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Supporting Information

Surface grafting of a dense and rigid coordination polymer based on tri-*para*-carboxy polychlorotriphenylmethyl radical and copper acetate

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Supporting Information.

SII. Scratching procedure.

In the scratching experiments, the applied force and the scan speed of tip are key parameters. The appropriate values depend on each specific tip-film-substrate system and their selection implies a series of tests prior to the experiments. In particular, to ensure that only the coordination polymer material is removed, these parameters have to be kept at values at which no Au substrate wear exists. Therefore, for each tip and prior to a set of experiments, a bare Au substrate has been scanned for different scanning conditions (force and velocity) to establish the wear onset. On the other hand, to determine the adlayer thickness, the whole grown film has to be removed in a sequential manner without changing these conditions. Exploiting the difference in mechanical properties between the adlayer and the Au, the two figures of merit employed to determine the end of the removal process are surface roughness and friction, magnitudes that can be measured independently but simultaneously during scratching. The so-called scratching procedure consists of different steps. First, a large area of the surface on which the polymer has been grown is imaged in a non-invasive manner, using dynamic intermittent contact mode and checking by successive imaging that no film damage exists. The SFM system is then driven into contact mode operation and a reduced area is repeatedly imaged at the selected load and speed determined for scratching.

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During this process, unstable topographic and friction signals indicate that material is being removed until, eventually, a steady state is reached. At this point the typical gold surface friction and roughness are measured. Tip sweeping is immediately stopped and the SFM is driven back to intermittent contact to avoid further debris. The scanning area is enlarged to record the resulting changes. Because intermittent contact mode measurements can give rise to wrong height measurements in heterogeneous samples¹, the results are always cross-checked by contact mode topographic measurements at the lowest practical force (pull off). As commented above, besides the topography differences, the simultaneous acquisition of the friction force² permits to ensure that the scratched area has been cleaned of any metal-organic material.

We note that because of the local surface plane subtraction used for figure 3 production, the color within the scratched region of that figure in the paper looks more inhomogeneous than expected from the surface rms. This is an enlarged color vertical scale effect which can be avoided if a region avoiding the borders of the scratched area as illustrated in figure SII is used.

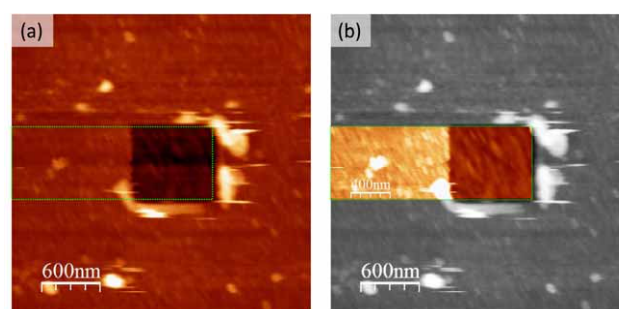


Figure SII. (a) Same as figure 3(a) in the main text. (b) In grey scale the same as in (a) and, superimposed in color, the selected region after a local plane subtraction avoiding the material accumulated at the right border.

SI2. ToF-SIMS chemical imaging.

Figure SI2 shows the chemical images obtained with the TOF-SIMS technique of a template gold surface, patterned with 20 μm squares of a MHDA SAM, where the PTMTC-copper coordination polymer (8 cycles) was grown under static flow conditions. The images correspond to ions with m/z of 37 (^{37}Cl ; left), 137 ($^{63}\text{Cu}^{37}\text{Cl}_2$; center), mainly present inside the MHDA squares, as indicated by the brightness, and 197 (^{197}Au ; right), present mainly outside the squares.

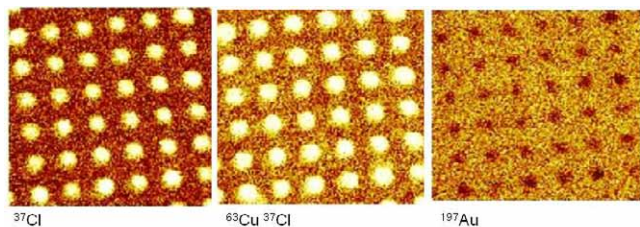


Figure SI2. ToF-SIMS of the 8 cycles PTMTC-copper polymer grown by under static flow conditions on a template gold surface patterned with a MHDA SAM of 20 μm size squares. The images correspond to ejected ions with m/z of 37 (^{37}Cl , left), 137 ($^{63}\text{Cu}^{37}\text{Cl}_2$, center), mainly present inside the MHDA SAMs squares, and 197 (^{197}Au , right), present mainly outside the patterned squares. The sample was prepared in parallel to the sample whose SFM topographical image is shown in Figure 4 in the main text.

SI3. Use of copper perchlorate as inorganic ligand.

By QCM-D it was checked whether the exposure of the sensing MHDA surface to an ethanolic solution of Cu(II) ions from copper perchlorate salt followed by PTMTC could lead to any change in the oscillation frequency over time. As shown in Figure SI3-I, when injecting copper perchlorate and PTMTC in a step-wise manner, no change in frequency (hence no mass uptake) was recorded. By substituting the copper perchlorate by copper acetate (Figure SI3-II), instead, a continuous mass uptake occurred. When switching back to copper perchlorate again (Figure SI3-III) no frequency change could be recorded. Eventually, when switching back to copper acetate and PTMTC (Figure SI3-IV), frequency changes could be recorded. This experiment suggests that, as in the case of other metal-organic frameworks, the paddle-wheel configuration of the Cu(II) ion used as synthon, plays a fundamental role to achieve the surface deposition of the coordination polymer.

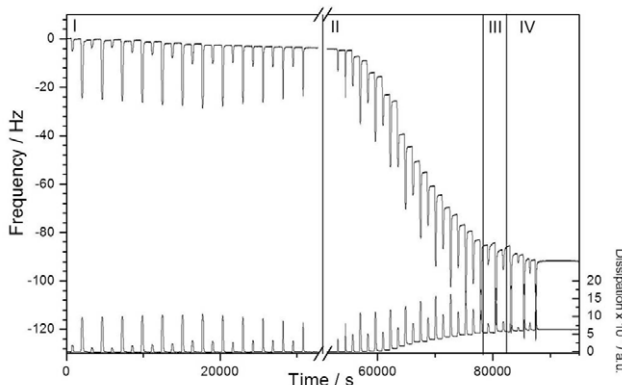


Figure SI3. QCM-D profile obtained with a gold template surface functionalized with a uniform MHDA SAM under continuous flow at 21°C; flow rate of 60 $\mu\text{l}/\text{min}$ and step duration of 4 min. Both frequency and dissipation refer to the third overtone. I) Deposition of copper perchlorate (0.5mM in ethanol) and PTMTC (0.05mM in ethanol) and of copper perchlorate (0.5mM in ethanol). II) Deposition of copper acetate (0.5mM in ethanol) and PTMTC (0.05mM in ethanol). III) Deposition of copper perchlorate (0.5mM in ethanol) and PTMTC (0.05mM in ethanol). IV) Deposition of copper acetate (0.5mM in ethanol) and PTMTC (0.05mM in ethanol).

Notes and references

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