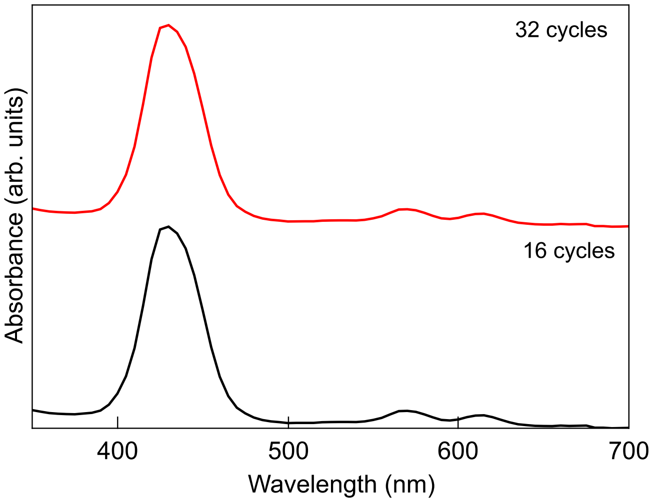

Figure S6. UV-vis spectra of pre-magnesiated **L2-MOF** as a function of cycles. Note that no demetalation occurs as indicated by the retention of two Q bands.

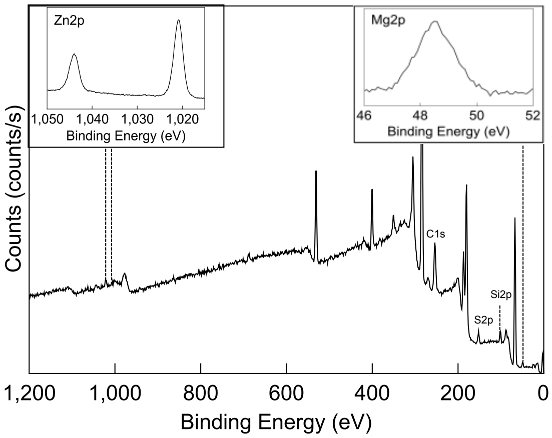

Figure S7. XPS spectra of **L2-MOF** under pre-magnesiation conditions.

Section S4. Calculation of effective refractive index of thin film and the volume fraction of analytes condensed in the MOFs before and after SALE and linker metallation.

To quantify the porosity of films, we turned to ellipsometry measurements of evacuated and solvent-filled films. Optical constants of the material were evaluated via ellipsometry. We chose *N,N*-dimethylformamide (DMF) as the MOF solvent, since it has a high boiling point and will not evaporate during room temperature ellipsometry. Sorption of volatile molecules (refractive index n_a>1) by the microporous MOF will displace the vacuum and increase the effective refractive index. The % porosity of the metal-organic framework (n_{fram}> 1) and the MOF cavities (vacuum, n_{vac} = 1) is given by:

$$\%porosity = \frac{n_{fram,A,V}^2 - n_{fram,V}^2}{n_a^2 - n_{vac}^2} x100\%$$

$n_{fram,A,V}$ and $n_{fram,V}$ are volume-weighted averages of refractive indices of the MOF films with and without solvent infiltration, respectively.

$$n_{fram,A,V} = n_{fram,A}V_{fram} + n_{solvent}V_{pores}$$
$$n_{fram,V} = n_{fram}V_{fram} + n_{vac}V_{pores}$$

where V_{fram} and V_{pores} are the volume fractions for the framework and pores, respectively. $n_{solvent}$ is the refractive index of the solvent used for infiltration (i.e. $n_{DMF} = 1.42$), and $n_{fram,A}$ is the refractive index of the solvent filled MOF film.

MOF Films	Estimated % Porosity	Actual Relative Change in % Porosity	Calculated Relative Change in % Porosity[a]
L2-MOF	29	-	-
SALEF-1	24	-0.82	-0.72
Mg-L2-MOF	30	+1.02	+1.06
Zn-L2-MOF	29	+1.00	+1.07

[a] Estimated from simulated single crystal XRDs of **L2-MOF**, **SALEF-1**, **Mg-L2-MOF**, and **Zn-L2-MOF**.

Table S2. Ellipsometry data shows that the porosity of the films (a) decreased after SALE treatment (**L2-MOF → SALEF-1**), and (b) stays nearly the same after post-assembly linker magnesiation (**L2-MOF → Mg-L2-MOF**) and zinc metalation (**L2-MOF → Zn-L2-MOF**). Note the actual and calculated relative changes in % porosity of the MOFs are in good agreement.

Section S5. References

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[1] H. K. Arslan, O. Shekhah, D. C. F. Wieland, M. Paulus, C. Sternemann, M. A. Schroer, S. Tiemeyer, M. Tolan, R. A. Fischer and C. Wöll, *J. Am. Chem. Soc.*, **2011**, *133*, 8158-8161.

[2] M. C. So, S. Jin, H.-J. Son, G. P. Wiederrecht, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, **2013**, *135*, 15698-15701.

[3] J. S. Lindsey, J. N. Woodford, *Inorg. Chem.* **1995**, *34*, 1063-1069.

[4] O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, **2011**, *133*, 5652-5655.