

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

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The step-by-step method is here presented as suitable to anchor on appropriately functionalized gold surfaces a metal–organic coordination polymer based on a non-planar trigonal tri-*para*-carboxy-polychlorotriphenylmethyl radical derivative and copper acetate. The structural characteristics of the grafted coordination polymer are derived during the step-wise growth from the real time changes in refractive index and oscillation frequency. The film thickness, as measured by scanning force microscopy, combined with the mass uptake value from the quartz crystal microbalance, are used to estimate an average density of the grafted metal–organic coordination polymer that suggests the formation of a dense and rather rigid thin film.

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## Introduction

Engineering at the molecular level of surface anchored multi-component architectures is a feasible but still challenging task since rather small changes in the chemical structure and geometry of the constituting building blocks, or synthons, can lead to unpredictable structures and novel properties. Recently, the solution-based methodology known as layer-by-layer, firstly described by Decher,<sup>1</sup> has been shown to be a valuable tool to control step-by-step the surface growth of Metal–Organic Frameworks (MOFs) on surfaces.<sup>2</sup> Indeed, by this method, it has been possible not only to anchor MOFs on template surfaces in an oriented way,<sup>3</sup> but also to produce frameworks with structures not achievable by conventional solvothermal synthesis.<sup>4</sup>

The growth of MOFs by the step-by-step method (Scheme 1) consists of exposing a template surface, properly functionalized either with a single component or a patterned self-assembled monolayer (SAM), to a solution containing the inorganic linker unit, followed by the abundant rinsing with pure solvent (step A, Scheme 1) and by the subsequent exposure to an organic ligand solution, again followed by rinsing with the solvent, until the complete removal of the not bound deposited material (step B, Scheme 1).

These steps are repeated as many times as desired, being possible to construct thin layers of coordination polymers with a controlled number of repeating metal–organic units. The step-wise exposure of the template surface to the solutions of the synthons forming the coordination polymer can be carried out either under continuous flow<sup>3a,3b</sup> or static conditions.<sup>3c</sup> While in this latter case the surface is let immersed in a vessel

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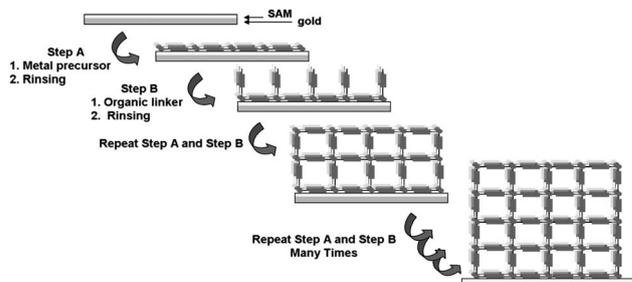
† Electronic supplementary information (ESI) available: Description of scratching procedure, ToF-SIMS of PTMTC-copper polymer multilayer on a patterned surface; SPR and QCM-D profiles recorded jointly during the step-by-step deposition of PTMTC and copper perchlorate under continuous flow conditions. See DOI: 10.1039/c2tc00037g

‡ Dedicated to Dr. Christian G. Claessens in his memory

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**Scheme 1** Scheme of the step-by-step methodology. Steps A and B can be performed either under continuous flow or static conditions.

containing the inorganic (or organic) synthon solution for a certain period of time, in the first case the synthon solutions are flowing during a given time period over the template surface. Both approaches lead to the preparation of surface anchored MOFs, the final composition and crystallinity of which can be assessed. The continuous flow approach has opened the way to the *in situ* and in real time characterization of the step-wise growth of the hybrid material by recording the changes of refractive index (as measured by surface plasmon resonance, SPR) and oscillation frequency (as measured by quartz crystal microbalance, QCM), if SPR and QCM sensors, respectively, are used as template surfaces. The outputs of these two techniques rely on different physical processes: while SPR is sensitive to the optical properties of the thin film, QCM-D is an electro-mechanical measurement that provides a quantification of the adsorbed mass, including the contribution of solvent molecules trapped within the thin film, providing therefore additional information on the film viscoelasticity. Since both techniques are very sensitive to changes related to material adsorption or deposition on the sensing template surface, they have been used independently<sup>5,6</sup> or jointly,<sup>7</sup> to monitor thin film deposition<sup>8</sup> or loading<sup>9</sup> of different types of molecules. For this reason these two complementary techniques can be considered very valuable to gain a deeper knowledge of the mechanisms of *in situ* growth of the thin films as well as the final structure of the grafted polymer, even in the absence of crystallographic data. In the present work, we report on surface grafting by the step-by-step method, both under continuous flow and static conditions, of a novel metal-organic coordination polymer, composed of the tri-*para*-carboxylic perchlorinated triphenylmethyl radical (PTMTC, Fig. 1) and copper acetate, in the quest for the preparation of crystalline and porous robust solid devices to match an always wider range of applications. The copper mediated anchoring of a mono carboxy-substituted perchlorinated triphenylmethyl radical derivative (PTMMC, Fig. 1) on a template surface was already achieved by the authors.<sup>10</sup> However, in order to build an extended and eventually porous surface anchored framework, we have moved a step further to investigate the use of a perchlorinated triphenylmethyl derivative with three carboxylic groups acting as potential coordinating sites, located in the three *para* positions with respect to the central sp<sup>2</sup> carbon atom. Even if the chosen PTMTC radical derivative can be seen as the enlarged version of the trimesic

acid (TMA), whose carboxylic groups can coordinate three inorganic synthons (as in HKUST-1),<sup>11</sup> its coordinated polymeric structure cannot be easily predicted *a priori*. Indeed, differently from what happens in the case of TMA, the steric hindrance exerted by the three pairs of chlorine atoms in *ortho* causes the torsion of the three perchlorinated rings,<sup>12</sup> while the ones in *meta* force the carboxylic groups in *para* to be perpendicular to the plane of the aromatic rings, generating thereby a non-planar rigid conformation. It is worth noting that ligands with similar trigonal non-planar geometry have not yet been used as synthons for the grafting of metal-organic coordination polymers. As it will be discussed herein, we have proved the feasibility of achieving by the step-by-step method laterally homogeneous thin layers of this coordination polymer, following the growth by recording the continuous change in the refractive index of the forming thin film, as well as its mass uptake. Moreover, by comparison of the recorded SPR sensorgram with the change in frequency, as measured by the QCM-D over time, an indication of the solvent uptake of the thin film has been extracted. Eventually, by combination of the mass uptake value and dissipation as determined by the QCM-D measurements with the thickness value as measured by scanning force microscopy (SFM), we have been able to propose that the PTMTC-based coordination polymer forms a rigid and dense surface grafted thin film. In addition, the deposition on a mercaptohexadecanoic acid (MHDA) patterned template surface of a PTMTC-Cu coordination polymer by the step-by-step method under static conditions and the obtaining of laterally confined metal-organic hybrid polymeric areas is also presented.

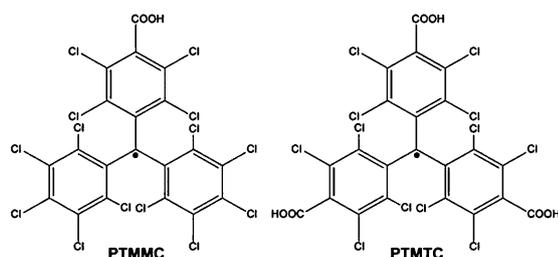
## Experimental section

### Materials

Mercaptohexadecanoic acid (MHDA) thiol, hexadecanethiol (HDT), monohydrate copper acetate (CuOAc<sub>2</sub>·H<sub>2</sub>O) and hexahydrate copper perchlorate (Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O) were purchased from Sigma Aldrich and used without further purification. 99.9% ethanol was purchased from Merck and Teknokroma. The tri-*para*-carboxylic triphenylmethyl (PTMTC) radical derivative was synthesized according to the literature.<sup>13</sup>

### Substrate preparation

Different types of gold substrates were employed: Au/glass (from Ssens BV; 12 × 12 × 1 mm; 50 nm Au) and Au/Si (from Albert Georg, 200 nm Au, 5 nm Ti). The Au/glass substrates were cleaned by immersion in a piranha solution (4 : 1 H<sub>3</sub>SO<sub>4</sub> : H<sub>2</sub>O<sub>2</sub>) for 30 seconds and then abundantly rinsed with water, ethanol and then dried with a gentle nitrogen flow. The Au/Si were used as received without further cleaning. SPR and QCM-D gold sensors were purchased from XanTec bioanalytics (GmbH, Düsseldorf, Germany) and LOT-Oriel (Quartz Crystal 5 MHz, AT-cut, gold electrode), respectively. Right before use, the sensors were cleaned in a UV/Ozone cleaner (from BioForce Nanosciences, Inc.) for 5–10 minutes and then rinsed with ultrapure ethanol and dried under soft nitrogen flow.



**Fig. 1** Chemical structure of PTMMC and PTMTC radicals. The rings' torsion is not represented.

### Self-assembled monolayers (SAMs)

Self-assembled monolayers (SAMs) of MHDA were prepared by immersion in the dark (72 hours) of the gold sensors in a 0.2 mM ethanolic solution of the MHDA thiol with acetic acid (10% in volume),<sup>14</sup> followed by abundant rinsing with ultrapure ethanol and drying under soft nitrogen flow. The resulting SAMs were used in the SPR and/or the QCM-D experiments right after their preparation. From now on, uniform SAMs made out of MHDA will be named as single component MHDA SAM.

### Patterned samples

Patterned samples were prepared by the micro-contact printing ( $\mu$ -CP) technique using a polydimethylsiloxane (PDMS) stamp with square-shaped ( $3\ \mu\text{m} \times 3\ \mu\text{m}$  or  $20\ \mu\text{m} \times 20\ \mu\text{m}$ ) motifs on Au/Glass. On the PDMS stamp, abundantly rinsed with ethanol and dried by nitrogen flow, a few drops of 1.0 mM ethanolic solution of MHDA with acetic acid (10% in volume) were deposited by a Pasteur pipette. After 3 to 5 minutes, the PDMS stamp was dried by nitrogen flow, gently pressed by hand on the gold sensor surface for 20 seconds and left after pressure release for another 2–3 minutes. After stamp removal, the sensor was immersed in a 1.0 mM ethanolic solution of HDT for 72 hours. The result was a completely covered but laterally heterogeneous functionalized gold surface exhibiting a pattern of squares with a lateral size of 3 (or 20)  $\mu\text{m}$  of MHDA surrounded by a SAM of HDT molecules filling the areas between the squares.

### Grafting of metal–organic coordination polymer

The single component MHDA SAM samples on SPR and QCM sensors were used as templates for the stepwise deposition of the synthons dissolved in ethanol under continuous flow conditions inside the SPR and the QCM-D equipment. For the deposition under static conditions Au/glass or Au/Si substrates were used. Patterned samples on Au/glass were used as template surfaces for grafting under static conditions.

### Continuous flow conditions

In a typical experiment, SPR and QCM gold sensors functionalized with MHDA SAMs were exposed to a sequence of cycles consisting of a flow of  $120\ \mu\text{L}\ \text{min}^{-1}$  of an ethanolic solution of copper acetate (0.5 mM) for 2 minutes followed by ethanol rinsing and then exposed under the same flow conditions to an ethanolic solution of PTMTC (0.05 mM) during the same time period. Based on previous experiments, the MHDA SAM was always exposed three times to the copper acetate solution, in order to coordinate most of the carboxylic end groups of the MHDA SAM with the copper ions, before injecting the radical ligand.

### Surface plasmon resonance

The SPR experiments were performed using a Reichert SR7000DC dual channel SPR instrument (Reichert Analytical Instruments, NY, USA). The setup is based on the configuration introduced by Kretschmann and Reather.<sup>15</sup> On top of the sample, the standard flow cell with two reaction channels

was used. The sample was kept at a constant temperature coinciding with the calibration temperature ( $21\ ^\circ\text{C}$ ) during the whole experiment and under a constant continuous flow of  $120\ \mu\text{L}\ \text{min}^{-1}$ .

### Quartz crystal microbalance with dissipation monitoring

Measurements were performed on the QCM-D E4 experimental platform from Q-Sense (BiolinScientific/Q-Sense). The equipment could be used connected in parallel to the SPR equipment by the Reichert SR7100 robotic autosampler. In order to do the latter, the flow from the injection loop of the autosampler ( $120\ \mu\text{L}\ \text{min}^{-1}$ ) was split into two tubes (internal diameter 0.010" ID), one connected to the left channel of the dual channel SPR flow cell and the other to one QCM-D cell.

### Static conditions

In the static case the gold template was let react with the inorganic ligand (1 mM in ethanol, 30 min, room temperature) in a small glass vessel. After evacuation of the vessel, the surface was abundantly rinsed with ethanol, and the vessel filled with an ethanolic solution of the PTMTC ligand (0.0125 mM, 60 min, room temperature). After a period of 60 min, the vessel was evacuated and the surface abundantly rinsed once more with ethanol in order to remove any deposited but not bound material. The cycle repetition on patterned samples was performed by means of a software controlled (FiaLab) multi-pump system connected to a multiposition valve from Valco Instruments Company Incorporated.

### Characterization techniques

SCANNING FORCE MICROSCOPY (SFM). Scanning force microscopy (SFM) measurements were performed under low humidity conditions (<5% RH, obtained by a continuous  $\text{N}_2$  gas flux) using a commercial head and software from Nanotec.<sup>16</sup> Si tips on Si cantilevers with  $k = 2.8\ \text{N}\ \text{m}^{-1}$  (Nanosensors) were employed as a compromise to combine both contact and dynamic modes, in the very same probe. We note that using the contact mode requires special care to avoid sample damage and film compression, but reliable height values (differences lower than 0.2  $\text{\AA}$ ) can be obtained if the applied load during imaging is kept at the lowest practical force (pull-off force).<sup>17</sup> Topographic SFM images were acquired by both methods, obtaining no significant difference in the measured layer's thickness for patterned surfaces, as given by the height difference between the topmost surface of the selectively grown material (within the squares of the pattern) and the surrounding surface. However, in order to determine the thickness of laterally continuous layers, we used scratching experiments, by which we locally removed material from surface until reaching the underlying substrate surface. The so called scratching procedure was the following: we first imaged a large area of the film surface using the SFM tapping mode to avoid film damage. The system was then driven to contact SFM mode and a small area was repeatedly imaged at a higher load (300–500 nN). During this process, an unstable topographic signal indicates material is being removed until eventually a steady state is reached. At that

moment, tip sweeping is stopped and the SFM is driven back to dynamic conditions, thus avoiding further material debris. The monitored area is enlarged to record the topographic changes. The material removed has been accumulated at the borders of the scratched region. Line profiles and height histograms between the inner and outer regions of the scratched region are used to determine the film thickness. More details on the scratching procedure are given in ESI1.†

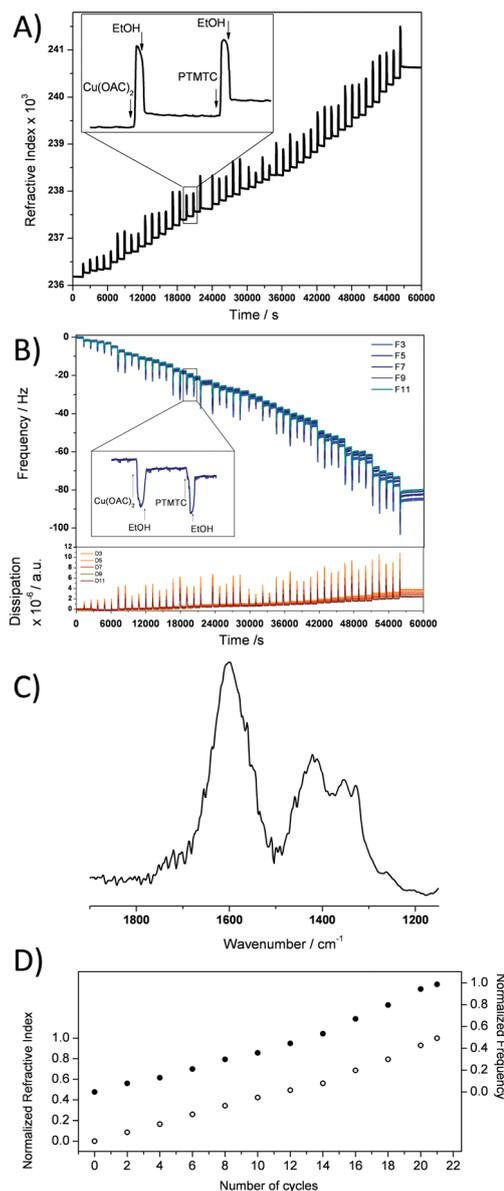
**INFRARED SPECTROSCOPY.** The prepared samples were characterized by infrared spectroscopy, both in grazing and attenuated reflection modes. Infrared reflection absorption (IRRAS) spectra were taken with a Biorad FTS-300 FT-IR equipped with a grazing incidence reflection unit, Biorad Uniflex, and a narrow band MCT detector. All spectra were recorded with  $2\text{ cm}^{-1}$  resolution at an angle of incidence of  $80^\circ$  relative to the surface normal and processed by using boxcar apodization. Attenuated total-reflection infra-red spectra (ATR-IR) were taken with a TENSOR 27 FT-IR spectrometer with a HYPERION 3000 FT-IR microscope, Bruker Optics. For IRRAS and ATR-IR characterizations, a single component MHDA SAM was prepared.

**TIME OF FLIGHT SECONDARY ION MASS SPECTROSCOPY (ToF-SIMS) IV.** A time of flight secondary ion mass spectrometry (ToF-SIMS) IV mass spectrometer (Ion-ToF GmbH, Münster, Germany) equipped with a bismuth cluster ( $\text{Bi}^3$ ) ion source and operated at a pressure of  $5 \times 10^{-9}$  mbar was used for these experiments (see ESI2†).

## Results and discussion

### A Grafting under continuous flow conditions

The step-by-step grafting of the copper-PTMTC coordination polymer was performed under continuous flow conditions following the step-wise change in optical and mechanical properties with the SPR and the QCM-D techniques simultaneously. For these experiments, a gold surface (an SPR and a QCM-D sensor) functionalized with a single component MHDA SAM was used as the sensing template surface. In a typical joint experiment, SPR and QCM gold sensors functionalized with MHDA SAMs were exposed to a sequence of cycles consisting of a flow of an ethanolic solution of copper acetate, followed by ethanol rinsing, and then exposed to a flow of an ethanolic solution of PTMTC. Fig. 2(A) and (B) show, respectively, the change in the refractive index (RI) as detected by SPR, and the change in the frequency ( $-\Delta f$ ), as observed by QCM-D, as a function of time. The sensorgrams have a ladder-like shape, as already seen for similar systems,<sup>18</sup> where each plateau, or step, corresponds to the uptake of material on the surface after complete rinsing. Note that the injection of either the inorganic or the organic synthons is characterized by an initial increase in RI or in  $-\Delta f$  followed by a decrease, due to solvent rinsing, in these parameters till a stable and constant value is reached (see insets in Fig. 2(A) and (B)). This behavior indicates that the large changes in both magnitudes (RI and  $-\Delta f$ ) recorded right after the injection are due to both specifically anchored and non-bound material, being this latter one which is removed from the surface by rinsing. Therefore, the constant refractive index and oscillation



**Fig. 2** Step-by-step deposition of copper acetate (0.5 mM) and PTMTC (0.05 mM) in ethanol on a template gold surface with a MHDA SAM under continuous flow conditions at  $21^\circ\text{C}$ ; flow rate of  $120\ \mu\text{L min}^{-1}$  and step duration of 2 min. SPR (A) and QCM-D (B) profiles obtained with equipment connected in parallel. The insets show the injections of copper acetate and PTMTC, corresponding to one cycle. For the QCM-D profile, the frequency and dissipation overtones (from the 3<sup>rd</sup> to the 11<sup>th</sup>) are shown in different colors and labelled as F3 to F11, and D3 to D11, respectively. (C) ATR-IR of the resulting coordination polymer at the end of the experiment shown in (B). (D) Parallelism in the normalized refractive index (open circles) and frequency change (filled circles) difference vs. number of cycles as derived from the time in seconds.

frequency values reached at each step indicate that only the chemically coordinated organic or inorganic synthon remain on the surface, contributing to the buildup of the grafted metal-organic hybrid coordination polymer. The ATR-IR (Fig. 2C) spectrum of the prepared sample shows, apart from the bands characteristics of the PTMTC ligand at  $1326$  and  $1260\text{ cm}^{-1}$ , vibrational bands at  $1602$  and  $1421\text{ cm}^{-1}$ , corresponding to the asymmetric and symmetric vibration of the

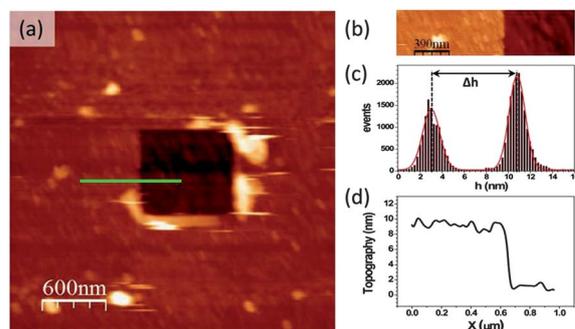
carboxylate groups. The presence of such bands, together with the absence of the carbonyl stretching of protonated carboxylic groups, at 1670 and 1712  $\text{cm}^{-1}$  (ref. 14) confirms that the PTMTC ligand is bound to the copper acetate. Interestingly, we found that the trend to form a paddle-wheel configuration of the metal unit is of fundamental importance for the surface growth of the PTMTC-Cu polymer. Indeed, when a copper salt with no paddle-wheel configuration was used, no step-wise growth of the PTMTC-based coordination polymer could be observed (see ESI3†), in agreement with what was observed for other surface grafted coordination polymers.<sup>3a</sup> On the basis of this experimental evidence, and considering the  $\Delta\nu_{(\text{asym-sym})}$  value (181  $\text{cm}^{-1}$ ),<sup>19</sup> we might suggest a bridging bidentate configuration of the copper in the step-wise grown polymer, as observed in many other coordination polymers grown on template surfaces. Nevertheless, further experimental evidence is needed to prove this hypothesis, as ascertained by Watkinson and coworkers.<sup>20</sup> By comparing the changes in refractive index and frequency shift, recorded jointly, vs. the number of cycles (Fig. 2D), it is also possible to extract some information about the solvent uptake within the coordination polymer. Note that, while the changes in refractive index of the hybrid grown thin film, are independent of the solvent uptake during an SPR experiment, the change in oscillation frequency depends on it. Therefore, if a quite large solvent uptake takes place, the SPR and the QCM-D sensorgrams would deviate from each other. In the present case, instead, a parallelism of the plots of normalized RI and  $-\Delta f$  vs. number of cycles is observed. This evidence seems to support the hypothesis that no important solvent uptake takes place. An analogous piece of information can be extracted by the almost complete absence of any spread among the recorded frequency overtones (Fig. 2(B)). This behavior, together with the very small (lower than  $3 \times 10^{-6}$  units, Fig. 2(B)) change in the dissipation parameter, that gives indication of the viscoelastic behavior of the film,<sup>6</sup> further suggests that the obtained coordination polymer is rather rigid. For this reason, it is reasonable to make use of the Sauerbrey equation<sup>21</sup> that directly correlates the changes in frequency with the mass uptake to determine the amount of adsorbed mass per square centimeter (*ca.*  $1450 \times 10^{-9}$   $\text{g cm}^{-2}$  for the 23 cycles). In the case of rigid and homogeneously distributed films, it is also possible to use the Sauerbrey equation to calculate the film thickness, being necessary to introduce as a constant parameter the density of the polymer. If, as a first and rough approximation, we use the density value of the largely porous framework MOROF-1 ( $0.94 \text{ g cm}^{-3}$ )<sup>22</sup> formed by the PTMTC radical, copper perchlorate and pyridine,<sup>23</sup> a Sauerbrey thickness of *ca.* 15.4 nm for the grown hybrid layer would be expected. Nevertheless, a different density value for the step-wise deposited PTMTC-copper coordination polymer could also be possible: as discussed above (Fig. 2(C)), the ATR-IR spectrum recorded for the 23 cycle QCM-D sample might suggest a bridging bidentate configuration of the copper, hence a structure for the coordination polymer different from the one reported in the bulk for porous MOROF1; in addition, the dissipation measurements suggest the absence of solvent in the structure, consistent with a non-

porous framework. For these reasons, we considered it necessary to determine the thickness of the grown film by SFM, and then eventually use this value to back-calculate the density of this novel coordination polymer and thus gain some more information on its structure. Since, in this case, a laterally continuous polymeric film is formed on the single component MHDA SAM, no direct measurement of the film thickness could be performed by SFM, and we instead used the so called scratching procedure, consisting of locally removing the polymeric material until reaching the underlying Au substrate surface (see ESI1†). As shown in Fig. 3, though some of the material removed has been accumulated at some borders of the scratched area, height histograms between the inner and outer regions of the scratched region, as well as topographic profiles (Fig. 3(c) and (d)), can be used to determine the film thickness. The 23 cycle copper-PTMTC thin film was measured by this method to be  $7.5 \pm 0.5$  nm thick for both SPR and QCM-D samples.

This value is almost half of the Sauerbrey thickness obtained, assuming for the coordination polymer the density of the porous MOROF1 framework, but otherwise matches with a density of  $1.9 \pm 0.27 \text{ g cm}^{-3}$ , a value compatible with a dense grafted structure.<sup>24</sup> Therefore, we have demonstrated that a PTMTC based coordination polymer can be grown as a thin film on a template surface in the presence of copper acetate, obtaining a dense and rather rigid structure for the formation of which the trend for a paddle-wheel configuration of the Cu(II) synthon seems to play a critical role.<sup>25</sup>

## B Grafting under static conditions

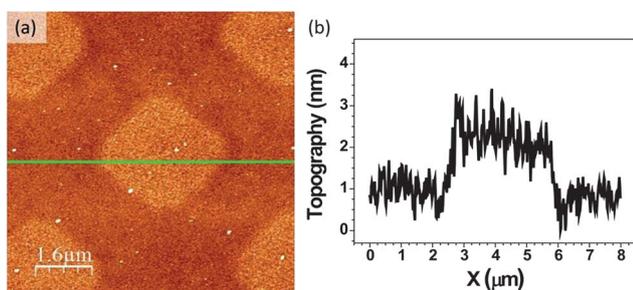
For such a grafting, patterned gold substrates (see experimental section), which have regularly spaced squared areas (3 and 20  $\mu\text{m}$ ) functionalized with carboxylic groups (MHDA) surrounded by methyl terminated HDT areas, were immersed and let react in a small vessel with an ethanolic solution of copper acetate for a time period of 30 min at room temperature, abundantly rinsed with ethanol, and then, without



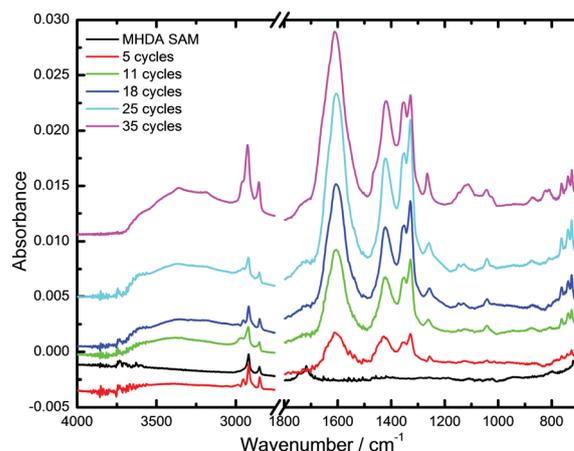
**Fig. 3** (a) Topographic SFM image of a continuous film of PTMTC-copper polymer grown by 23 cycles (under continuous flow conditions in the SPR) after a scratching experiment performed to estimate the film thickness from the height difference between the topmost polymer surface and the unvelled gold substrate. Zoom-in at the border of the scratched region (b) and the corresponding height histogram (c). The topographic line profile marked in (a) is presented in (d). More details in ESI1.†

drying, allowed to react with the organic ligand solution (60 min) at room temperature. As in the case of continuous flow, during the first step, the Cu(II) ions are expected to coordinate to the carboxylic end groups of the MHDA, hence to graft only on the patterned squares. The organic PTMTC ligand will subsequently coordinate these MHDA-Cu regions with one (or two) *para*-carboxylic groups, letting the MHDA-Cu-PTMTC patterned areas expose two (or one) PTMTC carboxylic groups. The repetition of such injection cycles for a given number of times results in a laterally confined selective grafting of the PTMTC-Cu coordination polymer, as indicated by the chemical composition mapping extracted from TOF-SIMS data (see ESI<sup>†</sup>) and imaged by SFM (Fig. 4). The thickness of the material grown was estimated by the SFM topographic difference between the squared areas and the surrounding bare HDT regions, where no coordination polymer was grafted. This thickness increases with the number of cycles, indicating that the PTMTC based coordination polymer can be step-wise deposited also under static conditions.

Infrared spectra in the grazing incidence mode were recorded for samples grown following the same procedure described above but on template gold surfaces uniformly covered by single component MHDA SAMs (Fig. 5). IRRAS spectra were recorded at specific times for the step-wise deposition, *i.e.* the cycle sequence was interrupted to record the IR spectrum after a given number of cycles and then re-immersed to continue with further cycles up to a total of 35 in this case. The presence of vibrational bands at 1607 and 1422 cm<sup>-1</sup>, attributed to the asymmetric and symmetric stretching of carboxylate groups, which increase their intensity with increasing number of cycles (Fig. 5), suggests that the carboxylic groups of the organic ligand underwent a complete deprotonation and are bound to the metal ions. The separation of symmetric and asymmetric stretching of the carboxylate group analogous to the samples prepared under continuous flow was recorded. In conclusion, also by working under static conditions, we have been able to graft on both patterned and single component surfaces a metal-organic coordination polymer based on PTMTC and copper, which is likely to be in a bridging bidentate configuration.



**Fig. 4** SFM topographic image of an ultrathin PTMTC-copper polymer (4 cycles) grown under static conditions on a gold template surface previously functionalized with a pattern of MHDA squares (3 μm × 3 μm) surrounded by HDT (a). The topographic profile in (b) corresponds to the line indicated in (a) and serves to estimate the polymer thickness from the height difference with respect to the HDT areas.



**Fig. 5** IRRAS spectra of a template gold surface with a uniform MHDA SAM on which the PTMTC-copper coordination polymer has been deposited under static flow conditions using different number of cycles.

## Conclusions

We have presented the use of the step-by-step method to anchor on a template surface, previously functionalized with a carboxylic terminated SAM, a coordination polymer based on copper acetate and a non-planar trigonal molecule, the tri-*para*-carboxylic polychlorotriphenylmethyl radical. As already shown in the case of other surface anchored MOFs, the trend to form a paddle-wheel geometry of the metal ion used during the step-wise preparation procedure (Scheme 1) seems to be the most suitable one for the surface anchoring and growth of these hybrid polymers.<sup>26</sup> The evidence that only with copper acetate salt a step-wise growth could be achieved, points to the need for a bridging bidentate configuration of the organic ligand carboxylate groups and the copper ion. As previously reported, one of the major advantages of the step-by-step method under continuous flow conditions is the possibility to monitor *in situ* and in real time the deposition of the organic and inorganic synthons, employing both SPR and QCM-D. In particular, the monitoring of the mechanical frequency change and of the dissipation has shown that the PTMTC based grafted metal-organic hybrid polymer is rather rigid. In addition, we have proved how information on the density could be obtained by independent measurement of the thickness of the film by scanning force microscopy (SFM). This latter technique allowed us to suggest that the bulk density parameter of a compound similar in composition cannot be used in the studied case, since the structure of the adsorbed thin film does not correspond to the one found in the 3D crystals and obtained using a different metal ion salt. The achievement of a dense and rigid film indicates that the step-by-step method does not always lead to surface anchored porous frameworks and that, instead, the final structure might depend on the geometry and conformational stiffness of the organic ligand used. To the best of our knowledge, ligands with similar geometries have been used to prepare MOFs only in bulk<sup>27</sup> but not yet on surfaces, where the achievement of a framework open structure and crystallinity might still represent a challenge.<sup>28</sup> To sum up, as a result of the

use of complementary characterization techniques, it has been possible to understand that the sequential deposition both under continuous flow conditions, followed in real time by QCM-D and SPR, and under static conditions, of copper acetate and PTMTC radical derivatives using ethanol as a vehicular solvent leads to the formation of a compact, homogeneous and rigid very thin film. The possibility to get a non-dense and porous film of copper and PTMTC using an additional linker, such as bipyridine is under investigation, similar to what has been reported for the non-planar triangular 1,3,5-tri-methyl-2,4,6-tri-carboxy-benzene in bulk.<sup>29</sup>

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## Notes and references

- G. Decher, *Science*, 1997, **277**, 1232.
- (a) H. Gliemann and C. Wöll, *Mater. Today*, 2012, **15**(3), 110; (b) D. Zacher, R. Schmid, C. Wöll and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2011, **50**, 176; (c) O. Shekhah, J. Liu, R. A. Fischer and C. Wöll, *Chem. Soc. Rev.*, 2011, **40**, 1081; (d) D. Zacher, O. Shekhah, C. Wöll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418.
- (a) O. Shekhah, H. Wang, D. Zacher, R. A. Fischer and C. Wöll, *Angew. Chem., Int. Ed.*, 2009, **48**(27), 5038; (b) O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, D. Zacher, R. A. Fischer and C. Wöll, *J. Am. Chem. Soc.*, 2007, **129**, 15118; (c) O. Shekhah, H. Wang, T. Strunskus, P. Cyanik, D. Zacher, R. A. Fischer and C. Wöll, *Langmuir*, 2007, **23**(14), 7440.
- O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A. Terfort, D. Zacher, R. A. Fischer and C. Wöll, *Nat. Mater.*, 2009, **8**(6), 481–484.
- J. Homola, *Anal. Bioanal. Chem.*, 2003, **377**, 528.
- I. Reviakine, D. Johannsmann and R. P. Richter, *Anal. Chem.*, 2011, **83**(23), 8838.
- (a) L. E. Bailey, D. Kambhampati, K. K. Kanazawa, W. Knoll and C. W. Frank, *Langmuir*, 2002, **18**, 479; (b) E. Reimhult, C. Larsson, B. Kasemo and F. Höök, *Anal. Chem.*, 2004, **76**(24), 7211; (c) F. Höök, B. Kasemo, T. Nylander, C. Fant, K. Sott and H. Elwing, *Anal. Chem.*, 2001, **73**, 5796.
- (a) J. C. Antunes, C. Leite Pereira, M. Molinos, F. Ferreira-da-Silva, M. Dessi, A. Gloria, L. Ambrosio, R. M. Gonçalves and M. A. Barbosa, *Biomacromolecules*, 2011, **12**, 4183; (b) M. Rodahl, F. Höök, C. Fredriksson, C. A. Keller, A. Krozer, P. Brzezinski, M. Voinova and B. Kasemo, *Faraday Discuss.*, 1997, **107**, 229.
- (a) O. Zybaylo, O. Shekhah, H. Wang, M. Tafipolsky, R. Schmid, D. Johannsmann and C. Wöll, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8092; (b) C.-Y. Huang, M. Song, Z.-Y. Gu, H.-F. Wang and X.-P. Yan, *Environ. Sci. Technol.*, 2011, **45**, 4490.
- O. Shekhah, N. Roques, V. Mugnaini, C. Munuera, C. Ocal, J. Veciana and C. Wöll, *Langmuir*, 2008, **24**, 6640.
- S. Chui, S. Lo, J. Charmant, A. Orpen and I. A. Williams, *Science*, 1999, **283**, 1148.
- (a) M. Ballester, *Acc. Chem. Res.*, 1985, **18**, 380; (b) J. Veciana and I. Ratera, in *Stable Radicals: Fundamentals and Applied Aspects of Odd-electron Compounds*, ed. R. G. Hicks, Wiley, New York, 2010, p. 33.
- D. MasPOCH, N. Domingo, D. Ruiz-Molina, K. Wurst, G. Vaughan, J. Tejada, C. Rovira and J. Veciana, *Angew. Chem., Int. Ed.*, 2004, **43**, 1828.
- R. Arnold, W. Azzam, A. Terfort and C. Wöll, *Langmuir*, 2002, **18**(10), 3980.
- E. Kretschmann and H. Reather, *Z. Naturforsch. A*, 1968, **23A**, 2135.
- I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.
- C. Munuera, E. Barrena and C. Ocal, *J. Phys. Chem. A*, 2007, **111**, 12721.
- O. Shekhah, *Materials*, 2010, **3**, 1302.
- G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
- D. Martínez, M. Motevalli and M. Watkinson, *Dalton Trans.*, 2010, **39**, 446.
- G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206.
- D. MasPOCH, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira and J. Veciana, *Nat. Mater.*, 2003, **2**, 190.
- The surface grafted PTMTC-copper coordination polymer is not expected to have the same crystal structure of the MOROF1, where the copper ion is monodentate and a pyridine molecule completes its coordination sphere. Nevertheless, the MOROF1 density is here used for a first approximated calculation considering it as the general density value for a framework made of polychlorinated ligands.
- As an example, the PTMMC-copper(II) paddle-wheel coordination complex bulk density is 1.75 g cm<sup>-3</sup>. D. MasPOCH, D. Ruiz-Molina, K. Wurst, C. Rovira and J. Veciana, *Chem. Commun.*, 2002, 2958.
- Unfortunately, for the prepared samples no X-ray characterization was possible, either due to the low thickness of the grafted film under investigation in this study or due to the low long-range order exhibited by this novel rigid and dense structure.

- 26 D. Zacher, K. Yussenko, A. Bétard, S. Henke, M. Molon, T. Ladnorg, O. Shekhah, B. Schüpbach, T. de los Arcos, M. Krasnopolski, M. Meilikhov, J. Winter, A. Terfort, C. Wöll and R. A. Fischer, *Chem.–Eur. J.*, 2011, **17**, 1448.
- 27 B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe and O. M. Yaghi, *Science*, 2001, **291**, 1021.
- 28 R. Kaminker, L. Motiei, A. Gulino, I. Fragalà, L. J. W. Shimon, G. Evmenenko, P. Dutta, M. A. Iron and M. E. van der Boom, *J. Am. Chem. Soc.*, 2010, **132**, 14554.
- 29 H. He, H. Yin, D. Wang, H. Ma, G. Zhang and D. Sun, *J. Inorg. Chem.*, 2010, 4822.