Electronic Supplementary Information

Metal-organic frameworks meet polymer brushes: enhanced crystalline film growth induced by macromolecular primers

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This supporting information contains 10 pages, including the details of synthesis and characterization for films used. This document includes **3** additional references, **7** figures, and this cover page.

1. Synthesis and characterization of Polymer Brushes.

Sulfopropyl methacrylate potassium salt polymer brushes were obtained by aqueous surface-initiated atom transfer radical polymerization (SI-ATRP) technique on Si/SiO_2 and gold coated quartz sensor. To this end, firstly ATRP initiator was grafted on the substrate surface according to already published procedure.[1]

ATRP initiator on Si/SiO_2 substrate. The Si/SiO_2 substrates were modified by immersion in a solution 2% v/v of 3-aminopropyltrimethoxysilane in ethanol for 1 hour at 30°C. The substrates were then washed with ethanol and cured for 1 h in an oven at 150°C. After, the silane-modified substrates were introduced in a solution 25 mM of α- bromoisobutyryl bromide (containing triethylamine, also in a concentration of 25 mM) in dry THF under N_2 at room temperature overnight. The activated substrates were washed with THF and dried under a stream of N_2.

ATRP initiator on gold coated quartz sensor. The sensors were modified by immersion in a solution of ω-mercaptoundecyl bromoisobutyrate in ethanol (5 mM) for 12 hours at room temperature. The washed substrate was dried under a stream of N_2.

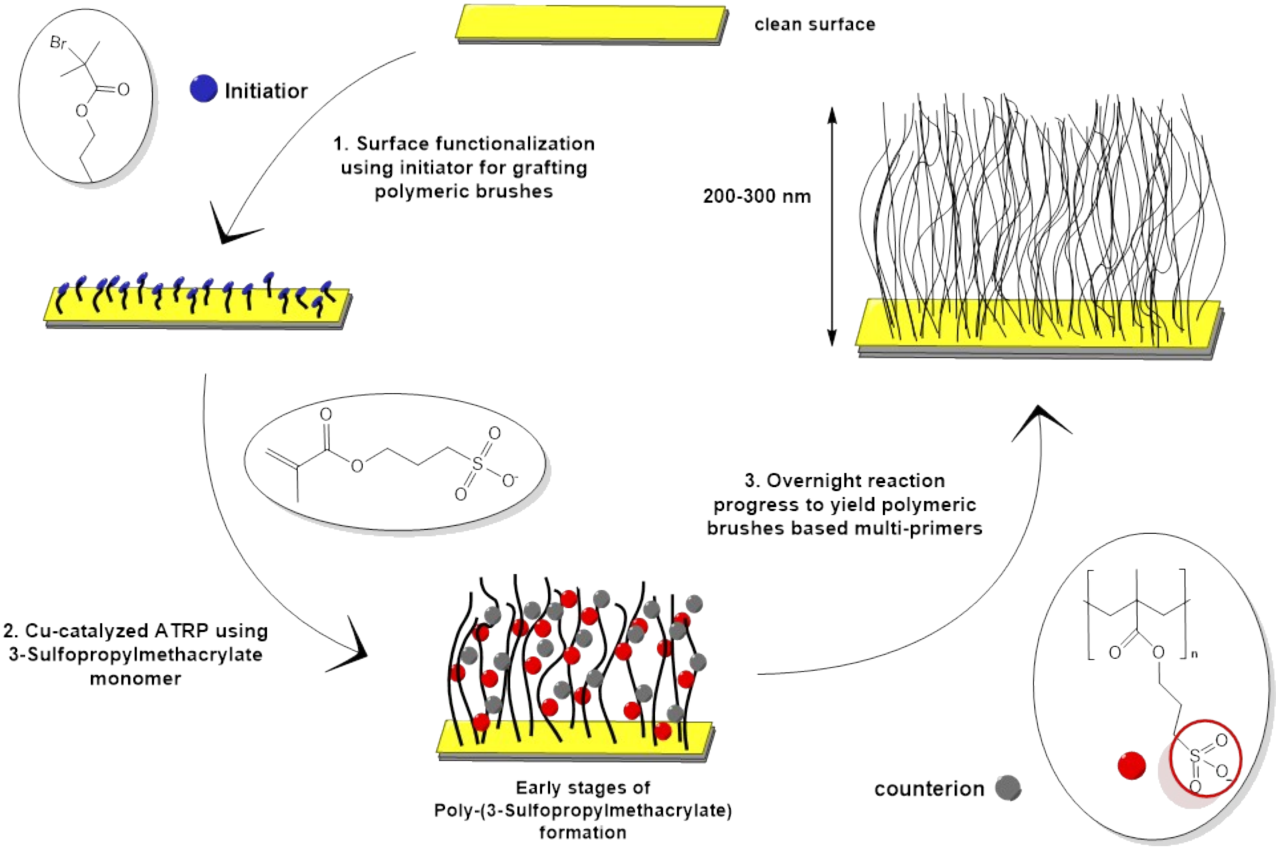


Figure S1. Schematic of synthetic route for the polySPM brushes.

Brushes growth. The ATRP polymerizations were carried out in the same way for both initiator substrates types, Si/SiO_2 and gold coated quartz sensor, according Ramstedt et al method.[2] A solution of 17.29 g of 3-sulfopropylmethacrylate potassium salt in 20 mL of methanol and 10 mL of water containing 0.651 g of BiPy and 0.0114 g of $CuCl_2$ was degassed by N_2 bubbling for an hour. Then 0.1648 g of CuCl was added and the mixture, under N_2, was left for 15 min. Simultaneously, both initiator substrates, Si/SiO_2 and gold coated quartz sensor, were sealed in a Schlenk tubes and degassed through vacuum/N_2 cycles. Then, the reaction mixture was syringed into these Schlenk tubes, adding enough volume to cover the samples completely. The mixture was left 2 days under N_2 and then, the substrates were removed and washed with deionized water and dried with N_2.

Figure S1 displays an schematic procedure of the above described process for brush growth. **Figure S2** shows a typical image obtained via Atomic Force Microscopy, in which brushes bundles can be observed on the otherwise smooth Si/SiO_2 substrate surface. **Figure S3** shows a comparison of native K^+ versus exchanged Zn^{2+} poly-SPM brushes as determined via ATR-FTIR.

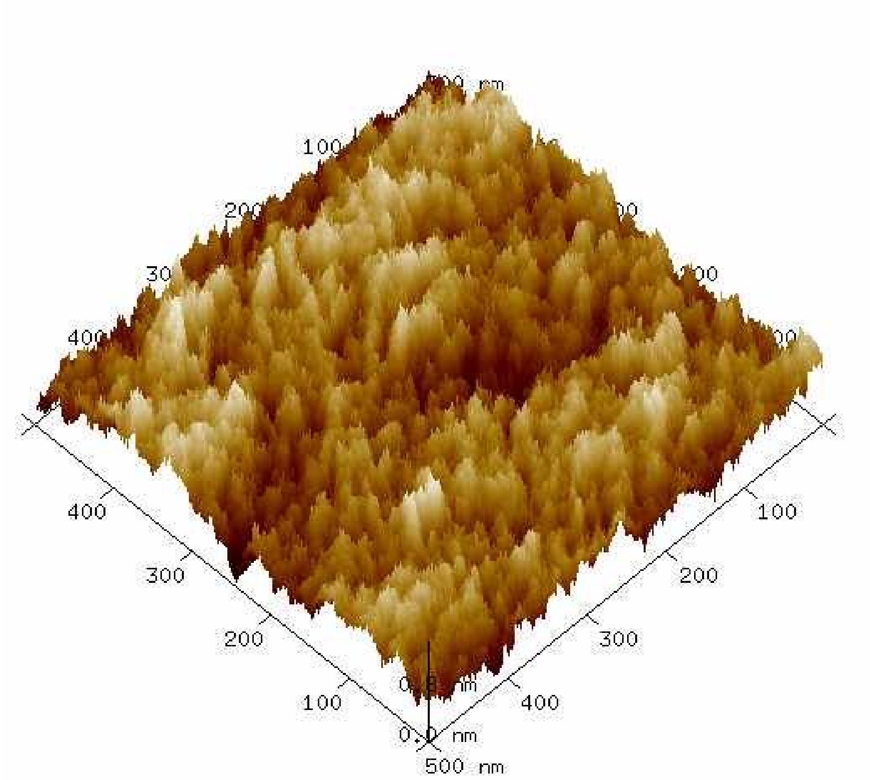


Figure S2. Atomic force microscopy (AFM) image showing 250 nm thick brush grown over Si substrate. Surface roughness over the scanned area using AFM was ≈ 1.4 nm.

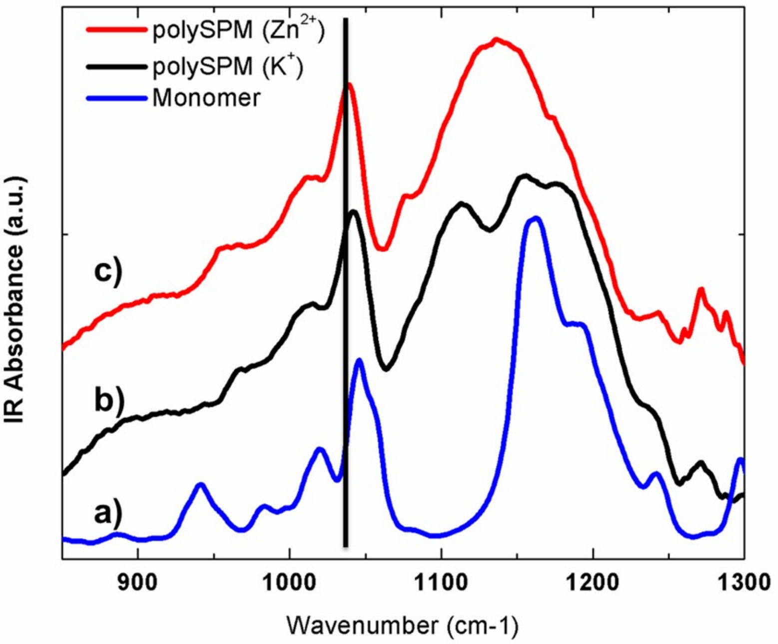


Figure S3. ATR-FTIR spectra of **(a)** SPM monomer, **(b)** as-synthesized polySPM brush, and **(c)** brush soaked in 50 mM Zn^{2+} methanolic solution. Changes in both asymmetric (≈ 1200 cm^{-1}) and symmetric sulfonate stretching (≈ 1045 cm^{-1}) modes, evidences the strong coordination between Zn^{2+} ions and sulfonate moieties.

2. Synthesis of ZIF-8 MOF.

Direct growth – QCM experiments. Synthesis of ZIF-8 was carried via room temperature mixture of methanolic $Zn(NO_3)_2.6H_2O$ 25 mM, and HmIm 50 mM / Sodium Formate 50 mM methanolic solutions in a flow cell Quartz Crystal Microbalance (QCM2000 Stanford Research Systems) setup.

Nanolayer-by-Nanolayer sequential-one-pot growth (NbN-SOP). In glass vials where the Si functionalized substrate (either with polySPM brushes or MPSA self-assembled monolayers) was placed obliquely, enough volume of the above described freshly prepared precursor solutions, was mixed for 10 minutes. After this time lapse, substrates were extracted, rinsed with methanol and dried with Nitrogen. This whole sequence constitutes one growth cycle. As non-invasive technique for film thickness determination in between SOP cycles, we used spectroscopic ellipsometry after drying. **Figure S4** shows the color change, arising not from colorless ZIF-8, but from optical interference in the visible region which depends on film thickness (all experiments were carried on a J.A. Wollam Co. – ALPHA-SE apparatus).

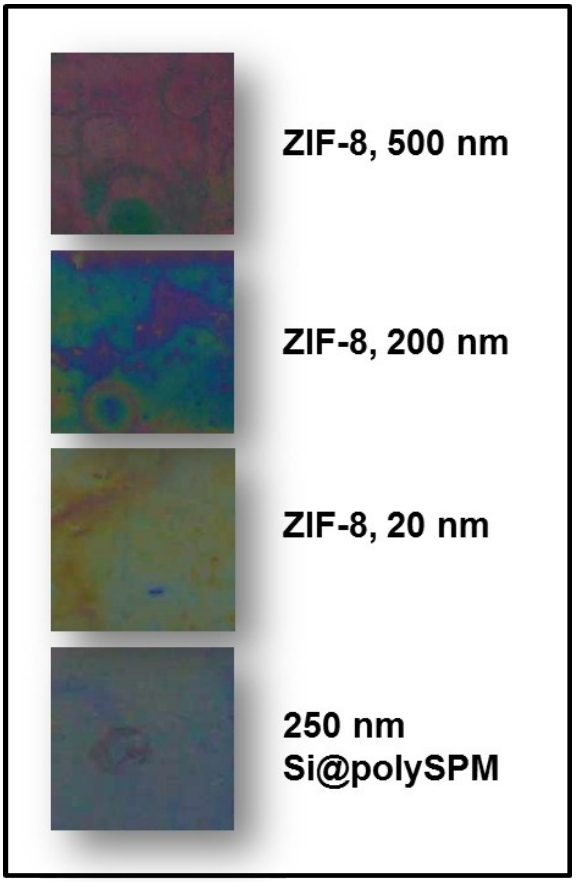


Figure S4. Films thickness evolution for ZIF-8 synthesis on Si@polySPM brushes (≈ 250 nm thick) substrates as the number of synthesis cycles increased. The different colors obtained arise from thickness-dependent interference phenomena.

X-ray diffraction. All calculated XRD were obtained from Cambridge Crystallographic Data Base ZIF-8 files using Mercury® software. ZIF-8 XRD patterns corresponding to all the synthesized films, were recorded at room temperature under ambient conditions on a Brucker D8 Discover X-ray diffractometer.

Scanning Electron Microscopy. ZIF-8 films were characterized using scanning electron microscope (SEM, Hitachi S-3200N, available at "*Servicio de Microscopía Electrónica de Barrido y Microanálisis del LIMF - Facultad de Ingeniería – UNLP*").

FTIR-ATR. ZIF-8 films show characteristic vibrational bands as reported in the literature as presented in **Figure S5**. All experiments were carried using Varian – 660-IR apparatus equipped with ATR accessory.

Figure S5. ATR-FTIR of synthesized ZIF-8 material.

3. Ellipsometry.

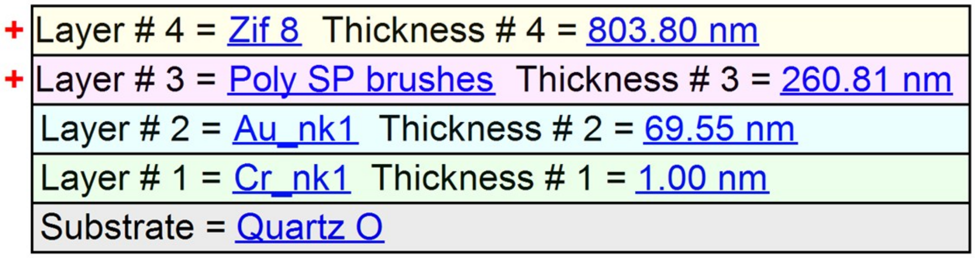
The refractive index and the thickness of thin films were measured by spectroscopic ellipsometry performed on a UV-visible (380-900 nm) spectroscopic ellipsometer ALPHA-SE from Woollam at an incidence angle of 70° , and the data analysis was performed with the *CompleteEASE®* software. The layered optical model built for data analysis for samples supported on QCM crystals is reported in **Figure S6**.

Polymer brushes layers are modeled using the Cauchy dispersion relation, which describes the optical behavior of a transparent film in the visible spectral range:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}$$

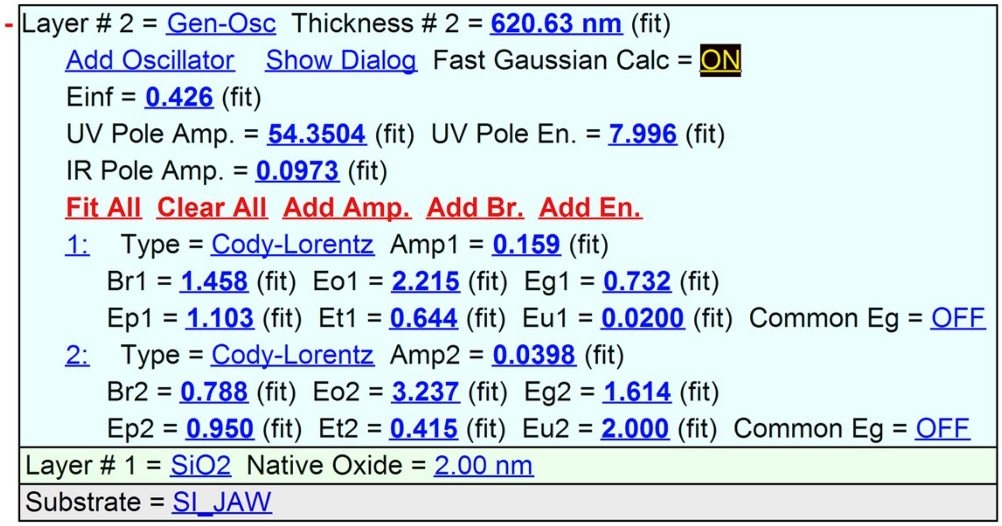
The A_n parameter relates to the approximate amplitude for the material refractive index, while B_n and C_n parameters provide the shape of the index versus wavelength.

MOF are modeled with a B-Spline layer in the first instance, and the optical constants obtained have been parametrized later with a Gen-Osc layer. The B-spline layer defines the optical functions by connecting a set of cubic polynominal splines, using a series of control points equally spaced in photon energy, allowing the optical constants to follow spectral features up to the B-spline resolution (spacing between spline nodes).[3] The Gen-Osc layer allows a combination of various oscillator lineshapes to match the shape of the material optical constants and parametrize them with a simple analytic expression. In the case of ZIF-8 films we parametrize the optical constants using two Cody-Lorentz oscillators, as reported in **Figure S7**.



+ Layer # 4 = Zif 8 Thickness # 4 = 803.80 nm
+ Layer # 3 = Poly SP brushes Thickness # 3 = 260.81 nm
Layer # 2 = Au_nk1 Thickness # 2 = 69.55 nm
Layer # 1 = Cr_nk1 Thickness # 1 = 1.00 nm
Substrate = Quartz O

Figure S6: Model used to analyze samples supported on QCM crystals: On the Quartz substrate there is a Chromium layer of 1 nm, then a Gold layer of about 70 nm, then the Polymer brushes layer and the Zif-8 MOF film on top.



- Layer # 2 = Gen-Osc Thickness # 2 = **620.63 nm** (fit)

Add Oscillator Show Dialog Fast Gaussian Calc = ON

Einf = **0.426** (fit)

UV Pole Amp. = **54.3504** (fit) UV Pole En. = **7.996** (fit)

IR Pole Amp. = **0.0973** (fit)

Fit All **Clear All** **Add Amp.** **Add Br.** **Add En.**

1: Type = Cody-Lorentz Amp1 = **0.159** (fit)

Br1 = **1.458** (fit) Eo1 = **2.215** (fit) Eg1 = **0.732** (fit)

Ep1 = **1.103** (fit) Et1 = **0.644** (fit) Eu1 = **0.0200** (fit) Common Eg = OFF

2: Type = Cody-Lorentz Amp2 = **0.0398** (fit)

Br2 = **0.788** (fit) Eo2 = **3.237** (fit) Eg2 = **1.614** (fit)

Ep2 = **0.950** (fit) Et2 = **0.415** (fit) Eu2 = **2.000** (fit) Common Eg = OFF

Layer # 1 = SiO2 Native Oxide = 2.00 nm

Substrate = SI_JAW

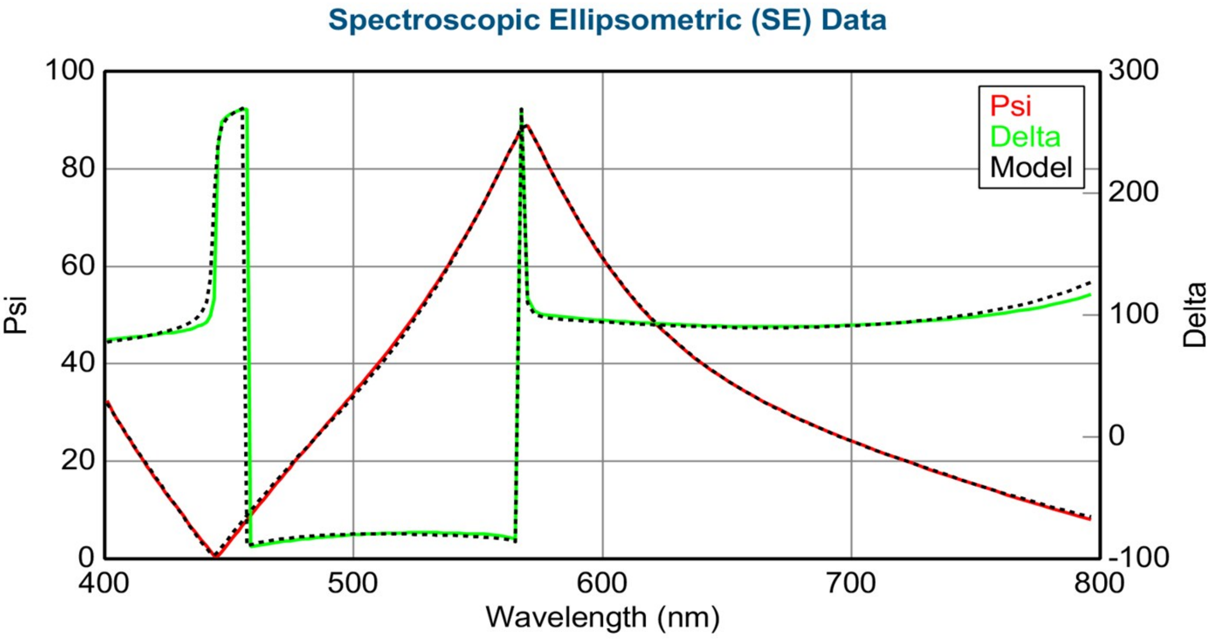


Figure S7: Model used to analyze Zif-8 MOF layers supported on silicon and match of the model (dashed black line) with experimental data (red and green lines). The MOF film is modeled with a Gen-Osc layer using two different Cody-Lorentz oscillators.

4. XPS experiments

Chemical composition of films, and the ion exchange effect were determined using X-ray photoelectron spectroscopy (XPS). XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Aluminum Kα line of 1486.6 eV energy and 300 W), placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 1.

The selected resolution for all the experiments presented was 30 eV of pass energy and 0.5 eV/step for the general survey spectra; and 15 eV of pass energy and 0.15 eV/step for each detailed spectrum. All measurements were made in ultra high vacuum (UHV) at a chamber base pressure of approx. $3x10^{-8}$ mbar. An electron flood gun was used to neutralize sample charging effect, and peak positions were calibrated by fixing the C 1s peak position at 284,6 eV.

5. Bibliography

(1) Brown, A. A.; Khan, N. S.; Steinbock, L.; Huck, W. T. S. *Eur. Polym. J.* **2005**, *41* (8), 1757–1765.

(2) Ramstedt, M.; Cheng, N.; Azzaroni, O.; Mossialos, D.; Huck, W. T. S.; Mathieu, H. J.; Huck, W. T. S. *Langmuir* **2007**, *23* (6), 3314–3321.

(3) Johs, B.; Hale, J. S. *Phys. status solidi* **2008**, *205* (4), 715–719.