

Supplementary Information

## Post Metalation of Solvothermally Grown Electroactive Porphyrin Metal-Organic Framework Thin Films

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### S1. Experimental Section

**1. Chemicals.** Meso-tetra(4-carboxyphenyl)porphine (H<sub>4</sub>TCPP, Frontier Scientific, >97%), benzoic acid (J. T. Baker, ≥99.5%), zirconyl chloride octahydrate (Alfa Aesar, 99.9%), N,N-Dimethylformamide (DMF, Macron, ≥99.8%), acetone (J. T. Baker, ≥99.5%), zinc chloride (Sigma-Aldrich, ≥98%), cobalt chloride hexahydrate (Alfa Aesar, 98.0–102.0%), potassium chloride (Sigma-Aldrich, 99.0–100.5%), sodium hydroxide (Sigma-Aldrich, ≥98%), and sodium nitrite (Sigma-Aldrich, ≥99.0%) were used as received. Deionized water was used as the water source throughout the work.

**2. Growth of the MOF-525 thin film.** The fluorine-doped tin oxide (FTO) conducting glass substrate (TEC-7, NSG America, Inc., New Jersey, USA, 7 Ω/□), with a size of 3.5 cm × 1.25 cm, was cleaned by sonicating in soapy water and acetone for 5 min sequentially.

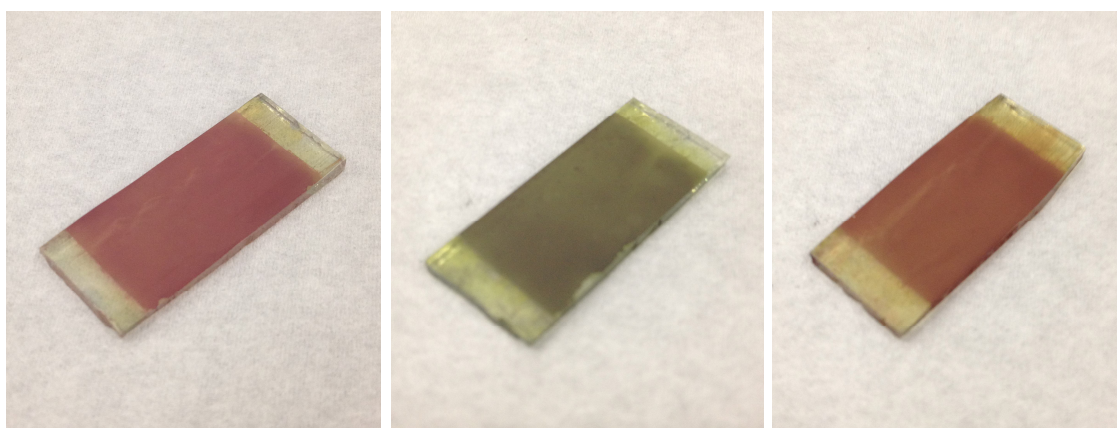
After drying under nitrogen flow, the substrate was further cleaned by an UV-ozone cleaning machine (Jelight Company, Inc., Model No. 42) for 15 min. Thereafter, the substrate was cooled down to room temperature and soaked in a solution of 0.5 mM H<sub>4</sub>TCPP in DMF for 12 h at room temperature. The substrate was then removed from the solution, washed with DMF, and air dried. Similar pretreatments of substrates have been proposed in previous studies for the growth of MOF thin films<sup>S1,S2</sup>. Thereafter, 2.7 g of benzoic acid and 105 mg of zirconyl chloride octahydrate were dissolved in 8 mL of DMF in a 20 mL screw-thread scintillation vial (28 mm × 61 mm) by sonication. The vial was closed with a urea cap and placed into an oven at 80 °C for 2 h. After cooling the solution to room temperature, 47 mg of H<sub>4</sub>TCPP was added into the solution, and the solution was sonicated at room temperature for 20 min. The pre-treated FTO substrate was then placed into the vial, with the conducting side facing down to the bottom. The vial was closed and placed on the bottom of a gravity convection oven with the temperature set at 70 °C for 24 h; similar procedures have been reported for the growth of other MOF thin films in a previous study<sup>S2</sup>. Thereafter, the substrate was removed from the vial and washed with DMF; a uniform thin film with dark red color was obtained. The obtained thin film was washed with acetone for several times and soaked in acetone for one day. After drying under vacuum, the MOF-525 thin film was obtained (Fig. S1(a)). The precipitation in the vial was also collected by centrifugation. The obtained powder was then washed with DMF and acetone twice sequentially and soaked in acetone for one day. After drying under vacuum, the MOF-525 powder with dark red color was obtained as well.

**3. Post metalation of the MOF-525 thin films.** 2 mM solution of zinc chloride was prepared in a mixture of 19.8 mL of DMF and 0.2 mL of water in a scintillation vial. The MOF-525 thin film was placed into the vial, and the closed vial was placed into an oven at 100 °C for 24 h. Thereafter, the obtained thin film was removed from the solution, washed with acetone for several times, soaked into acetone for one day, and dried under vacuum. The Zn-MOF-525 thin film, which shows a dark green color, was obtained (Fig. S1(b)). The Co-MOF-525 thin film (Fig. S1(c)) was prepared by simply using cobalt chloride hexahydrate in the procedure mentioned above.

**4. Instrumentation.** X-ray diffraction (XRD) patterns of the MOF thin films and powder were obtained by an X-ray diffractometer (X-Pert, the Netherlands). Nitrogen adsorption-desorption isotherm of the MOF-525 powder was measured on Micromeritics ASAP 2020. The morphologies of MOF-525 thin films and powder were investigated by using a scanning electron microscope (SEM, Nova NanoSEM 230). Energy dispersive X-ray spectroscopy (EDS) experiments were also conducted on the same SEM. UV-visible spectra were measured by a UV-visible spectrophotometer (UV-VIS-NIR, V670, Jasco Co., Japan). For the measurements of digested MOF thin films, a small piece of the MOF thin film was dissolved in 1.0 M NaOH aqueous solution. The obtained solution was then added into a quartz cell (1.0 cm) for UV-visible measurement.

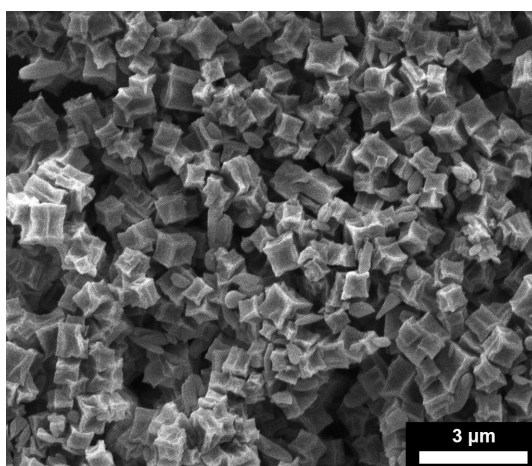
Cyclic voltammetric (CV) curves of the MOF thin films were measured on a CHI 440 electrochemical workstation (CH Instruments, Inc., USA), using a conventional three-electrode setup. The MOF-525 thin film, metalated MOF-525 thin film, or bare FTO

glass, with an exposed area of  $0.25 \text{ cm}^2$ , was used as the working electrode. A Ag/AgCl/KCl (sat'd) electrode (homemade) and a Pt foil ( $4 \text{ cm}^2$ ) were used as the reference and counter electrodes, respectively. 10 mL of aqueous solution containing 0.1 M of KCl was used as the electrolyte for each CV experiment.



**Figure S1.** Photos of the (a) as-prepared MOF-525 thin film, (b) Zn-MOF-525 thin film, and (c) Co-MOF-525 thin film grown on FTO substrates.

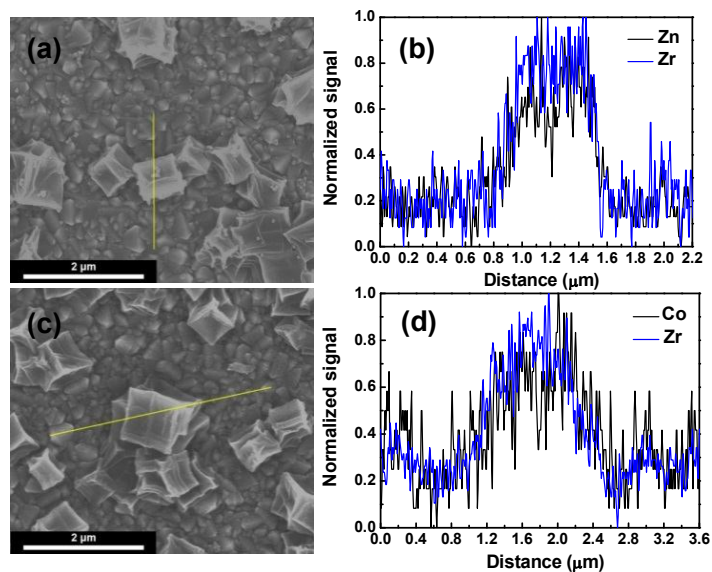
## S2. SEM image of the MOF-525 powder



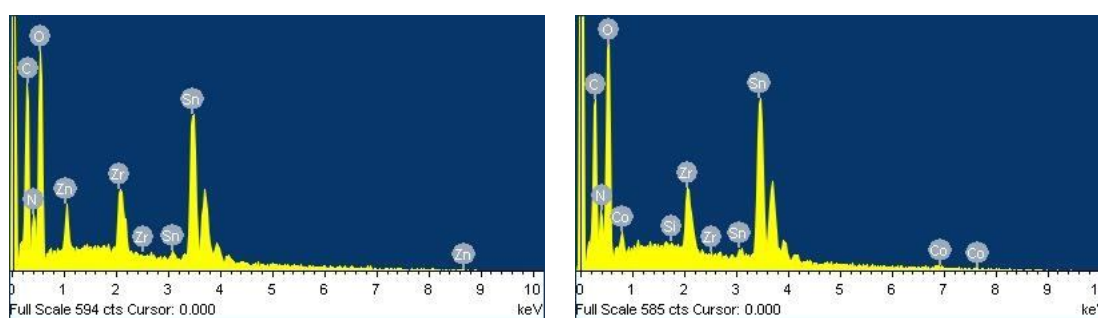
**Figure S2.** SEM image of the MOF-525 powder obtained during the growth of thin film.

### **S3. EDS spectra and elemental line scans of the metalated MOF-525 thin films**

To investigate the distributions of Zn and Co inside the MOF crystals of the metalated MOF-525 thin films, EDS elemental line scan was done across an isolated crystal found on each metalated MOF thin film (Fig. S3). The regions for line scan on the Zn-MOF-525 and Co-MOF-525 thin films are shown in Fig. S3(a) and S3(c), respectively. The normalized EDS signals collected from the lines in Fig. S3(a) and Fig. S3(c) are shown in Fig. S3(b) and S3(d), respectively. It can be observed that the distribution of Zn in the Zn-MOF-525 crystal and the distribution of Co in the Co-MOF-525 crystal (in Fig. S4(a) and S4(b)) are uniform cross the cubic crystals of the MOF-525 thin film. The average Zn/Zr ratio in the Zn-MOF-525 thin film and the average Co/Zr ratio in the Co-MOF-525 thin film, quantified from 3 different regions of each film by EDS, are 0.47 and 0.51, respectively. Since the molecular formula of MOF-525 contains three TCPP linkers and six Zr atoms, this result suggests a high degree of metalation in both Zn-MOF-525 and Co-MOF-525 thin films.



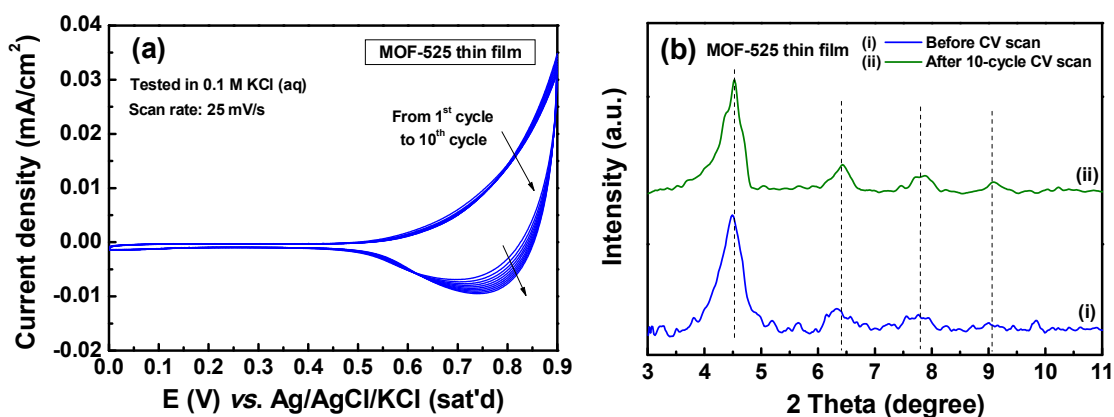
**Figure S3.** SEM images of the isolated crystal selected for EDS elemental line scan on (a) Zn-MOF-525 thin film, and (c) Co-MOF-525 thin film. Normalized EDS signals for (b) Zn and Zr collected from the yellow line shown in (a), and (d) Co and Zr collected from the yellow line shown in (c).



**Figure S4.** EDS spectra of (a) Zn-MOF-525 thin film and (b) Co-MOF-525 thin film.

#### S4. Electrochemical stability of the MOF-525 thin film

Electrochemical stability of the MOF-525 thin film was also briefly studied by cycling the film voltammetrically for 10 cycles in the KCl aqueous solution. CV curves recorded during 10 cycles of scan are shown in Fig. S5(a); the result shows that the CV curve of MOF-525 thin film tends to be stable after a few cycles of scan. After scanning for 10 voltammetric cycles, the MOF-525 thin film was removed from the solution, washed with water, and soaked in acetone for one day. After drying the film under vacuum, crystallinity of the obtained thin film was studied by XRD (Fig. S5(b)). The thin film shows the same XRD pattern after 10 CV scans, suggesting that the porous framework of MOF-525 thin film is stable during the CV experiment in the KCl aqueous solution.

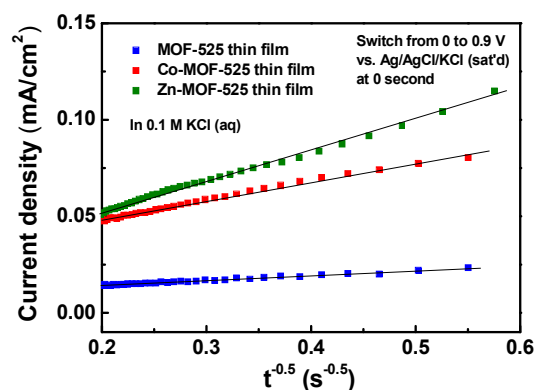


**Figure S5.** (a) 10-cycle CV curves of the MOF-525 thin film, measured in 0.1 M KCl aqueous solution at a scan rate of 25 mV/s. (b) XRD patterns of the MOF-525 thin film (i) before the CV scan, and (ii) after 10-cycle CV scan in 0.1 M KCl aqueous solution.

## S5. Chronoamperometric results

Chronoamperometric curves of all the Zn-MOF-525, Co-MOF-525, and MOF-525 thin films were conducted with the same setup as CV experiments. The working electrode was initially held at 0 V, and switched to 0.9 V (*vs.* Ag/AgCl/KCl (sat'd)) at 0 s. The current was recorded with increasing time (*t*), and the plot of current density *vs.*  $t^{-1/2}$  in linear region is shown in Fig. S6. The apparent diffusion coefficient ( $D_{app}$ ), which can be affected by the charge transport between redox moieties in the film, the ion diffusion into or out of the film to maintain electroneutrality, and/or the rate of physical diffusion of the redox moieties in the film, can be estimated from the slopes in Fig. S6 by using the Cottrell equation<sup>S3,S4</sup>. Since the concentration of redox moieties (porphyrinic centers) in the MOF thin film ( $C_0$ ) cannot be precisely estimated, the values of  $D_{app}$  for all the films cannot be quantitatively determined. However, by assuming all the MOF thin films possess the same  $C_0$ , the slopes in Fig. S6 are proportional to  $D_{app}^{1/2}$ <sup>S5</sup>. It can be observed that the Zn-MOF-525 thin film exhibits the largest slope in Fig. S6, and the MOF-525 thin film shows the smallest slope; this tendency is in consistent with the redox signals observed in Fig. 4. Since the physical movement of porphyrinic centers in the MOF thin films is neglectable, this observation suggests that the Zn-MOF-525 thin film provides either faster charge hopping or faster ion diffusion compared to the Co-MOF-525 and MOF-525 thin films, which may be the reason for its much higher redox signal compared to those of the Co-MOF-525 and MOF-525 thin films in the CV curves shown in Fig. 4.





**Figure S6.** Plot of current density vs.  $t^{-1/2}$  of the Zn-MOF-525, Co-MOF-525, and MOF-525 thin films. A potential step was applied to the films from 0 to 0.9 V (vs. Ag/AgCl/KCl (sat'd)) at  $t=0$  s for each experiment.

## S6. Reference

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