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Shedding Light on the Dark Corners of MOF Thin Films: Growth and Structural Stability of ZIF-8 Layers Probed by Optical Waveguide Spectroscopy

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Abstract

Due to its many features and possible applications, metal-organic frameworks have attracted increasing attention in recent years. Within this type of materials, hydrophobic zeolitic imidazolate framework constituted of Zn^{2+} metal centers, coordinated by 2-methylimidazolate organic linkers (ZIF-8); has proved to be a highly versatile porous support compatible with diverse applications ranging from sensing platforms to electronics or energy-related devices. However, the study of a crucial parameter such as their structural stability towards exposure to different aqueous environments (relevant for a wide range of applications), remains only partially addressed and constitutes one of the main goals of the present work. By synthesizing mono- and multimode ZIF-8 optical waveguides for both optical waveguide and surface plasmon resonance spectroscopy, it was possible to characterize the ZIF-8 film growth, and its stability in different sensor-relevant liquid environments. Additionally, characterization of polyelectrolyte-modified films was explored, as it constitutes a relevant strategy in order to confer differential properties and enhanced stability to the films.

Introduction

Metal Organic Frameworks (MOFs)[1,2] can be defined as infinite porous coordination networks constituted by non-covalently linked organic and inorganic units, and offer numerous attractive properties including high surface area, chemical versatility and relatively high chemical and thermal stability. Owing to these features, MOFs have been used to pursue a wide range of applications; to name a few, gas sensors,[3] adsorbents for liquid and gas phase separations,[4] supports for drug-delivery systems,[5] or as separation membranes.[6] Moreover, the facile synthesis methods, and versatility regarding structural and surface chemistry fine-tuning via either pre or post-synthetic procedures[7,8] adds additional appeal to the integration of MOFs in catalytic and adsorption related mixed platforms.[9–11] This relatively new class of materials can be used to prepare films using different strategies depending on the targeted application; e.g., direct spin-coating using colloidal dispersions of nano/microcrystals generate thick and eminently non-smooth films, while surface mounted MOF quasi-monolayer thin films (SURMOFs), allow for the observation of non-bulk physical and chemical properties.[12–14] SURMOFs can be synthesized via the Langmuir-Blodgett method, or directly on top of substrates exposing suitable moieties which would act as primers for growth enhancement. It was also previously demonstrated, that post-synthetic modification of porous films (not only for MOF growth but in general; *e.g.*, mesoporous silica) using polyelectrolytes, can yield a pH-responsive material, or to allow modulation of polar character.[15–19]

An extensively used MOF is the so-called ZIF-8 (Zeolitic Imidazolate Framework, available commercially as BASF-BASOLITE-Z1200®); and features a sodalite-like crystalline microporous network based on Zn^{2+} clusters tetrahedrally coordinated by 2-methylimidazolate ions (mIm^-). ZIF-8 was successfully employed for separations,[20–22] in mixed membranes,[23–25] and

even for the synthesis of hybrid membranes.[26–29] There are many different strategies for synthesizing ZIF-8 films, but the hydro/solvothermal method remains the most popular, both in terms of simplicity and reproducibility. One of the areas in which the use of MOFs in general, and ZIF-8, in particular, is gaining increasing interest is sensor technologies,[30–32] which takes advantage of its high microporosity and surface area. A recent example of ZIF-8 films use for sensing applications is the work of Lu and Hupp,[33] in which the authors took advantage of the effect of different adsorbed analytes on the Fabry-Pérot interference phenomena (which gives rise to different colors) in order to detect such chemicals via UV-vis transmission spectroscopy. Propane, ethanol, water and water/ethanol mixtures were used taking in consideration the hydrophobicity of ZIF-8 micropores. In a similar fashion, Li *et al*. presented a photonic crystal fabricated with a structured ZIF-8 thin layer with narrow spectral resonances.[34] Time-resolved reflectometry performed on this material allowed for the monitoring of acetonitrile adsorption in the ZIF-8 layer. Another possible strategy is to probe the interaction between analyte and MOF indirectly with an external optical element. This strategy was followed by Tao *et al.* who used a ZIF-8 coated Micro Ring Resonator (MRR). Detection of Volatile Organic Compounds (VOCs) such as methanol, propylene, and benzene at concentration levels as low as ppb, was reported based on the induced refractive index (RI) changes, which detunes the MRR resonant wavelengths.[35] In a similar way, Kim *et al.* used a ZIF-8 coated optical fiber for monitoring a selected gas phase analyte.[36] Chocarro-Ruiz *et al*. recently developed an interferometric CO_2 sensor using a multilayer architecture which includes a Si_3N_4 waveguide coated with an adsorbing ZIF-8 nanocrystals layer, and a final protective polydimethylsiloxane (PDMS) coating. Detection limits of such sensor are 3130 ppm at room temperature and 774 ppm at room temperature.[37]

MOFs' stability towards aqueous solutions, or gases/water vapor mixtures is a matter of great importance[38–42] in order to harness their potential in practical applications. However, the literature shows that MOFs present different degrees of stability in aqueous media[43] and it is actually a matter of debate. For example, XRD analysis showed that ZIF-8 colloidal dispersions remain stable at room temperature and in boiling water, even for seven days.[44,45] Contrary to these observations, Zhang *et al.* showed that thin α-alumina supported ZIF-8 membranes are not stable towards water exposure and highly dependent on the pH value.[41] These examples show that characterization of both, surface and bulk properties, are necessary to address MOFs' stability in a definitive way.

Optical Waveguide Spectroscopy (OWS) technique and the close-related Surface Plasmon Resonance (SPR) spectroscopy, offer a convenient way for answering the above discussed questions, and eventually provide a tool for assessing changes in MOF layers exposed to different conditions. One of the earliest examples of the use of SPR and OWS for characterization of functional materials was given by Knoll.[46] Of course, each specific material acting as waveguide would bring new specific features for analyte detection or stimuli-responsive behavior. The review presented by Ma *et al*.[47] provides a compilation of a great variety of polymeric materials used as waveguides that can act as probes for many processes occurring inside nanoporous materials; e.g.,[48,49] characterization of block copolymers in thin films,[50] detection of structural changes on such films after exposure to different physical and chemical stimuli,[51] and variations on lateral film structure due nanoparticle incorporation.[52]

Synthesizing porous crystalline materials such as MOFs with the capability of acting as waveguides, opens the path not only for sensing applications but also for the observation of their structural stability. The synthesis of Lanthanide-based MOFs capable of acting as waveguides

has been reported already by Yang *et al.*[53] Considering the physical characteristics required for a material to be used as an optical waveguide,[54] and the typical properties and morphologies reported for MOF films and membranes,[55] it might look like a difficult task to bring these two worlds together. However, Hou *et al.* showed that it is possible to achieve sufficiently uniform ZIF-8 films by a method which can be classified as Liquid-Phase Epitaxial growth, taking advantage of appropriate surface-anchoring moieties.[56]

We hereby report the use of ZIF-8 MOF films as optical waveguides for the first time to the best of our knowledge. ZIF-8 optical waveguides were constructed on surface-modified gold substrates, in order to characterize film growth process and to determine structural stability towards the exposure to different aqueous environments. The suitability of this approach to elucidate the interaction of ZIF-8 films with modifying agents such as polyelectrolyte solutions (post-synthetic modification allows for the application of many different fine tuning steps in terms of material's structure-response as recently reported)[19,57] is demonstrated. In conjunction with effective medium theory, the optical response of ZIF-8 films can be quantified in terms of thickness, surface mass density and porosity variations, which are of the utmost importance for any sensor-related application.

EXPERIMENTAL SECTION

Chemicals

Sulfuric acid, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, or ZnN), 2-methylimidazole (or HmIm), 3-mercapto-1-propanesulfonic acid sodium salt (MPSA), 70 kDa Poly(4-styrenesulfonic acid sodium salt) (NaPSS), anhydrous methanol, sodium chloride, sodium phosphate monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$) and sodium phosphate dibasic dihydrate ($Na_2HPO_4 \cdot 2H_2O$) were purchased from Sigma Aldrich and used without further purification. Ultrapure *Milli-Q* water

(18,24 MΩ cm) was used for all the aqueous solutions and washing steps. Further details on the solutions used can be found in the supplementary information.

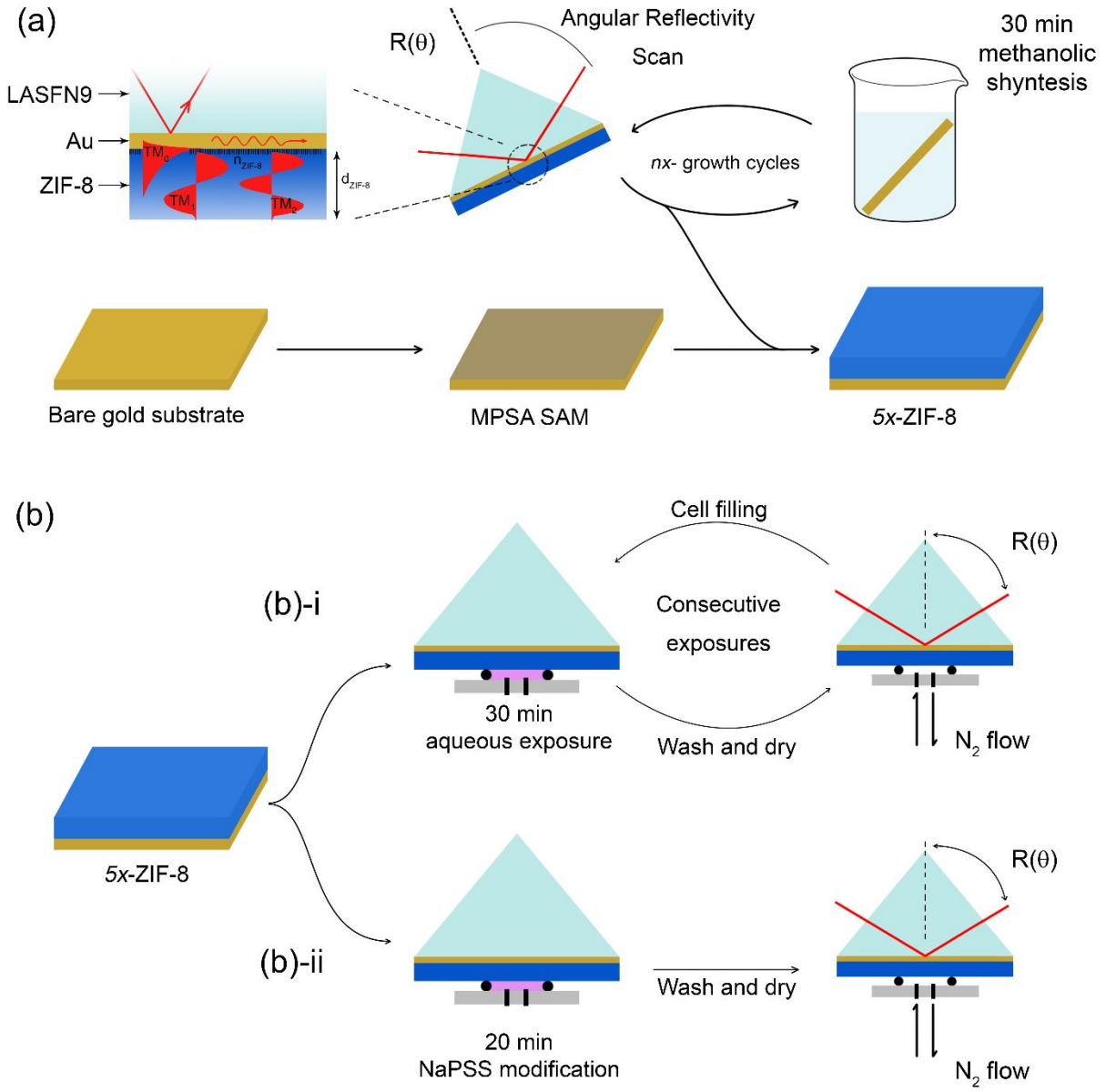
Optical setup

A HeNe laser beam (2 mW, λ=632,8 nm) was coupled to a right-angle LASFN9 glass prism in an SPR spectrometer instrument, operated in the Kretschmann configuration, see scheme S1. The ZIF-8 layers were grown on a LASFN9 glass substrate that was optically matched to the prism base by using immersion oil. All measurements were carried out under N_2 flow over the ZIF-8 waveguide surface by using a flow-cell that was clamped at the prism base. The angle of incidence θ of the laser beam incident on the ZIF-8 surface was controlled by a rotation stage (from Huber) and its polarization was set by Glan-Thompson polarizer as transverse electric (TE) or transverse magnetic (TM). The intensity of laser beam reflected at prism base with ZIF-8 waveguide film was recorded by a photodiode detector connected to a lock-in amplifier as a function of incidence angle R(θ). WINSPALL software (version 3.02, Max Planck Institute for Polymer Research, Germany) was used to fit the experimental data R(θ), based on Fresnel equations. In the fitting protocol, we assumed a single and isotropic layer that represents the ZIF-8 waveguide layer on top of the Cr and Au layers (see supplementary information file, table S1).

Synthesis of ZIF-8 films

Initially, the glass substrates were washed via subsequent 15 minutes ultrasonication steps: 1% Hellmanex III solution, pure water, and ethanol. Then 50 nm thick gold layer was prepared by thermal sputtering using a UNIVEX 450C apparatus (Leybold, Germany) on top of a LASFN9 glass substrate with a 2 nm Cr adhesion-promoting layer. ZIF-8 thin films were synthesized on

the top of the gold surface according to previously reported protocols.[19] Briefly, a gold-coated substrate was placed overnight in MPSA aqueous solution. Then, the substrate was washed with *Milli-Q* pure water and dried under a stream of N_2. The gold substrate with the MPSA self-assembled monolayer (SAM) exposing sulfonate-moieties was placed vertically in a 25 mM ZnN solution prepared in anhydrous methanol and then, an equal volume of 50 mM HmIm solution (also prepared in anhydrous methanol) was added. After 30 minutes, the substrate was washed generously with anhydrous methanol and dried under a N_2 stream. This sequence represents a single "growth cycle". By repeating these growth cycles, it is possible to control the thickness of the formed ZIF-8 film in a step-wise manner (see Scheme 1*a*). The films prepared in such way will be referred to as *nx*-ZIF-8, where *n* indicates the number of growth cycles used.



Scheme 1. Schematics of (a) ZIF-8 film growth, (b)-i *in-situ* probing of *5x*-ZIF-8 films in aqueous environments and (b)-ii *in-situ* probing of polyelectrolyte infiltration on *5x*-ZIF-8 films.

In-situ probing in aqueous environment

For *in-situ* experiments, a ~10 μL flow cell was mounted on top of the ZIF-8 layer surface. The cell was composed of a rubber O-ring pressed against the ZIF-8 surface by an acrylic slide

with inlet and outlet ports connected to tubing with a diameter of 0,8 mm. The flow-cell was filled with the tested solution and after the elapsed exposure time (30 minutes) in static conditions, the solution was removed from the flow-cell by using a syringe, subsequently rinsed with water, and completely dried with N_2 flow for 30 minutes (see scheme 1*b*-i). The N_2 flow was kept during the angular reflectivity scan R(θ).

***In-situ* probing of polyelectrolyte infiltration**

Modification with the NaPSS solution was carried *in situ*, similar to the exposure to the exposure to aqueous environments above mentioned: the polyelectrolyte solution was injected into the flow-cell for 20 minutes and then the surface was washed with water and dried in N_2 (see scheme 1*b*-ii). The film treated this way will be hereafter referred as *nx*-ZIF-8+PSS.

RESULTS AND DISCUSSION

Films growth and properties

Firstly, ZIF-8 film growth was optically characterized using resonantly excited waveguide modes. As Figure 1 shows, this excitation is manifested as a series of dips in the angular reflectivity spectrum R(θ) in both, TM and TE polarization, which change positions after each growth cycle. The waveguide modes supported by ZIF-8 films arise from the total internal reflection of light at the outer film interface and from the reflection at the inner gold surface. Depending on the thickness $d_{ZIF\text{-}8}$ and the refractive index $n_{ZIF\text{-}8}$ of the film, multiple guided waves referred to as TM_m or TE_m (m is the number of nodes of that particular field distribution) can be excited with the optical beam launched into the prism and hitting the layer structure (see

Scheme 1a). The excitation of guided waves is resonant, and occurs only at specific angles (θ), at which the laser beam is phase-matched with TM_m or TE_m modes traveling along the surface.

The synthesis of ZIF-8 film was characterized by performing angular reflectivity spectra R(θ) measurements after each growth cycle. As can be seen in Figure 1, R(θ) prior to ZIF-8 first growth cycle shows one resonance in the TM polarization (TM_0 mode corresponding to surface plasmon – SP – at the gold/air interface) and no resonance in TE polarization. After the first cycle of ZIF-8 growth, the resonant angle at which the SP is excited shifts by almost 30° and the excitation of the first guided mode TE_0 occurs in TE polarization. With the subsequent growth cycles (*nx = 2x, 3x…5x*), the SP angular position does not change significantly, TE_0 guided mode shifts to higher angular values, and additional higher order guided modes in both TM and TE polarizations, respectively, occur. After the complete film synthesis (five growth cycles), TM_0 (SP) and four guided modes $TE_{0,1}$ and $TM_{1,2}$ are observed. The measured reflectivity curves R(θ) have been fitted with a Fresnel reflectivity-based model in order to determine changes in the thickness $d_{ZIF\text{-}8}$ and refractive index $n_{ZIF\text{-}8}$ of the synthesized ZIF-8 films. For the first growth cycle, the fitting of two observed resonances due to SP and TE_0 mode, allows for determination of both $d_{ZIF\text{-}8}$=174±4 nm, and $n_{ZIF\text{-}8}$=1,357±0,005 parameters. For the films obtained after subsequent growth cycles (*nx = 2x* to *5x*), fitting all the observed resonances becomes not possible using the model, and the experimental SP angular position exhibits a slight deviation (between 1° and 1,3°) respecting to the fit. This difference can be attributed to the fact that probing distance of the SP is only around 100 nm from the gold surface, and thus it only partially overlaps with the first layer and it does not allow for probing of the increased thickness gained after additional synthesis steps. On the contrary, the guided modes $TM_{1,2}$ and $TE_{0,1}$ exhibit a more delocalized profile of electromagnetic field, and thus probe the entire thickness of ZIF-8

layer. These discrepancies indicate that effective optical properties of ZIF-8 films at the very interface with the gold surface (as observed via SP mode variations) may be slightly different than those values obtained from thickness-averaged determinations when probing the entire structure (as observed by $TM_{1,2}$ and $TE_{0,1}$). Further discussion addressing this point will be given, together with MPSA monolayer effect (see below).

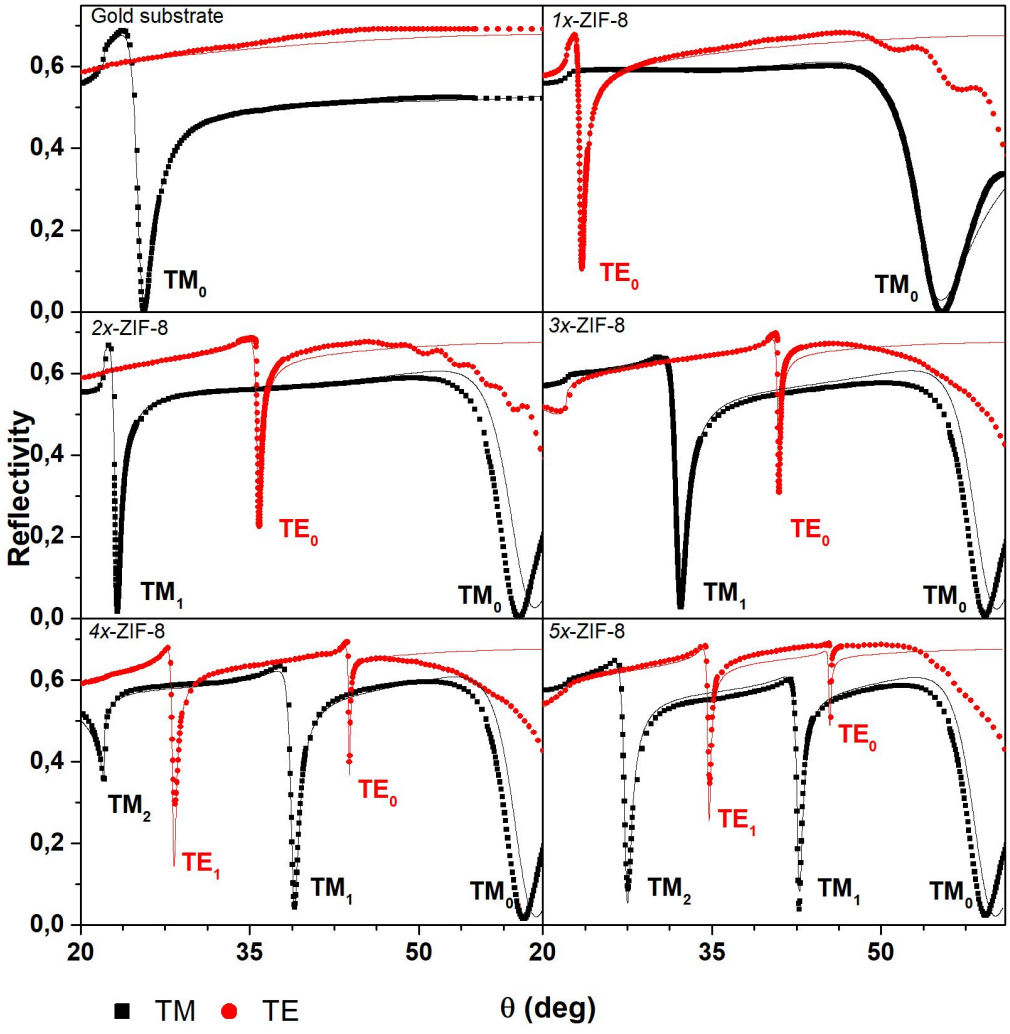


Figure 1. Cycle-by-cycle progression of the resonant coupling of guided modes under TM (black squares) and TE (red circles) polarization, and model fitting (full lines) for the 5x-ZIF-8 film construction.

It is possible to tackle the problem of the observed difference between the experimental and fitted curves for the SP angular position by adopting a slightly more complex bilayer model. Under this approach, the first layer would have the thickness found for the *1x*-ZIF-8 films, while the thickness of the second layer will change according to the increasing number of growth cycles (total thickness would be the sum of both assumed layers). Regarding the refractive index (RI), the values would change for each layer, in order to correctly fit the experimental curves. Fig. 2 shows as an example of how the two-layer model describes accurately the SP resonant angular position as well as all the guided modes.

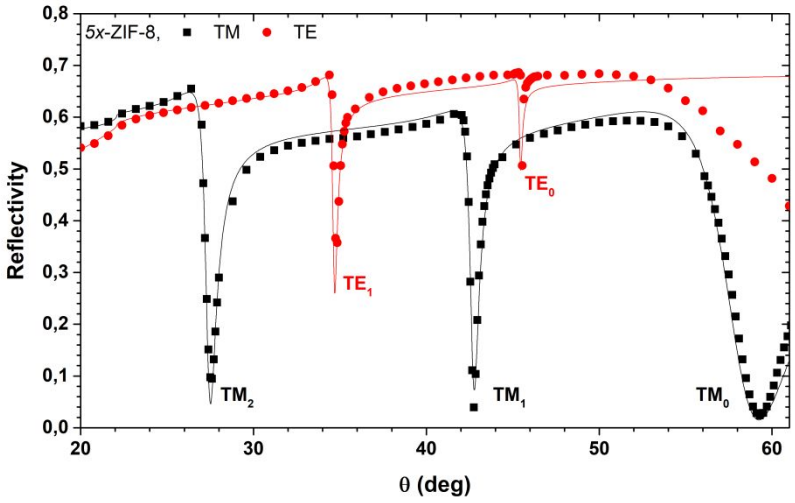


Figure. 2: Resonant coupling for the *5x*-ZIF-8 film under TM (black squares) and TE (red circles) polarization. Experimental points were fitted with a bilayer model (full line).

Although there is better agreement between experiments and fittings when using this two-layer model, the parameters obtained are quite similar to what is obtained using the much simpler one-layer model; *e.g.*, thickness progression was found to be exactly the same (138±3 nm/cycle). However, the two-layer model results in a RI value for the first layer which is lower than the RI obtained for the second layer. Moreover, having in mind that film porosity should only depend on its crystalline structure, one can safely disregard the two-layer model, since the porous

fraction was found to be larger for the first layer than for the second layer after applying Bruggeman's theory. Additionally, structural stability of ZIF-8 film after post-synthetic modifications (see below) can be better understood by assuming the existence of a single unit rather than a two-layer structure. Based on the above discussion, we selected the one-layer model for describing the observed behavior.

The parameters $d_{\text{ZIF-8}}$ and $n_{\text{ZIF-8}}$ were determined for each subsequent growth cycle, as presented in the supplementary information (Table S2). Evolution of film thickness is shown in Figure 3. These experiments reveal a linear increase in the thickness per growth cycle with a slope of 138±3 nm/cycle. The standard deviation in thickness of about 2% indicates a highly reproducible synthesis process as determined by comparing four equivalent *5x*-ZIF-8 films, each of which was measured and fitted on three different spots. From this analysis, it was also possible to calculate an average real part of the refractive index of ZIF-8: $\text{Re}\{n_{\text{ZIF-8}}\}$=1,352±0,004 at λ=632,8 nm, in good agreement with previously reported values.[42] Using the Bruggeman's Effective Medium Theory (calculation details can be found in the supporting information) porous fraction of 0,6 was determined for all prepared *5x*-ZIF-8 films. This result is in line with previously reported porosity values for similar ZIF-8 crystals (58,8 %).[58]

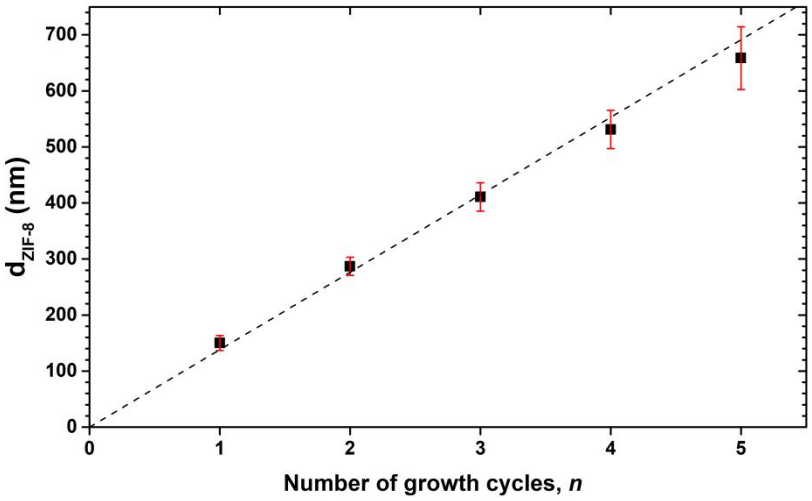


Figure 3. Thickness evolution ($d_{ZIF\text{-}8}$) upon sequential synthesis of *5x*-ZIF-8 films. Each value was averaged from measurements on 4 different samples and 3 distinct spots. Error bars correspond to standard errors and the dashed line represents the linear fit (r^2 = 0,998) of the measured values.

Interestingly, the observed growth rate of 138 ± 3 nm/cycle is significantly higher than what previously reported in the literature (~70 nm/cycle)[56]. This difference can be ascribed to the effect of sulfonate moieties introduced to the gold interface by the MPSA SAM primer.[59,60] These anchoring moieties are crucial for obtaining an homogenous ZIF-8 layer that can serve as an efficient slab waveguide. For comparison, Figure S1 (see supporting information) shows the progression of the angular reflectivity scans R(θ) for the growth of ZIF-8 at bare gold surfaces; *i.e.*, without MPSA. The experiment reveals that the angular width of TM_0 (SP) resonance is significantly broader and that higher waveguide modes are not apparent. This can be ascribed to the strongly deteriorated lateral homogeneity of the ZIF-8 film, which can be quantified by the use of the effective extinction coefficient κ of the ZIF-8 layer (imaginary part of the refractive index $\mathrm{Im}\{n_{ZIF\text{-}8}\}$). This parameter can be determined by the fitting analysis of R(θ) and

increasing κ is typically associated with a broadening of the observed dips in R(θ). Effective extinction coefficient κ takes into account scattering on defects with a size comparable or higher than the used wavelength λ and it is important to note neither Zn^{2+} nor mIm^- (which are used to synthesize the ZIF-8 films) exhibit absorption at selected wavelength λ.

Table 1 provides the comparison of thickness $d_{ZIF\text{-}8}$ and extinction coefficient κ determined for the films prepared on a gold surface without and with an MPSA SAM. MPSA was expected to promote heterogeneous nucleation of ZIF-8 on the surface triggered by pre-coordination of Zn^{2+} ions by the surface-exposed sulfonate moieties .[60] There were two main results supporting the assumption above. First, thickness value $d_{ZIF\text{-}8}$ for the *1x*-ZIF-8 is almost 20 times higher when using MPSA anchoring, but for the next growth cycles these differences start to decrease, and at the end, *5x*-ZIF-8 synthesized on an MPSA SAM is only 1,5 times greater than when no MPSA SAM is present. Second, the extinction coefficient κ of films prepared on MPSA SAM is at least one order of magnitude lower than that without this anchoring layer. In other words, by providing these initial nucleation points distributed across the gold surface, a higher density of (probably smaller) nuclei is achieved, and ultimately causes a much more homogeneous film compared to what is obtained when nucleation occurs preferentially in the homogeneous phase and nanocrystals thus formed start to aggregate to form the film. The fact that the extinction coefficient κ decreases with film growth progression over MPSA SAM also supports the hypothesis, as each growth cycle is influenced by the presence of the previously synthesized ZIF-8 layer. The above interpretation brings further support for the use of a single layer model to describe the system; *i.e.*, each growth cycle does not generate layers with different morphology but rather contribute to a one-block structure with increasing thickness.

Growth Cycle (*nx*)	Thickness $d_{ZIF\text{-}8}$ (nm)		ratio	Ext. coefficient κ		ratio
	With MPSA	Without MPSA	d_{wo}/d_w	With MPSA	Without MPSA	κ_{wo}/κ_w
1	150	8,8	0,06	0,0035	0,312	89
2	287	39	0,14	0,0030	0,276	92
3	410	91	0,22	0,0016	0,150	94
4	530	359	0,68	0,0017	0,049	29
5	658	426	0,65	0,0017	0,036	21

Table 1. Comparison of thickness ($d_{ZIF\text{-}8}$) and extinction coefficient (κ) for *5x*-ZIF-8 films synthesized on a gold surface with and without an MPSA nucleation layer.

Structural stability of ZIF-8 films in aqueous environment

The stability of the ZIF-8 film is crucial for determining its possible applications. A useful quantity to evaluate this feature is the layer surface mass density Γ, which takes into account the potential loss in the porous material due to etching caused by exposure to different solvents. Surface mass density can be shown to be proportional to the term $d_{ZIF\text{-}8}(1\text{-}f_{pores})$, where the volume fraction of pores f_{pores} can be obtained from fitted $\mathrm{Re}\{n_{ZIF\text{-}8}\}$ by Bruggeman effective medium theory (see supporting information).

In order to study the stability of synthesized materials, *5x*-ZIF-8 films were investigated after they were exposed to *Milli-Q* water, NaCl 50 mM aqueous solution, and finally to 10 mM PBS, pH=8, aqueous buffer. NaCl was chosen in order to regulate ionic strength because Na^+ and Cl^- ions were proved to have no effect on the crystalline structure of ZIF-8.[61,62] Figure 4 shows the relative changes between final and initial thicknesses as $(d^f_{ZIF-8} - d^i_{ZIF-8})/d^i_{ZIF-8}$ (top), and the relative changes between final and initial Γ as $(\Gamma_f - \Gamma_i)/\Gamma_i$ (bottom) after sequential (30 min)

static exposure to each of the above solutions. Results obtained reveal that films exposed to Milli-Q water and NaCl experiment some swelling; a 15% thickness increase was detected compared to what observed for freshly prepared films after five exposure cycles (equivalent to 150 min). Such swelling is accompanied with a decrease in surface mass density Γ, which reaches a 20% loss of ZIF-8 mass after five exposures (see table S3 for the further details). Interestingly, ZIF-8 films were found to behave dramatically different in PBS solution. The film underwent an initial thickness increase by 12% after 30 min exposure of PBS followed by a gradual decrease to a final value of 50% after five exposure cycles. In addition, Γ shows a continuous decrease until a loss of almost 65%.

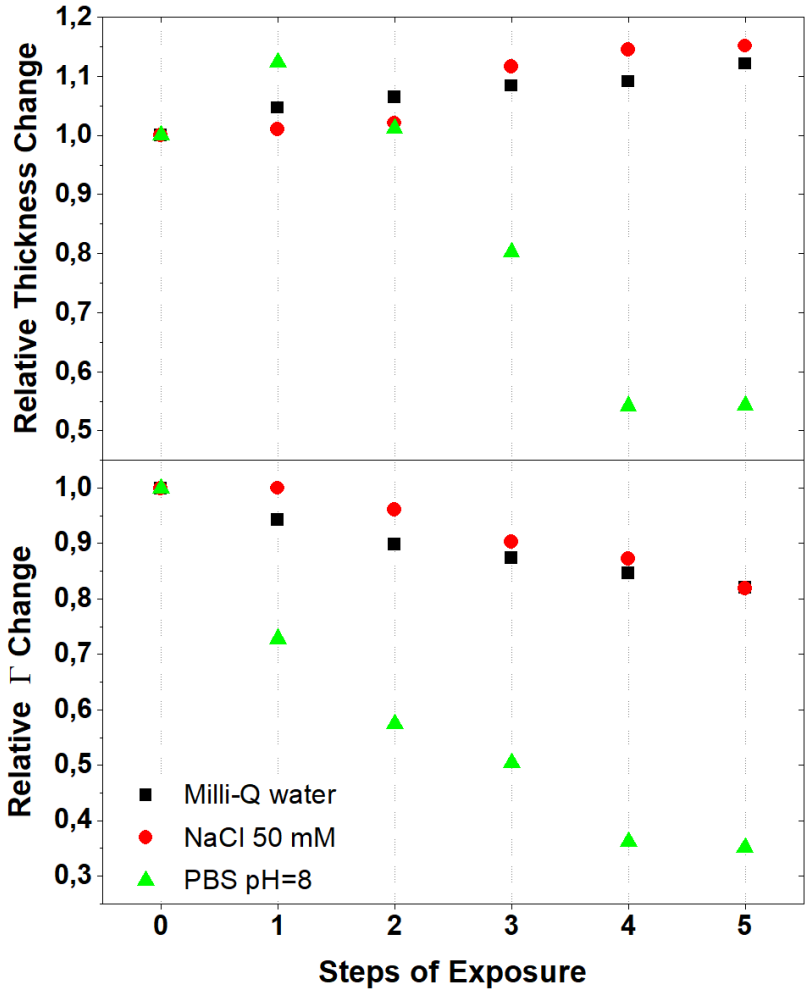


Figure 4. Relative changes on Thickness (top) and Γ (bottom) for *5x*-ZIF-8 films after five consecutive 30 min exposures to *Milli-Q* water (black squares), 50 mM NaCl (red circles) and 10 mM PBS, pH=8 (green triangles).

The observed changes in Γ can be ascribed to variations in the thickness as well as in the porous fraction, f_{pores}. Figure 5 provides this information, which confirms that ZIF-8 films gradually undergo an irreversible swelling together with a release of occluded material when exposed to *Milli-Q* and NaCl 50 mM solution. Contrary to these experiments, the porous fraction f_{pores} abruptly increases by 20% after the first exposure to PBS and afterward it does not change substantially. These observations indicate that, after exposure to *Milli-Q* water and 50 mM NaCl solution, the film slowly swells and the porosity f_{pores} increases. On the other hand, exposure to PBS causes the film to experience an initial thickness increase followed by a gradual material loss without collapsing, which decreases its thickness although porosity shows no variation. It is worth mentioning that Wang et al. already reported such effect for ZIF-8 exposed to PBS solutions[61] but higher pH values were used (9,0 and 13,2), for which the material is not expected to be stable towards hydrolysis. Additionally, in the same reported work, higher concentrations were used which translates to almost 100 mM ionic strength and means that no direct comparison is possible to the results hereby presented.

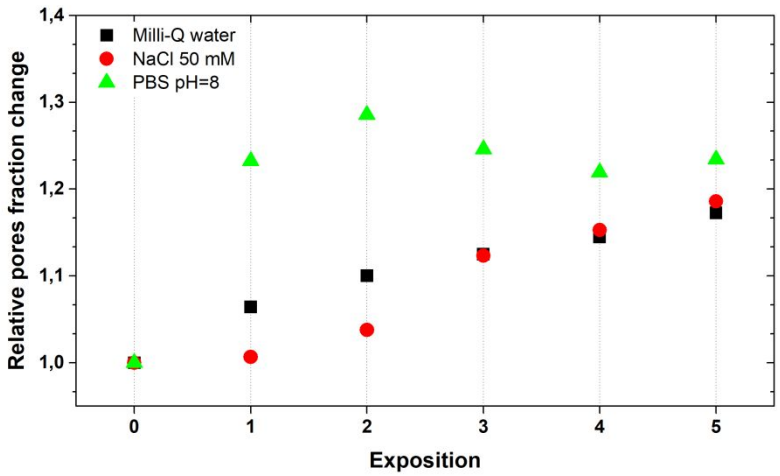


Figure 5. Relative porous fraction change for *5x*-ZIF-8 films after five consecutive exposures to Milli-Q water (black squares), 50 mM NaCl (red circles) and 10 mM PBS, pH=8 (green triangles).

Polyelectrolyte/ZIF-8 interaction

It was previously reported that PSS can modify the polar character of ZIF-8 films' porosity, which in turn, alters effective diffusion coefficients.[19] This opens the path for the use of diffusion-reaction approach for the synthesis of film-embedded metal nanoparticles. The successful polyelectrolyte capping of films constituted by porous materials depends on the nature and strength of the interactions between capping agent and the pore walls. Possible architectures obtained are either confined (polyelectrolyte remains segregated on a different phase causing no effect on the porous material) or segregated (polyelectrolyte percolates the entire porous structure causing a change on the overall films' polar character). In order to gain insight into the outcome of such processes, a series of OWS measurements were carried out on films that were

exposed to PSS polymer solutions (PSS was selected due to both its anionic nature and its affinity towards Zn^{2+} moieties on ZIF-8). Figure 6 shows a comparison of reflectivity curves R(θ) before (*5x*-ZIF-8) and after modification with PSS (*5x*-ZIF-8+PSS). These curves reveal that the angles at which the resonant coupling to guided waves occurs are shifted by about 3°. By fitting experimental data obtained, a (relatively) strong increase in RI from $n_{ZIF\text{-}8}$=1,352 to 1,375 was determined, together with a small (1,74%) increase of film thickness $d_{ZIF\text{-}8}$. Since the strong refractive index increase relates to a decrease in f_{pores}, it can be assumed that PSS efficiently percolates the entire film. This assumption is supported by the fact that, if the PSS would remain mostly surface-confined, the SP (TM_0) resonance angular position should not change. However, the surface plasmon waves probing the gold/ZIF-8 interface, show a distinct angular change which indicates that PSS was distributed through the whole film (see supporting information). Although the experimental data was successfully fitted by using a single and isotropic layer, the observed shifts on the different guided modes allow for hypothesizing that, even though PSS percolates the whole film structure, some lateral gradient concentration of PSS could be expected. By applying effective medium theory, it was possible to calculate the remaining porous fraction after PSS modification and to obtain an estimation of the polymer fraction in the film (see supporting information). Briefly, the final composition obtained was 40,9% of ZIF-8 (framework), 55,2% empty pores, and 3,9% of polymer. It is possible to say thus, that PSS modification does not represent a significant decrease in film porosity, which is a core property when thinking MOFs as sensing platforms.

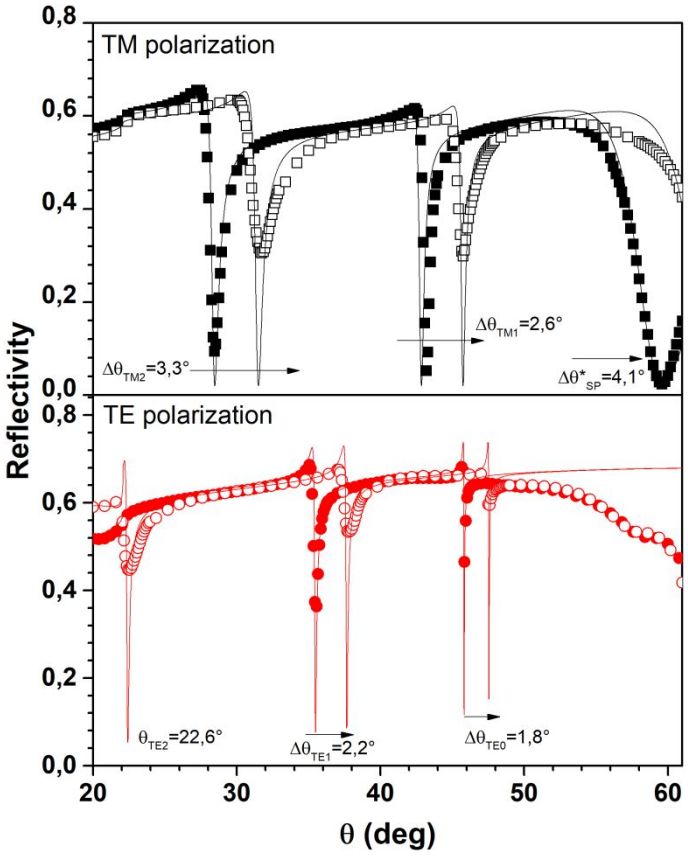


Figure 6. Resonant coupling of guided modes under TM (black squares, top) and TE (red circles, bottom) polarization for a *5x*-ZIF-8 film (filled dots) and *5x*-ZIF-8+PSS film (empty dots).

CONCLUSIONS

Surface plasmon resonance in combination with optical waveguide spectroscopy provided new insight into the growth and structural stability of ZIF-8 films towards exposure to aqueous solutions relevant for a wide range of applications. For this end, we have for the first-time synthesized wave-guiding MOF-films. We have found a linear thickness increase for films growth cycles and showed how each of those cycles is strongly influenced by the previous step in terms of the chemical identity of the starting layer. The experimental setup used allowed us to

confirm that substrate surface modification with MPSA monolayer primer is critical in order to achieve ZIF-8 layers that can effectively act as monomode or multimode slab optical waveguides. We have shown also, that ZIF-8 films are structurally stable under *Milli-Q* water and NaCl 50 mM solutions, and that the choice of a proper buffered media needs to be carefully considered (i.e., PBS buffer was shown to be deleterious for film stability in the case of ZIF-8 MOF). It was demonstrated that polyelectrolyte post-synthetic modification of ZIF-8 films modify their surface properties without detrimental effects on the porosity, thus providing a powerful tool for fine-tuning their transport properties.

Supporting Information

The Supporting Information is available free of charge on the ACS website: A brief description of OWS-SPR technique as well as experimental relevant data.

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