

# Surface Anchoring of Lanthanide Metal-Organic Frameworks by Electrochemical Deposition

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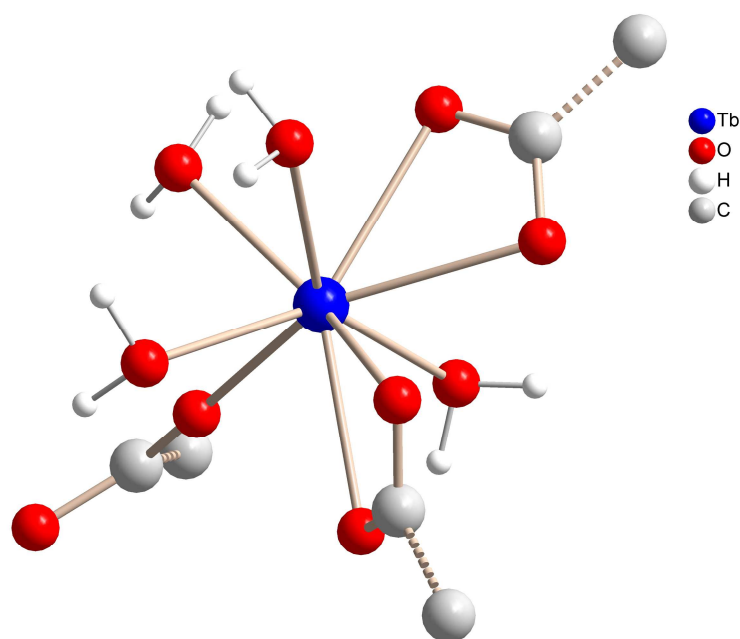
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Electrochemical deposition is a widely applied technique to produce defined thin films for various applications. For surface anchored metal-organic frameworks (SURMOFs) this technique is rather rarely applied, since not all MOFs form under electrochemical conditions. Some examples showed the deposition of MOF powders, forming a thin film via electrochemical deposition. We herein show a sophisticated way to produce the thin, defined, crystalline SURMOF Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub> films and further characterized them with X-ray diffraction. The Ln-MOF consisting of Tb<sup>3+</sup> and mellitic acids (bhc) shows highly luminescent properties, even in water - without quenching - as shown on photographs, which makes it a great candidate for different kinds of sensorics applications.

## Introduction

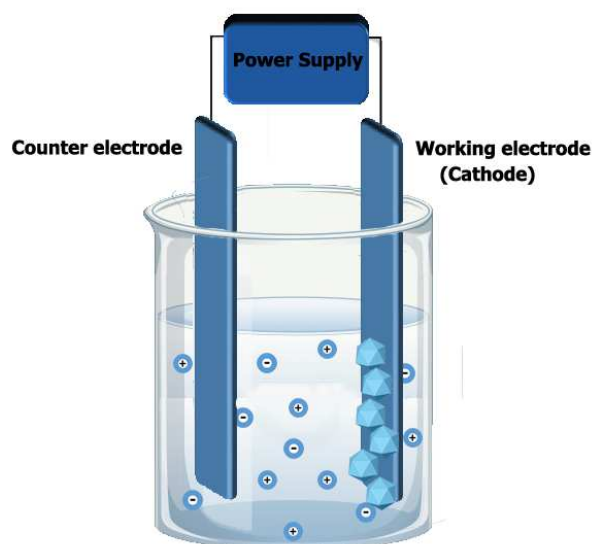
Among metal-organic frameworks (MOFs), build up from metal-nodes and organic linker molecules, lanthanide-based MOFs have attracted great attention due to their fascinating characteristic coordination and unique optical properties arising from 4f electrons (1–3). The narrow bandwidth fluorescence of the lanthanides metal nodes and the wide absorption of the chromophores in the linker, which act as antennae to excite the shielded f-orbitals of lanthanides metal-nodes, contributed to the numerous applications in luminescent sensors (4), light-emitting devices (5) and anticounterfeiting barcodes (6). Moreover, tuning the emission color by mixing the ratio of different lanthanides are also the advantage of Ln-MOFs, because the Ln-MOFs, with Eu(III)/Gd(III)/Tb(III)/Dy(III), etc. and the same linker, are nearly isostructural (7). However, powder materials of Ln-MOFs have a number of drawbacks for optical applications, including unwanted light scattering effects and opaque characteristics. And a very efficient energy transfer (FRET) from Tb(III) to neighboring Eu(III) existed in random Ln metals centers MOFs, which would cause unwanted quenching effects and severely complicates for the color tuning (8). Usually, a quenching also happens when water goes into the pore. As shown in this study for Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub>-MOF (Figure 1) which has been reported earlier (9), the MOF contains coordinated crystal water but still does not show quenching effects, but a rather strong luminescence.



**Figure 1** The coordination around the Tb atom in the  $\text{Tb}_2(\text{bhc})(\text{H}_2\text{O})_6\text{-MOF}$ . On 3 directions it coordinates with carboxy groups of the linker, whereas it coordinates to 4 water molecules as crystal water at the same time.

To address these challenges, surface-anchored metal-organic frameworks (SURMOFs) were designed and applied in optical Ln-MOFs thin film fabrication. In 2009, a procedure to mount MOFs on a gold substrate, which was functionalized with a self-assembled monolayer, was created to fabricate SURMOFs thin film by layer-by-layer method (lbl) (10). And in 2019, the first transparent, oriented, crystalline Ln- SURMOFs was synthesized by lbl method (11). The thickness of the Ln- SURMOFs can be easily controlled, maintaining the transparent nature, which makes them attractive for the wide field of optical coatings. Moreover, by depositing Tb-SURMOF on Eu- SURMOF, the energy transfer from Tb(III) to Eu(III) was reduced and results in an optimized fabrication of Ln-MOFs thin film with straightforward modulation of the emission color.

The electrochemical deposition of Metal–Organic Frameworks (MOFs) has generated a great deal of interest in recent years. Electrochemical deposition is an electric current driven method that provides precise control of coating the species in the form of nanoparticles, nanowires, thin films, and so on, onto a conductive target material. Even an electric field during the synthesis is capable of forcing MOF structures in a special direction, making synthesis of non-accessible structures possible (12, 13). The advantage of electrochemical deposition techniques is that the product grows directly attached to the substrate, and in comparison to other techniques, crystallographic orientation, thickness, and morphology of the nanostructured materials and thin films can be controlled by adjusting the operational conditions (14).



**Figure 2** Schematic depiction of the electrochemical deposition of metal-organic frameworks.

This technique can be categorized into three types: anodic electrodeposition (AED), cathodic electrodeposition (CED) and electrophoretic deposition (EPD). Anodic electrodeposition and cathodic electrodeposition methods involve the *in-situ* synthesis of MOFs on the substrate while electrophoretic deposition is a technique to deposit pre-synthesized MOFs.

Former methods propose even a charge transfer during the deposition to produce the metal or oxide layer on top of the electrode. In other words, positively charged ions in the electrolytic solution is reduced upon an external electric field applied so that they could be deposited onto a target material (15). In AED, a metal anode is electrochemically oxidized in the solution and then deposit on the anode, and in a CED process, components (ions, clusters...) are reduced and deposited onto the cathode from solution precursors. However, in the EPD, deposition occurs without any chemical reaction involved. In fact, the principal driving force for EPD is the charge and the electrophoretic mobility of the positively charged particles in the solvent under the influence of an applied electric field. Compared with AED and CED, EPD is a two-step method, which includes an extra step for the synthesis of MOF particles (16, 17).

In this work, cathodic electrodeposition (CED) has been used in the fabricating of Ln-MOF due to its low cost, precise control of coating, short formation time, and higher deposition rates.

## Experimental

### Materials:

Terbium (III) trifluoromethanesulfonate (98%) and Mellitic acid (hbc) (97%) were obtained from Sigma-Aldrich and used without any further purification.

## Synthesis of Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub> thin film

Terbium (III) trifluoromethanesulfonate was initially dissolved in water with formic acid (60mL water + 2 drops of concentrated formic acid). Mellitic acid ligand was added to the solution. The MOF thin films were electrodeposited in a gold-coated Si substrate using DC power supply. The electrochemical cell was equipped with two electrodes, a working electrode (thin film), and a counter electrode and operated at 6V for 10min. The electrochemical deposition was done using a Komerici power supply model QJ1502C. The metal and organic linker solutions were prepared in Milli-Q water with the same concentration ratio.

## Substrate preparation

Gold-coated substrates were prepared by coating Si wafers with a thin (5 nm) titanium adhesive layer, followed by a 100 nm gold layer. These substrates were cleaned with ultrapure ethanol and 5min Ozone cleaner before the thin film deposition.

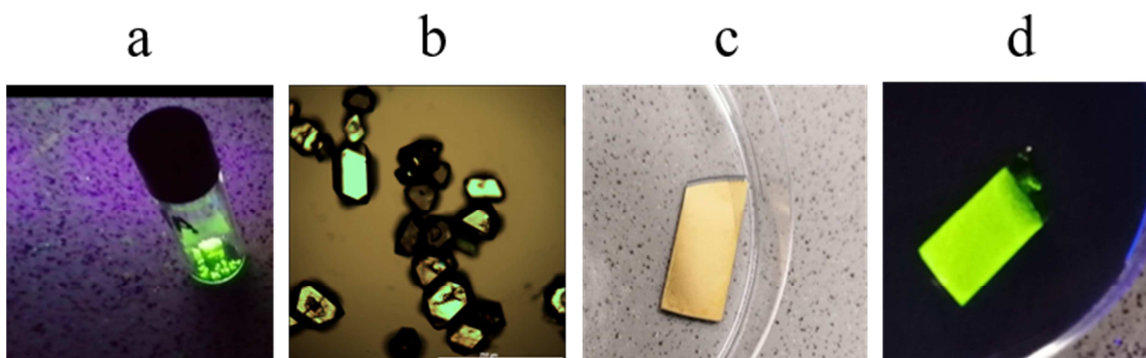
## X-ray diffraction (XRD)

The out-of-plane (co-planar orientation) XRD measurements were collected on a Bruker D8-Advance diffractometer equipped with a position sensitive detector Lynxeye in  $\theta - 2\theta$  geometry, variable divergence slit, and 2.3° Soller-slit was used on the secondary side. The measurement was carried out in the range of  $2\theta = 6^\circ - 25^\circ$  at a scan step of 0.018° at 40 kV and 40mA utilizing Cu K $\alpha$ 1,2-radiation ( $\lambda = 0.154018$  nm).

## **Results**

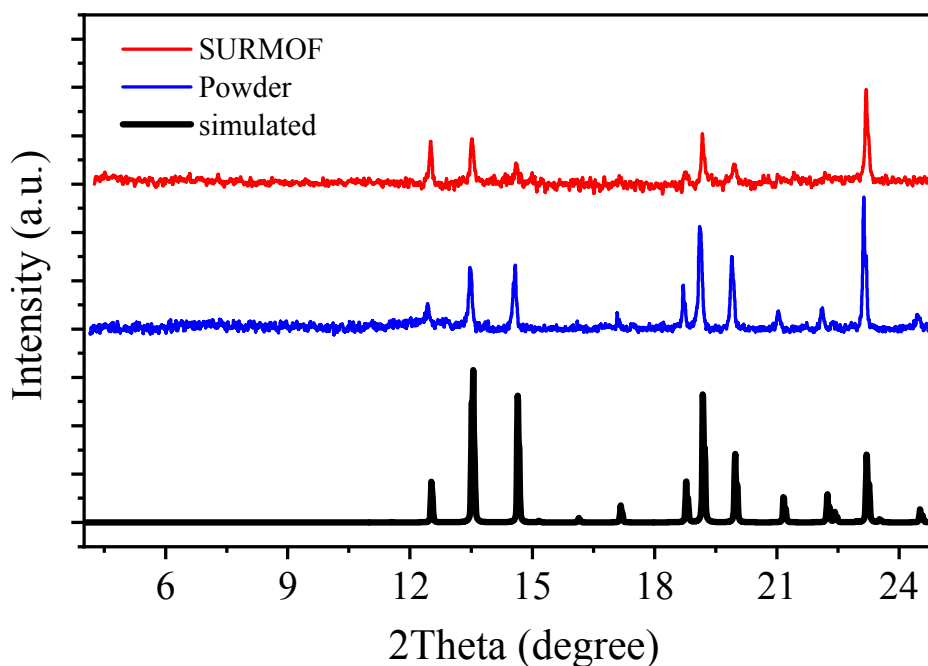
There are many methods to produce thin SURMOF films, however, the most widely used is the layer-by-layer (LbL) assembly deposition. This sequential deposition is rather distinct than the solvothermal powder synthesis, the LbL preparation can be done in controlled environment, but with a limited range of temperature, since the solvents should not evaporate during the process. For trivalent lanthanides ions, this is one big drawback, since it is rather difficult to predict and control Ln-MOF structures and small changes in the synthesis (such as solvent choice and temperature) lead to rather different crystal structures. We herein present the electrochemical synthesis of Ln-SURMOF films of Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub>. It was not possible, using the traditional LbL approach, to prepare Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub>-MOF as a thin film that we already prepared as a powder. We chose electrochemical deposition, which we found as an alternative to prepare Ln-SURMOFs with well and clearly determined structures. We are able to control the conditions and receive a defined SURMOF. The only drawback here is the crucial need of a conductive surface and no real control over the morphology and orientation.

We successfully prepared luminescent SURMOF thin films using an electrochemical deposition on an Au-coated Si-wafer in a really short deposition method of only 10 min. The large Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub>-MOF particles and the corresponding Tb<sub>2</sub>(bhc)(H<sub>2</sub>O)<sub>6</sub>-SURMOFs are the same are shown in Figure 3. A clearly visible luminescence is observable under UV irradiation in **Figure 3** a and d and the homogeneous formation of the film on the Au-coated Si-wafer can be assumed to be successfully.



**Figure 3** Single crystals prepared under solvothermal method under UV radiation (254nm) (a) Optical microscope images of the single crystals (b). Photograph of SURMOF prepared on gold coated Si substrate by electrochemical deposition (c) and the SURMOF under UV radiation (Exc. 254nm) (d).

The XRD pattern of the film matches the pattern of our single crystals that were solvothermally synthesized as shown in Figure 4. Also, the simulated XRD pattern for this structure is given. The out-of-plane XRD comparing the SURMOF prepared under electrochemical deposition with the powder and simulated XRD is in perfect accordance and proves the formation of the  $Tb_2(bhc)(H_2O)_6$ -MOF on the Au-surface.



**Figure 4** Out-of-plane XRD data of the polycrystalline thin-film SURMOF  $Tb_2(bhc)(H_2O)_6$  and a comparison with the powder and the simulated pattern.

### Conclusion

It was shown that electrochemical deposition can be applied on the growth of Ln-MOFs, anchored on flat substrates at the example of  $Tb_2(bhc)(H_2O)_6$ . We gave an insight into electrochemical deposition techniques of polycrystalline SURMOFs on conductive

substrates and show for the first time that the  $\text{Tb}_2(\text{bhc})(\text{H}_2\text{O})_6$ -MOF can be successfully deposited on the surface of an Au-coated Si-wafer. The XRD shows the exact framework parameters as the simulated pattern. The MOF is highly luminescent under UV irradiation and very uniform at the same time, as shown on photographs. The  $\text{Tb}_2(\text{bhc})(\text{H}_2\text{O})_6$  framework is a highly interesting one and further work is on-going to find an application for our SURMOF.

## Acknowledgement

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