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Polyelectrolyte Brushes as Ink Nanoreservoirs for Microcontact Printing of Ionic Species with Poly(dimethyl siloxane) Stamps**

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In this work a new variation of microcontact printing is described, which is used to transfer chemical patterns onto different substrates. The approach is based on the use of conventional elastomeric stamps modified with polyelectrolyte brushes. It is demonstrated that, by using stamps modified with brushes acting as preconcentrating/sorbent nanolayers, it is possible to control the uptake of aqueous inks containing ionic species. This controlled uptake can be easily used for site-selective delivery of the loaded species by means of soft lithography. The potential of this approach is demonstrated by creating patterned counterion domains in a flat polyelectrolyte brush and by promoting a site-selective metallization through galvanic displacement reactions with reactive species.

1. Introduction

The ability to transfer chemical species onto surfaces in an accurate and controlled manner has become of particular relevance in diverse nanotechnology-related disciplines like materials science, surface chemistry, and biology. During the last decade many interesting strategies have been developed in order to achieve this goal. Major technologies include dip-pen nanolithography (DPN),^[1] nanopipette writing (nPW),^[2] and microcontact printing (μ CP).^[3] DPN and nPW are serial writing techniques based on scanning a nanoscale probe over a surface through a feedback loop. Although this renders the patterning slow, the big advantage of both techniques is the ability to deliver controllable amounts of molecules to the surface. On the other hand, gaining control over the amounts of material deposited when stamping chemical domains onto a surface, by means of an “inked” elastomeric stamp (μ CP), is not an easy matter. This aspect of μ CP is the aim of current research efforts within diverse groups devoted to understanding the physico-

chemical aspects of the inking process.^[4,5] Remarkably, μ CP has been demonstrated to be a suitable technique for patterning 20 in. wafers in one step.^[6,7]

The possibility of transferring complex patterns onto large surfaces in a single step makes μ CP a simple, practical, and convenient strategy for introducing a variety of molecules, ranging from biomolecules to inorganic complexes, onto substrates of different natures.^[8–12] The different noncovalent interactions in the system “stamp–ink–substrate” have been exploited recently to further broaden the scope of μ CP. One illustrative example is supramolecular μ CP, where host molecules are site-selectively delivered onto substrates modified with guest monolayers acting as molecular “printboards”.^[13,14] The surfaces of the poly(dimethyl siloxane) (PDMS) stamps traditionally used in μ CP have also been modified to broaden the range of inks that can be printed. Delamarche and co-workers fabricated PDMS stamps with amino-terminated poly(ethylene glycol) monolayers to print polar inks from ethanolic solutions.^[8,9] Other routes involve the use of hydrogel stamps for the patterning of ionic species.^[15,16] In this case, the hydrogel stamps promote a considerable ink uptake, enabling the patterning of different chemical species.^[17–19] However, hydrogel stamps do not show the same chemical and mechanical stability as the PDMS ones. Finally, Rogers and co-workers have shown that thin metal films deposited on PDMS stamps can be transfer-printed reliably as well.^[20]

The aim of this work is to establish a new variation on μ CP that has the capability to deposit controlled amounts of material without sacrificing the advantages of robust, large-area patterning. In this work we show that polyelectrolyte brushes grown on PDMS stamps can be used as “ink nanoreservoirs”, enabling controlled uptake as well as site-selective delivery of the ionic species. In particular, we demonstrate the potential of our approach by creating counterion domains in a flat polyelectrolyte brush and by promoting a site-selective metallization with reactive ionic species.

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2. Results and Discussion

For this work we used surface-initiated cationic poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PME-TAC) brushes. These brushes were grown from initiator-modified PDMS stamps (Fig. 1) as well as on Si/SiO₂ surfaces by aqueous atom-transfer radical polymerization^[21] (details are described in the Experimental section).

Besides the well-known collapse upon increasing ionic strength (electrostatically driven collapse), PMETAC brushes also collapse via specific interactions in the presence of certain ions like ClO₄⁻, SCN⁻, and I⁻.^[22–24] An important feature of ion-pairing-driven collapse is that, unlike the electrostatic case, it is not immediately reversible in the presence of pure water. Experimental observations reported by us indicate that the interaction of quaternary ammonium (QA⁺) moieties, which constitute the pendant groups in a PMETAC brush, together with the surrounding counterions (anions) play a major role in determining the uptake/release characteristics of the polyelectrolyte brush.^[24] Scarcely hydrated, large, and highly polarizable species (like ClO₄⁻) interact very strongly with the QA⁺ groups through ion-pairing interactions, giving rise to preferential retention of these species in the brush layer. This retention is clearly observed using the quartz crystal microbalance (QCM) technique. Figure 2a shows the QCM trace in different electrolytic environments for a gold-coated quartz crystal modified with 20 nm thick PMETAC brushes. When passing from water to a 1 M LiClO₄ solution, we observed an abrupt increase in the frequency, at approximately 420 Hz. This change is mainly associated with a reduction in the water content of the brush during collapse. The first rinse with MilliQ water resulted in a further increase of the frequency up to 580 Hz, instead of a return of the frequency and dissipation to their original values. The following washings performed after different time intervals showed a progressive and slight decrease in the frequency, indicating the slow release of electrolyte from the polyelectrolyte brush. After a 24 h measurement with progressive washings the frequency had not reached a constant value (not shown). This slow release of electrolyte was confirmed by measuring the conductivity of the rinsing water depleted from the QCM chamber after each rinsing step (Fig. 2b). The first wash-

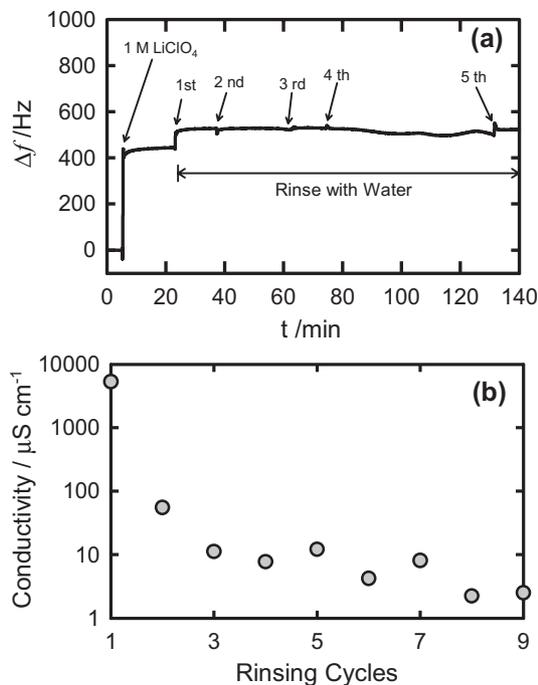


Figure 2. a) QCM frequency response (Δf) when 20 nm METAC brushes are in the presence of 1 M LiClO₄, and repeatedly rinsed with water. b) Conductivity measurements of the rinsing water depleted from the QCM chamber after performing the experiments with a 1 M LiClO₄ electrolyte solution.

ing, which involved the exchange of the 1 M LiClO₄ solution, had a very high conductivity of 5290 $\mu\text{S cm}^{-1}$, which then decreased to 55 $\mu\text{S cm}^{-1}$ in the second washing and to 7.7 $\mu\text{S cm}^{-1}$ in the third. The conductivities for the following rinsing cycles varied between 2 and 12 $\mu\text{S cm}^{-1}$ depending on the rinsing time in the QCM chamber.

After an interval of 12 h between two washing cycles the conductivity of the washing solution reached a value of 30.3 $\mu\text{S cm}^{-1}$. As an indication of the amount of electrolyte released, it must be noted that the conductivities of 0.01, 0.05, 0.1, and 0.5 mM LiClO₄ standard solutions are 224, 600, 1076, and 4900 $\mu\text{S cm}^{-1}$, respectively. In our experiments, each washing cycle required passing 5 mL of water through the QCM

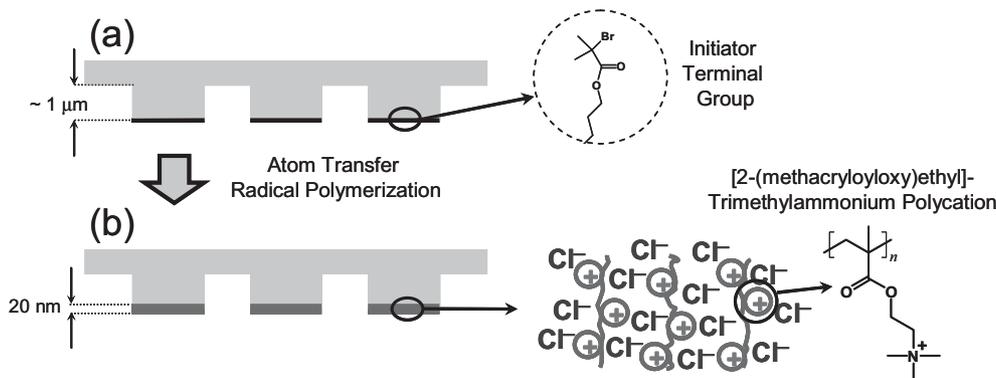


Figure 1. Simplified scheme describing the preparation of PMETAC-modified PDMS stamps. Brushes are grown from initiator-modified stamps using aqueous atom-transfer radical polymerization (a), leading to the formation of a 20 nm thick layer on the relief structures of the stamps (b).

chamber; the volume of the chamber is 80 μL . Consequently, there is a 60 \times dilution in each washing step. Taking this into account, the concentration of LiClO_4 between washings would vary from a few millimoles at the shorter time intervals to approximately 0.01 mM at the 12 h interval. The conductivity values of the washing solutions confirm that LiClO_4 is slowly released from the brush after the first rinse, and that the amount washed out of the brush can be controlled.

To explore the potential of PMETAC brushes as nanoreservoirs, we proceeded to the site-selective release of ClO_4^- counterions from a stamp modified with PMETAC into a flat Cl^- -coordinated PMETAC brush (Fig. 3a), thus promoting the creation of patterned counterion domains inside the same polyelectrolyte matrix, PMETAC (Fig. 3b).

The PMETAC-modified PDMS stamp was immersed in a 1 M LiClO_4 aqueous solution for five minutes. This led to a full collapse of the PMETAC brushes, trapping considerable amounts of ClO_4^- anions. After rinsing with water, the stamp was brought into conformal contact with the flat Cl^- -coordinated METAC brush (Figs. 3a,b). The transfer of ClO_4^- ions onto the sample was monitored using Fourier transform infrared (FTIR) spectroscopy in the region corresponding to the Cl-O stretching vibration (1105 cm^{-1}), characteristic of ClO_4^- species (Fig. 4).

For printing times shorter than 1–3 min the observed Cl-O signal was rather weak, and the spectra were similar to that of

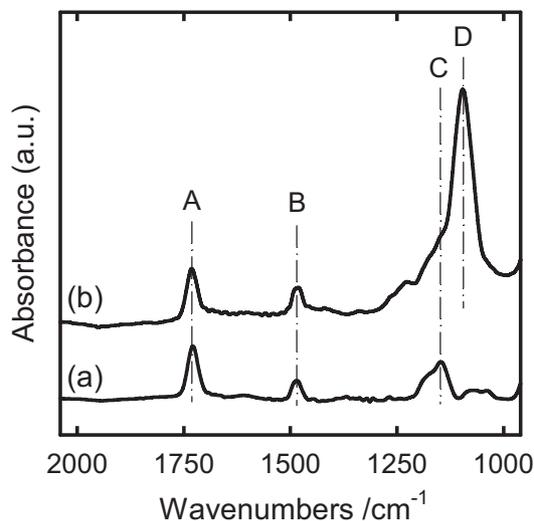


Figure 4. FTIR spectra corresponding to a) as-synthesized PMETAC brushes and b) PMETAC brushes contact-printed with ClO_4^- anions for five minutes. The IR signals labeled from A to D correspond to the: A) C=O stretching vibration, B) $(\text{CH}_3)_4\text{N}^+$ bending vibration, C) Si-O stretching vibration, and D) Cl-O stretching vibration.

the Cl^- -coordinated PMETAC brushes (Fig. 4a). The optimum printing time was 5 min (Fig. 4b), and longer times produced

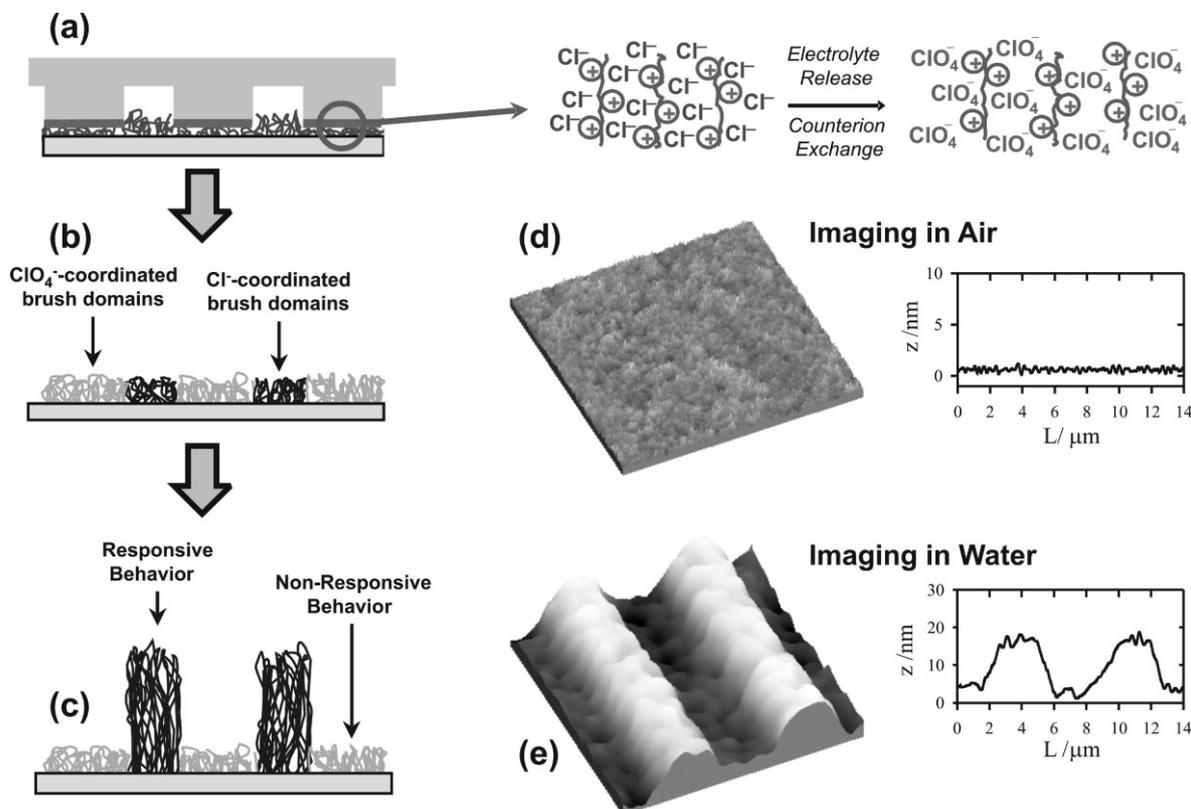


Figure 3. Schematic showing the contact printing procedure for transferring ClO_4^- into Cl^- -coordinated PMETAC flat brushes by using a PMETAC-modified PDMS stamp: Initially the modified stamp is inked with a 1 M LiClO_4 solution and, after rinsing with water, it is brought into conformal contact with the flat PMETAC surface for 5 min (a). After contact printing the counterion domains (b), the brush is immersed in water (c). The 3D atomic force microscopy (AFM) images shown ($14\text{ }\mu\text{m} \times 14\text{ }\mu\text{m}$) with their cross-sectional analyses correspond to: d) contact-printed ClO_4^- domains imaged in air and e) contact-printed ClO_4^- domains imaged in water.

no significant changes in the Cl–O stretching signal. The generation of patterned domains of ClO_4^- and Cl^- anions on the same PMETAC enables the synthesis of macromolecular films with different responsive characteristics. In the presence of water, the Cl^- -coordinated domains would show an extended swollen conformation as a consequence of the interplay between the solvation forces and the repulsion between the charged moieties. In contrast, in the presence of water, the ClO_4^- -coordinated domains would remain collapsed (hydrophobic) as a consequence of the changes introduced by the ion pairing of the ClO_4^- with the QA^+ moieties (Figs. 3b,c). In agreement with this picture, atomic force microscopy (AFM) characterization showed that surfaces with a smooth flat morphology in air (Fig. 3d) develop a patterned corrugation when imaged under water (Fig. 3e) as a result of the contact printing of ions. These counterion domains are relatively well defined and stable for at least 2 h after imaging under water. Prolonged times involves a significant diffusion of counterions within the polyelectrolyte brush and, consequently, the pattern vanishes.

The ability to print ions also allows the delivery of ionic species that can react with the substrate, as in the case of the so-called “metal-displacement reactions” also known as “galvanic displacements”.^[25] This process involves the spontaneous reduction of an ion species by a “less noble” metal, according to the electromotive series. A classic example is the case of a copper surface in the presence of PdCl_4^{2-} anions, in which the Cu is anodically dissolved while the PdCl_4^{2-} anions are cathodically electroplated on its surface.

One of the advantages of using polyelectrolyte brushes as nanoreservoirs is the control over stamp inking that it affords. In other words, it is possible to achieve a reproducible and predictable relationship between the content of ionic species on the stamp surface and the ink concentration. This has been demonstrated by measuring the change in the uptake of Pd^{II} species on the stamp surface for different PdCl_4^{2-} ink concentrations (Fig. 5). PdCl_4^{2-} species have a well-defined charge-transfer band in the UV range of the electromagnetic spectrum at

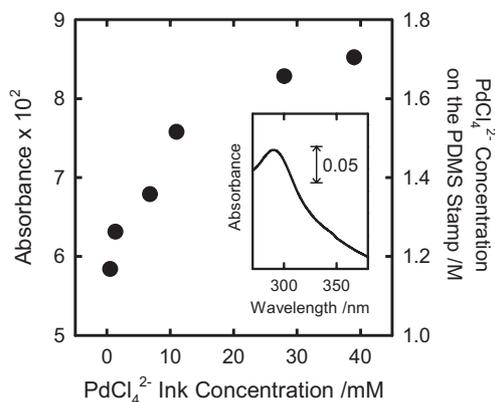
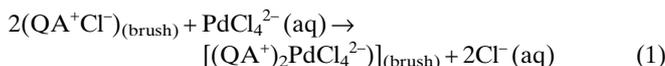


Figure 5. Absorbance measurements (at 295 nm) corresponding to PdCl_4^{2-} uptake in the PMETAC-modified PDMS stamp for an inking time of 15 min. The inset depicts the UV-absorption characteristics of the Pd^{II} species immobilized on the modified PDMS stamp.

~ 300 nm,^[26,27] a region where PDMS is still transparent (Fig. 5, inset). By using this distinctive feature, the change in absorbance of the Pd^{II} species retained in the brushlike layer after immersing the PMETAC-modified PDMS stamp for 15 minutes in solutions of different ink concentrations was measured (Fig. 5). To quantify the Pd^{II} uptake, the “molar concentration” of PdCl_4^{2-} in the 20 nm thick polyelectrolyte layer was estimated from the absorbance values using the Lambert–Beer law. For this estimation, a PdCl_4^{2-} -species molar absorptivity (ϵ) of $8.25 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, as reported in the literature,^[28] was used.

It can be observed that ink concentrations in the range 10–40 mM give rise to “molar concentrations” in the 20 nm brush layer of nearly 1.2–1.8 M in a similar fashion to an adsorption isotherm. The driving force for this enhanced uptake is correlated to the high affinity of QA^+ groups in the METAC brush for PdCl_4^{2-} species in solution. In other words, the equilibrium describing the ink uptake (1),



favors the displacement of Cl^- anions by PdCl_4^{2-} species.

It should be noted that the affinity of QA^+ groups for chloro-complexes of precious metals is commonly used in extracting and preconcentrating metal-ion solutions with ion-exchange resins like Amberlite.^[29,30] In our case, we used the PMETAC brushes as ion-exchanging/ion-pairing sorbent nanolayers to preconcentrate the ink on the stamp surface and, consequently, to selectively deliver the loaded species.

Contact-printing of the PdCl_4^{2-} species was performed by immersing the PDMS stamps modified with 20 nm thick PMETAC brushes in a 40 mM PdCl_4^{2-} solution for 15 minutes. After rinsing and removing the water with a gentle nitrogen stream, the inked stamp was placed in conformal contact with the copper surface. Immediately after placing the stamp onto the surface (less than five seconds) a patterned array of Pd lines was deposited on the Cu surface (Fig. 6).

These contact-printed Pd lines were 3 μm wide and 100 nm high, as derived from AFM measurements (Fig. 6b). In addition, the presence of Pd on the contact-printed Cu surface was corroborated by elemental analysis using Auger-electron spectroscopy (AES, Fig. 7).

3. Conclusions

In summary, we have described a novel soft-lithographic approach, which combines the outstanding mechanical and chemical properties of traditional PDMS stamps with the advantageous characteristics of hydrogel stamps, to print aqueous and ionic inks. It was demonstrated that, by tailoring the surface chemistry of PDMS stamps with polyelectrolyte brushes, it is possible to control the uptake or “load” of aqueous inks containing ionic species. Polyelectrolyte brushes can act as preconcentrating/sorbent nanolayers in combination with conventional PDMS stamps to promote site-selective delivery of ionic species onto diverse substrates with different chemical characteristics.

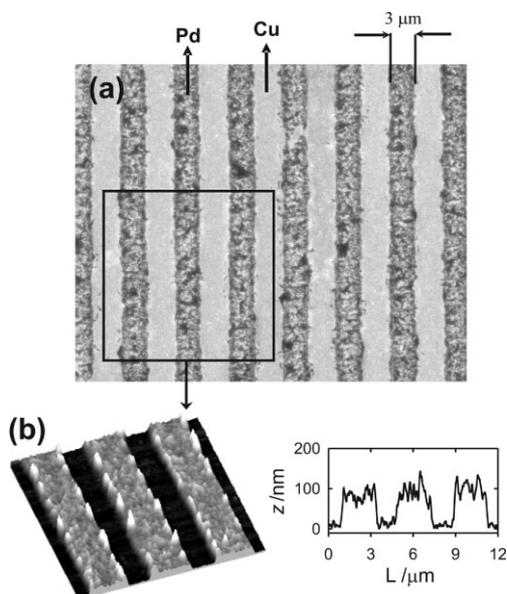


Figure 6. a) Scanning electron microscopy (SEM) image showing the Pd domains contact-printed onto the Cu surface. b) AFM image and its corresponding cross-sectional analysis showing the relief structure of the transferred Pd lines.

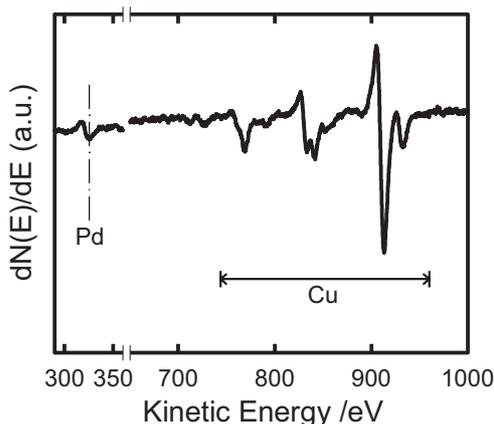


Figure 7. AES spectrum of the Cu surface contact-printed with the PdCl_4^{2-} anions. The spectrum gives evidence of the relevant AES signals for Pd (MNN, 323 eV) and Cu (LMM, 750–950 eV) N : electron intensity; E : energy.

4. Experimental

Modification of PDMS Stamps with PMETAC Brushes: PDMS stamps (Sylgard 184, Dow Corning) were oxidized with O_2 -plasma treatment for 30 s using an EmiTech plasma oxidizer. A few drops of initiator solution (50 μL of 2-bromo-2-methyl-propionic acid 3-trichlorosilylanyl-propyl ester in 6 mL of dry hexane) were put onto a flat PDMS stamp (“ink pad” method). Then, the solvent (hexane) was immediately (10 s) evaporated using a gentle stream of Ar. After “drying” the PDMS pad, the plasma-oxidized PDMS stamp was placed (in conformal contact) onto it for 1 min. For the preparation of the polymerization solution, commercially available (75 wt %, Aldrich) 2-(methacryloyloxy)ethyl trimethylammonium chloride (METAC) (46.3 g) was dissolved in MeOH (46 cm^3) at 20 °C and degassed by passing a continuous stream of dry N_2 through the solution whilst being

stirred (20 min). To this solution was added 2,2'-dipyridyl (2.411 g), $\text{Cu}^{\text{I}}\text{Cl}$ (0.611 g), and $\text{Cu}^{\text{II}}\text{Cl}_2$ (0.083 g). The mixture was then further stirred and degassed with a stream of dry N_2 (15 min). Initiator-modified PDMS stamps were sealed in Schlenk tubes, degassed (4 \times high-vacuum pump/ N_2 refill cycles), and left at 20 °C under N_2 . The polymerization solution was then syringed into each Schlenk tube, adding enough solution to submerge each stamp completely. The samples remained in the polymerization solution for 3–4 h. After polymerization the samples were removed, washed with MeOH and water, and dried under a stream of N_2 .

Characterization Techniques: Fourier transform infrared spectra were recorded with a BioRad spectrometer using PMETAC brushes grown on silicon wafers. Spectra were taken with a resolution of 4 cm^{-1} by accumulating 128 scans on each run. The sample compartment was carefully purged with nitrogen to reduce the interference of water and carbon dioxide absorption from the gas phase. Surface elemental analyses with Auger electron spectroscopy (INIFTA, La Plata) were carried out using a single-pass cylindrical mirror analyzer (CMA, Physical Electronics). All the spectra were recorded in the differential mode $dN(E)/dE$. Atomic force microscopy experiments were carried out in a liquid cell using a MacMode PicoSPM magnetically driven dynamic force microscope (Molecular Imaging). Images were taken using commercially available type II MACLevers with a nominal force constant of 2.8 N m^{-1} at a driving frequency of 19 Hz in the liquid environment.

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