Electronic Supplementary Information

Patterned Growth of Luminescent Metal-organic Framework Films: A Versatile Method for Electrochemical-assisted Microwave Deposition

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1, Materials and instrumentation

1.1 Materials. Tri-p-tolylphosphine was purchased from Adamas Reagent, Ltd. Potassium permanganate ($KMnO_4$) and sodium nitrate were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. $Ln(NO_3)_3 \cdot 6H_2O$ was purchased from Beijing HWRK Chem Co., Ltd. They were all used without further purification. All reagents and solvents were commercially available and used as received. Ultrapure water (18.24MΩ cm^{-1}) is used directly from a Milli-Q water system. Poly(dimethylsiloxane) (PDMS; Sylgard 184) was obtained from Dow Corning company.

1.2 Instrumentation. X-ray diffraction (XRD) patterns of the films were collected on a Bruker Advance D8 using graphite-monchromated Cu Kα radiation in the 2θ range of 3-50° with step size of 0.02°. The grazing incident angle is 1.0°. The scanning electron microscopy (SEM) measurement was carried out on a Phenom G2 instrument. Voltage supply was performed by Epsilon electrochemical workstation. Microwave syntheses were carried out in a microwave oven (Initiator 8 EXP, 2450 MHz frequency, Biotage Corp.). Fluorescence spectroscopy data were recorded on a FLS920 fluorescence spectrophotometer. The thicknesses of deposited layers were measured by DEKTAK XT step profile instrument. The simulated powder patterns were calculated using Mercury 2.0. The optical photos were obtained from a Canon Digital IXUS 9901S camera.

2, Preparation of $Ln(OH)_3$ layer by electrochemical preparation. The lanthanide hydroxides were deposited onto FTO glass at room temperature in a bath containing 0.1 M $Ln(NO_3)_3$ and 0.2 M $NaNO_3$ in a solvent of 20 ml ethanol and deionized(DI) water (V/V=1:1) using cyclic voltammetry (CV) at the rang of potential of open circuit potential to -1.4 V.

3, Preparation of patterned $Ln(OH)_3$ layers on FTO using electrochemical methods. The Poly(dimethylsiloxane) (PDMS) prepolymer (mixed in a 10:1 ratio with cross-linking catalyst) was written on a transparent FTO surface using hollow pen to create a desired pattern. Because of the insulation of PDMS, the $Ln(OH)_3$ layers can only be electrochemically deposited on the area without PDMS. Hence, the desired pattern was formed on a FTO surface.

4, Converting patterned $Ln(OH)_3$ layers into LMOFs using microwave irradiation. The $Ln(OH)_3$ layers or patterned $Ln(OH)_3$ layers were loaded into DMF/H_2O/EtOH(V/V/V, 3:3:1) mixture solution in 30 ml microwave tube, adding another 200 μL ice acetic acid. The side of

$Ln(OH)_3$ was face down in order to avoid precipitate on the FTO glass. Subsequently, the microwave was transferred to microwave instrument for reaction.

5, Supporting Figures.

Equation S1: Basic principle of electrochemical reduction of NO_3^- :

$$NO_3^- + H_2O + 2e^- = NO_2^- + 2OH^- \quad (1)$$

$$2H_2O + 2e^- = 2OH^- + H_2 \quad (2)$$

$$Ln^{3+} + 3OH^- = Ln(OH)_3 \quad (3)$$

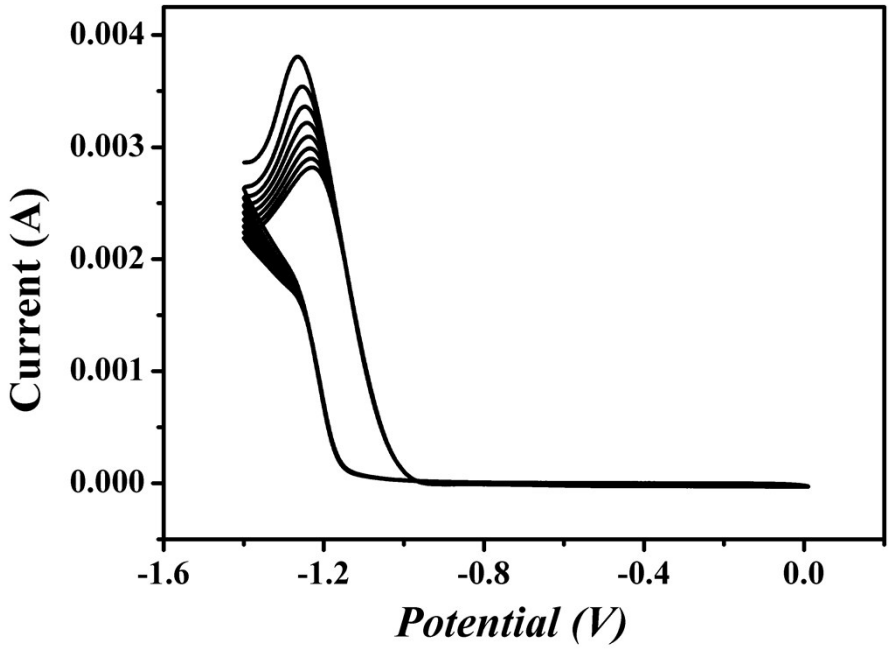

Figure S1 Electrochemical preparation of $Ln(OH)_3$

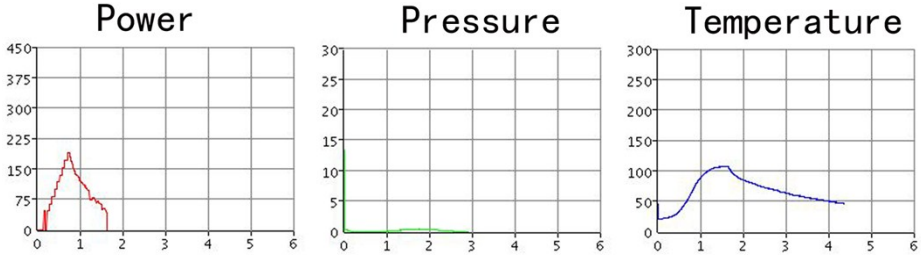

Figure S2 Converting $Ln(OH)_3$ into Ln-MOFs by microwave irradiation.

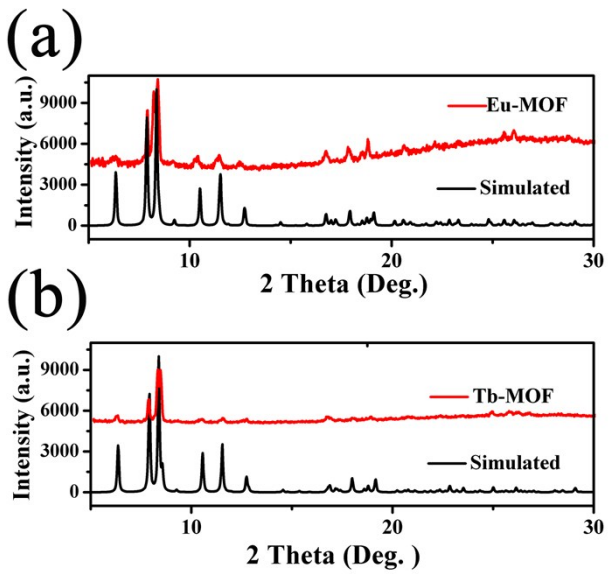

Figure S3 (a) PXRD of Eu-MOF layers on FTO surface. (b) PXRD of Tb-MOF layers on FTO surface.

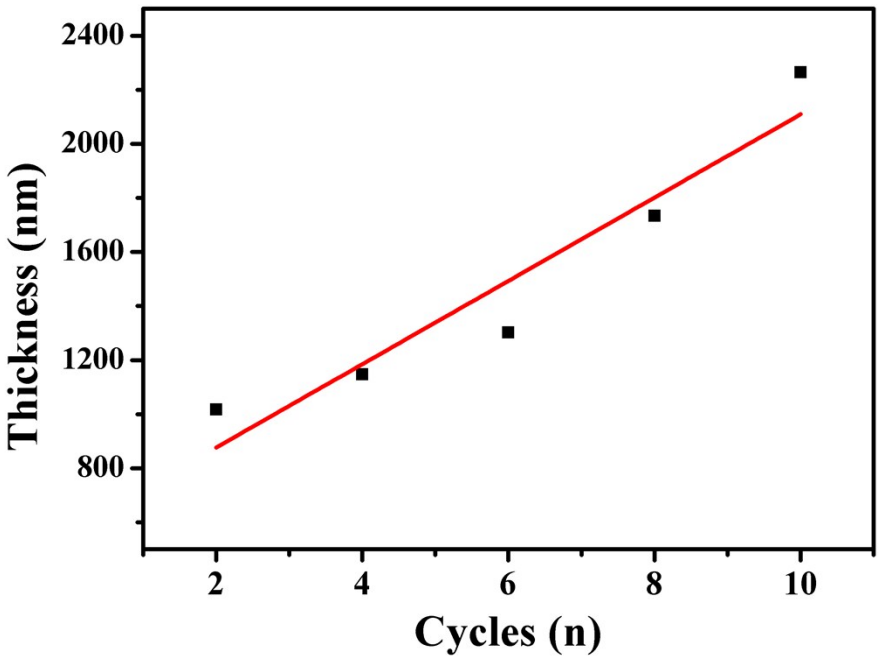

Figure S4 Linear relationship between the electrochemical deposition and thickness of $Tb(OH)_3$ Layers.

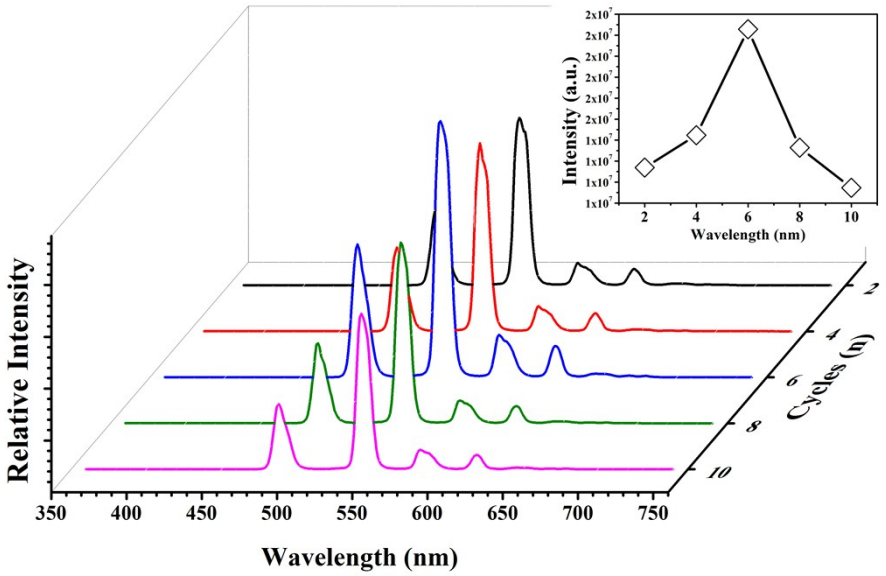

Figure S5 Line profiles of the emission spectra for different deposition cycles. Inset: Linear relationship between the emission intensity at 544 nm and deposited cycles.

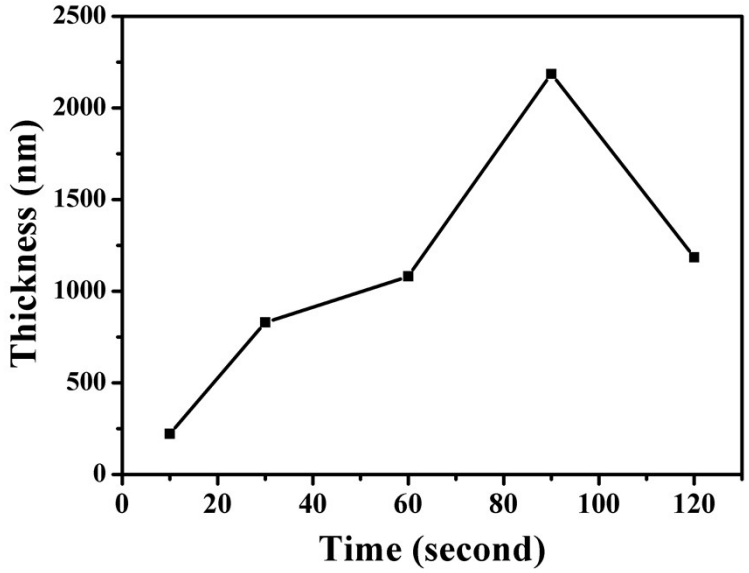

Figure S6 Relationship between the microwave reaction time and thickness of Tb-MOF Layers.

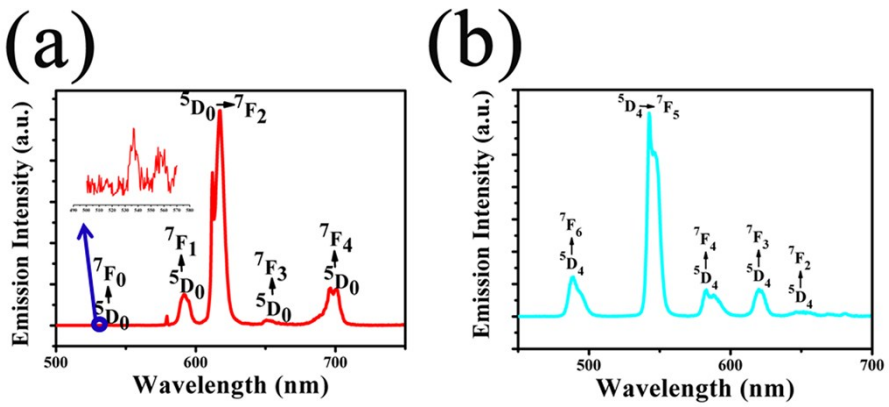

Figure S7 (a) Emission spectra of Eu-MOF. (b) Emission spectra of Tb-MOF.

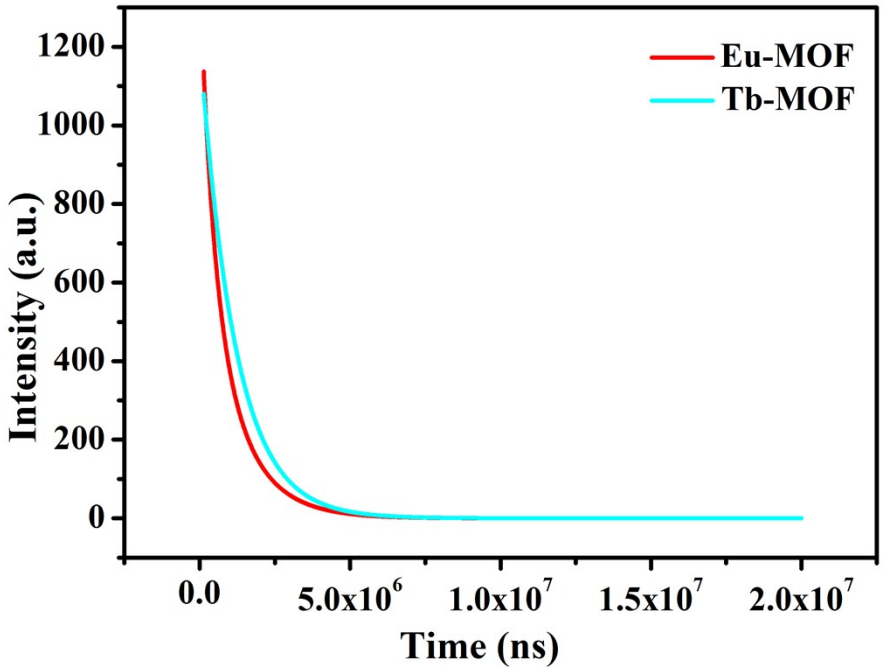

Figure S8 The decays of prepared Eu-MOF films and Tb-MOF films.

Table S1. Comparative ratio of theoretical Tb/Eu and experimental Tb/Eu

Theoretical Tb/Eu	Experimental Tb/Eu
0.4	**0.31**
1.0	**1.12**
1.5	**1.53**
2.7	**2.78**
3.0	**3.46**

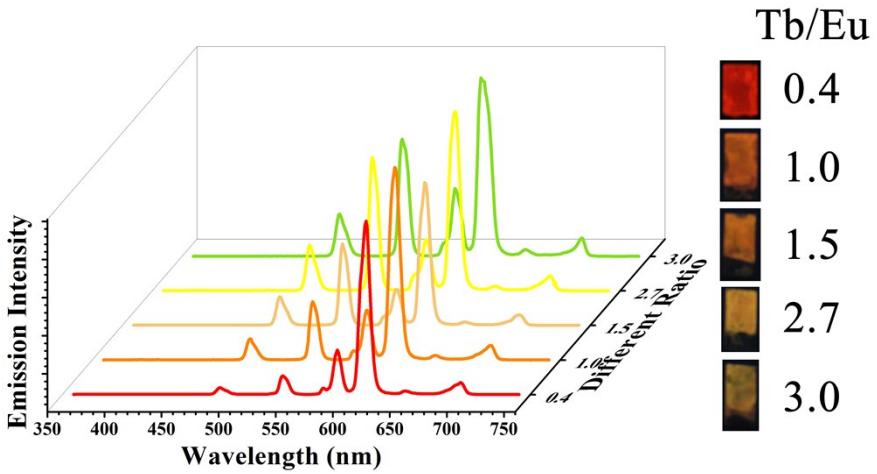

Figure S9 Photoluminescent spectra of as-prepared Eu_{1-x}/Tb_x-MOF films with Tb^{3+}/Eu^{3+} mol ratio of: 0.4, 1.0, 1.5, 2.7, and 3.0, respectively.

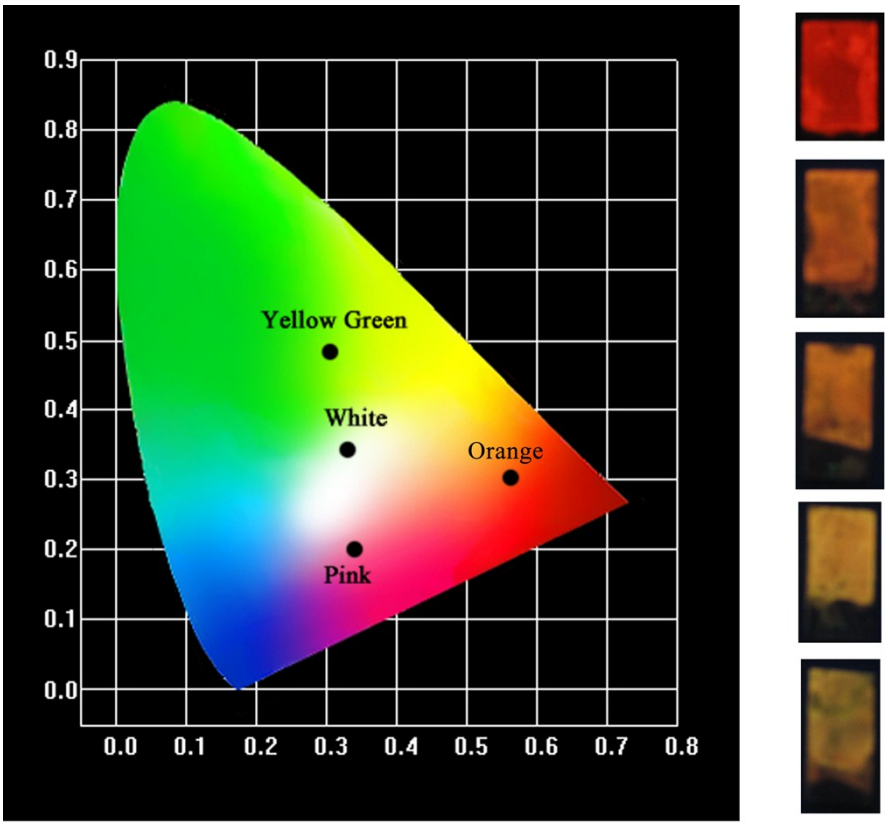

Figure S10 Comparison of the color of calculated chromaticity with that of the measured (on the right side). Tb^{3+}/Eu^{3+} mol ratio: 0.4, 1.0, 1.5, 2.7, and 3.0.

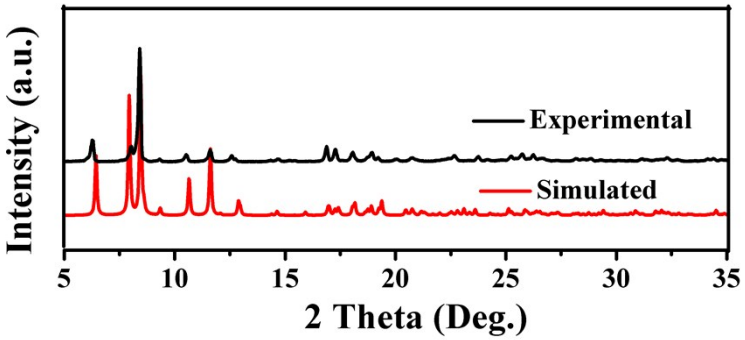

Figure S11 PXRD of Yb-MOF film.

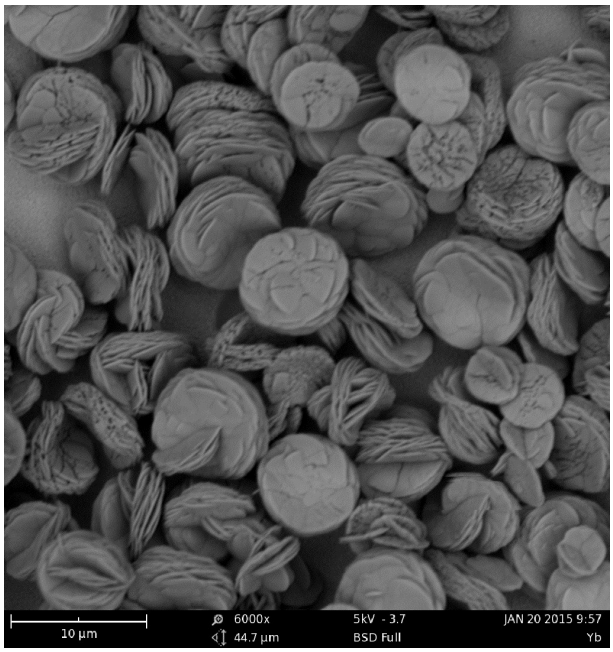

Figure S12 SEM images of Yb-MOF films on FTO surface.

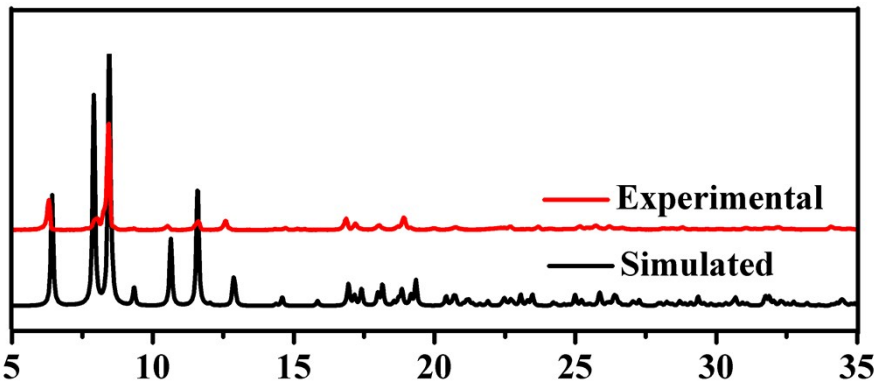

Figure S13 PXRD of Er-MOF films.

Figure S14 SEM images of Er-MOF films.