

# Direct X-ray and electron-beam lithography of halogenated zeolitic imidazolate frameworks

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## **Abstract**

Integrating metal-organic frameworks (MOFs) in microelectronics has disruptive potential because of the unique properties of these microporous crystalline materials. Nanoscale patterning is a fundamental step in the implementation of MOFs in miniaturised solid-state devices. Conventional MOF patterning methods suffer from a low resolution and poorly defined pattern edges. Here, we demonstrate for the first time resist-free, direct X-ray and e-beam lithography of MOFs. This process avoids etching damage and contamination, and leaves the porosity and crystallinity of the patterned MOFs intact. The resulting high-quality patterns have a record sub-50 nm resolution, far beyond the state of the art in MOF patterning and approaching the mesopore regime. The excellent compatibility of X-ray and e-beam lithography with existing microfabrication processes, both in research and production facilities, provides an avenue to explore the integration of MOFs in microelectronics further. This approach is the first example of direct lithography of any type of microporous crystalline network solid, and marks an important milestone in the processing of such materials.

## Main

To structure matter at the (sub-)nanometre scale, both bottom-up and top-down strategies are pursued. Bottom-up approaches, inspired by biological systems, seek to have molecular building blocks self-assemble into the desired arrangement. However, precise control over the localisation of the self-assembly sites is a challenging task. In contrast, top-down approaches use external stimuli to remove the undesired part of a larger area to create the desired shapes in the preferred location. The convergence of self-assembly and top-down approaches would lead to multiscale control over the organisation of matter, from arranging molecular building blocks to shaping the materials they form.<sup>1-4</sup> For instance, high-resolution patterning can be achieved by using lithographically defined guiding patterns to direct the self-assembly of engineered block copolymers.<sup>5</sup> In this case, self-assembly serves solely to achieve smaller-pitch patterns since the block copolymer is sacrificed. An anticipated next step in bringing together bottom-up and top-down approaches is the patterning and integration of self-assembled materials with desired properties as functional components.

Metal-organic frameworks (MOFs) are crystalline nanoporous materials that form through the self-assembly of metal ion nodes and multitopic organic linkers.<sup>6,7</sup> Because of their porous, crystalline, and modular nature, MOFs offer unique prospects in microelectronics and related applications, including displays, photovoltaics, low-k dielectrics and chemical sensors.<sup>8-15</sup> Thin film deposition and patterning are the fundamental steps to integrate any novel material in a device. However, patterning techniques for MOFs are still in their infancy, and suffer from a low resolution and poorly defined pattern edges (Supporting Information Section 1).<sup>15-18</sup> In conventional lithography, the pattern generated in a resist layer is etched into a film of the material of interest, followed by stripping the resist mask.<sup>19</sup> The few reported examples of lithographic MOF patterning follow this approach.<sup>20-23</sup> Direct, resist-free lithography of functional materials is desirable to minimise the number of process steps and possible contamination sources, especially for highly porous materials.<sup>24-26</sup> For instance, direct patterning of low-k dielectrics could eliminate resist contamination and the exposure to damaging plasma.<sup>26-28</sup> Herein, we report for the first time the resist-free lithography of MOFs at the micro- and nanoscale by X-ray and e-beam lithography (XRL and EBL, respectively; Figure 1). This straightforward approach enables high-quality MOF patterns in which all desirable material properties are maintained. A sub-50 nm resolution is demonstrated, which is two orders of magnitude improvement over previous lithographic MOF patterns.<sup>20-23</sup>

In XRL, a mask is used to pattern an X-ray-sensitive layer with a resolution down to 100 nm.<sup>29</sup> In contrast, EBL is a mask-less technique based on direct writing in an e-beam-sensitive material, with a resolution down to sub-10 nm.<sup>30,31</sup> In both techniques, the solubility of the irradiated layer changes, which enables selective dissolution of either the exposed or non-exposed region during the developing step. To evaluate the feasibility of direct lithography of MOFs, we screened the X-ray sensitivity of a variety of zeolitic imidazolate frameworks (ZIFs,<sup>32,33</sup> a subclass of MOFs) by exposing ZIF powders to X-rays (2-30 keV; Supporting Information Section 2). All halogenated ZIFs exhibited a clear solubility switch from a threshold dose onwards, regardless of their topology or structural metal ion. The studied halogenated ZIFs include ZIF-71, ZIF-71\_Co, ZIF-72, ZIF-8\_dclm, ZIF-8\_Cl and ZIF-8\_Br (Figure 1a). While the pristine halogenated ZIFs are entirely insoluble in dimethyl sulfoxide (DMSO), they readily dissolved in this solvent after X-ray irradiation. In contrast, non-halogenated ZIFs did not show solubility changes in any common solvent, although the collapse of the crystalline structure occurred at high X-ray doses, in consistent with the previous report.<sup>34</sup>

To further evaluate halogenated ZIFs as positive-tone materials in direct lithography, films were grown through chemical vapour deposition (CVD). The two-step MOF-CVD process consists of depositing a ZnO precursor layer and subsequently converting it to the desired ZIF in an imidazole linker atmosphere.<sup>21,35</sup> The ZIF films were characterised by grazing-incidence small-angle X-ray scattering (GISAXS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and ellipsometry (Supporting Information Section 3). To evaluate the lithographic process, an XRL mask with dots and holes of different shapes and dimensions was used (ranging from 10 to 150  $\mu\text{m}$ ; Figure S1). Taking 300 nm ZIF-71 films as an illustration case, the optimal volume dose was found to be 60  $\text{kJ cm}^{-3}$ . The crystal structure of non-irradiated ZIF-71 was maintained throughout the XRL process, as confirmed by GISAXS (Figure 2a). Through the removal of the irradiated areas, even the smallest features of the mask are replicated with high fidelity in the ZIF-71 layer (Figure 2b). Profilometry together with energy-dispersive X-ray spectroscopy (EDX) mapping suggest that the irradiated area was completely removed, as further confirmed by AFM (Figure 2c, d). Furthermore, both SEM and AFM demonstrate the sharp edges of the ZIF-71 pattern (Figure 2d and S28). Besides ZIF-71, the same XRL protocol can be employed for the direct patterning of other halogenated ZIF films, with similar optimal exposure doses (60-100  $\text{kJ cm}^{-3}$ ; Supporting Information Section 4).

XRL is capable of patterning thick layers (up to mm), due to the deep penetration of the high-energy X-rays.<sup>36</sup> To leverage this capability, XRL was performed on 50-200  $\mu\text{m}$  ZIF-8\_dclm single crystals. Positive and negative hexagonal grid masks enabled to cleanly slice through the entire crystal, in a 'cookie cutter' fashion, to yield crystals with hexagonal holes and freestanding hexagonal rods, respectively (Figure 2e, f and S46). To validate the retention of the single-crystalline nature of these particles, single-crystal X-ray diffraction was conducted. The starting ZIF-8\_dclm crystallizes in the cubic  $Im\bar{3}m$  space group.<sup>37</sup> Remarkably, the diffraction patterns of the single crystals after XRL were of high enough quality to determine the unit cell parameters as identical to those of the starting crystals (Table S3), thus demonstrating that XRL maintains the single-crystalline nature. This patterning approach could enable hierarchical structures with highly ordered porosity at multiple length scales, which are of interest in a range of applications.<sup>38-40</sup>

To leverage MOFs in solid-state devices, patterning should not alter their desirable properties, especially their porosity. Notably, such tests have not been considered previously.<sup>15,16</sup> The porosity of patterned ZIF-71 films was studied by krypton (Kr) and methanol physisorption on MOF-coated micropillar arrays and quartz crystal microbalance (QCM) substrates, respectively (Figure 3a-d). The MOF-CVD process enables conformal ZIF-71 coatings on the pillar arrays, resulting in a geometric surface area enhancement that enables Kr sorption measurements (Figure S29).<sup>21</sup> The resulting type I isotherm and the Brunauer-Emmett-Teller (BET) surface area per film area of 247  $\text{m}^2 \text{m}^{-2}$  demonstrate the microporous nature of the ZIF-71 coating before X-ray irradiation (Figure 3c). Based on the calculated ZIF-71 density (1.17  $\text{g cm}^{-3}$ ) and measured film thickness (200 nm), a specific BET surface area of 1055  $\text{m}^2 \text{g}^{-1}$  is found, similar to values reported for powder samples.<sup>41</sup> After X-ray irradiation and removal of the coating on half of the pillar array, the BET surface area of the remaining ZIF-71 film was virtually unchanged (236  $\text{m}^2 \text{m}^{-2}$ ; Figure 3c). Gravimetric QCM monitoring shows an S-shaped methanol adsorption isotherm (Figure 3d), in good agreement with data reported for ZIF-71 powder samples.<sup>42</sup> By using the removed film fraction as a correction factor, the gravimetric methanol isotherms of the patterned and unpatterned ZIF-71 films overlap. These results illustrate the remaining ZIF-71 film after XRL fully retains its porosity.

Due to their periodicity, the ZIF-71 patterns formed by XRL are efficient diffraction gratings for light in the visible range (Figure 3e, f).<sup>43</sup> Taking advantage of the MOF's porosity, a ZIF-71 pattern on a transparent substrate was used as a diffraction grating vapour sensor (Figure 3g). When guest molecules adsorb in the pores, the phase difference resulting from the ZIF-71 pattern increases together with the refractive index of the MOF layer. Therefore, guest adsorption can be transduced through monitoring the intensity changes of the first-order diffraction spots.<sup>43</sup> This principle was illustrated for methanol vapour sensing using a 200 nm thick ZIF-71 diffraction grating covering a  $4 \times 4 \text{ mm}^2$  area (Figure 3g, h). The resulting sensing data are in excellent agreement with the *in situ* ellipsometry and QCM reference adsorption experiments. Despite its simplicity, this example illustrates the potential of scalable high-resolution patterning of MOF films.

The initially white halogenated ZIF powders turn brown upon X-ray exposure (Figure S6), indicating a chemical change of the imidazolate linkers. X-ray-induced changes typically comprise primary and secondary phenomena. Primary bond breaking occurs because of the interaction between the X-rays and the irradiated material through photoelectric, Compton or Auger effects.<sup>34,44</sup> Secondary reactions are the result of radiolytic products such as free radicals generated by the energetic electrons.<sup>45,46</sup> Since halogenated ZIFs undergo both decomposition and a solubility switch, while non-halogenated ZIFs only exhibit amorphisation (Supporting Information Section 2), halogen atoms on the structural linkers evidently play a vital role in these processes. GISAXS data show that ZIF-71 films become amorphous at X-ray doses over  $10 \text{ kJ cm}^{-3}$ , while a dose higher than  $60 \text{ kJ cm}^{-3}$  is required for a complete solubility switch (Figure 4a). This result suggests that low X-ray doses induce the amorphisation because of primary damage, and further reactions take place at higher doses. While the solution <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum of the pristine dclm linker has only one peak at  $\sim 7.5 \text{ ppm}$ , a large number of peaks appear in the 6.5-9 ppm and 2.5-1.5 ppm ranges after X-ray irradiation (Figure 4b). The peaks indicate bond cleavage of imidazolate ring and the formation of different imines, C-H bonds or amines. These chemical changes are likely catalysed by Cl radicals that are sufficiently reactive to initiate C-H activation, C-C bond cleavage, and ring-opening reactions.<sup>47-50</sup>

The X-ray-induced changes of ZIF-71 films were studied by X-ray photoelectron spectroscopy (XPS). No obvious changes were found in the Zn 2P spectra, indicating no reduction of  $\text{Zn}^{2+}$  (Figure S47). In the N 1S XPS spectra, both C-N and Zn-N peaks decrease along with an increase of the N-H signal, suggesting cleavage of the imidazole ring C-N bonds and the framework Zn-N bonds (Figure 4e, f). The decrease of C-Cl signal together with the rise of the Zn-Cl signal suggests the formation of Cl radicals by the homolysis of C-Cl bonds (Figure 4d, f). These Cl radicals likely initiate the cleavage of C-C, C-N, and Zn-N bonds, resulting in further reactions between the formed fragments. No change in composition is observed (Table S4), suggesting that negligible material is lost through volatilisation during X-ray exposure. Figure 4c displays the elemental analysis of the water-soluble and -insoluble fractions of X-ray irradiated ZIF-71. Both fractions contain C, N, and Cl, while only the water-soluble fraction contains Zn. Therefore, the X-ray-induced breakdown of the dclm linker seems to result in an at least partially polymerised organic fraction and a water-soluble fraction consisting of Zn-Cl salts, and Zn-N or Cl-Zn-N complexes. In contrast, the imidazolate linkers of non-halogenated ZIFs remain intact upon X-ray induced amorphisation.<sup>34</sup> Therefore, the crucial role of the halogen atoms is to catalyse the imidazolate ring fragmentation upon X-ray exposure, thus enabling dissolution and direct lithography.

XRL resists can commonly also be applied in EBL, since the electron beam has the same effect as the photoelectrons generated by X-rays.<sup>31,51</sup> It was previously observed that repeated scanning during

electron microscopy can induce amorphisation of non-halogenated ZIFs, resulting in a less soluble amorphous deposit.<sup>52</sup> Analogous to the different behaviour of non-halogenated and halogenated ZIFs in XRL, the latter behave as positive-tone materials in direct EBL. The optimal e-beam area dose for ZIF-71 patterning was found to be  $\sim 1000 \mu\text{C}/\text{cm}^2$  (Supporting Information Section 6). The irradiated part cannot be developed completely at lower irradiation doses, while higher doses resulted in a mismatch between the developed and exposed areas due to scattering of the primary, secondary and backscattered electrons.<sup>53–55</sup> Patterns with different shapes and feature sizes were obtained by direct e-beam writing in a 100 nm thick ZIF-71 film and subsequent development in DMSO. Straight lines with sharp edges were achieved for features down to 50 nm (Figure 5a-d and S57). In all patterns, the ZIF-71 crystal facets remain clearly visible, suggesting that the patterned MOF remained intact, as during XRL. AFM data (Figure 5b) suggests that most of the irradiated area was developed, except for a small residue that probably formed by e-beam-induced cross-linking of linker fragments. High-resolution patterning with features below 50 nm can be realized, although the pattern edge quality deteriorates because of proximity effects (Figure 5e, f and S58). Higher resolution may be achievable by systematic optimisation of patterning parameters such as beam energy, beam current, field parameters and deflection mode.<sup>56</sup>

## Conclusion

In summary, we demonstrated for the first time the direct lithographic patterning of MOFs, without the use of resist layers. This approach is the first example of direct lithography of any type of microporous crystalline network solid, and marks an important milestone in the processing of such materials. The resulting patterns have a high uniformity and edge quality, with a record sub-50 nm resolution, far beyond the state of the art in MOF patterning and approaching the mesopore regime. The crystallinity and porosity of the patterned MOF films is maintained. The excellent compatibility of XRL and EBL with established microfabrication processes will considerably expedite the integration of MOF materials in microelectronics and related applications requiring, for example, state-of-the-art low dielectric constant, low refractive index or low density/high surface area materials.

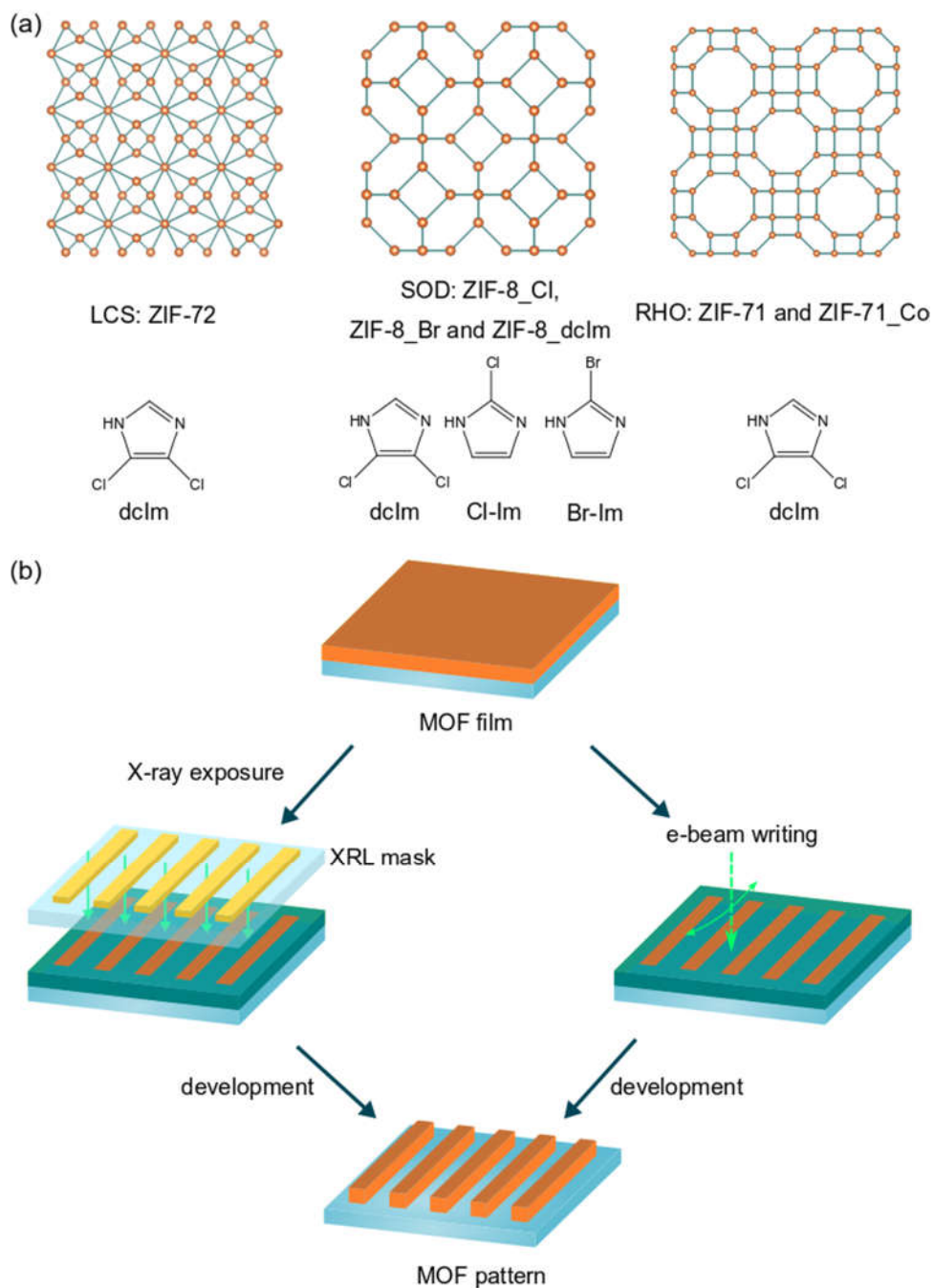


Figure 1. Direct patterning of MOF films by XRL and EBL. (a) Ball-and-stick representation of halogenated ZIFs that can be directly patterned by XRL and EBL. Capitalised three-letter codes are used to describe ZIF topologies. Cl-Im, Br-Im and dclm represent the linkers of 2-chloroimidazole, 2-bromoimidazole and 4,5-dichloroimidazole, respectively. All ZIFs are Zn based except ZIF-71\_Co. (b) Schematic illustration of direct top-down patterning of MOF films by XRL and EBL.

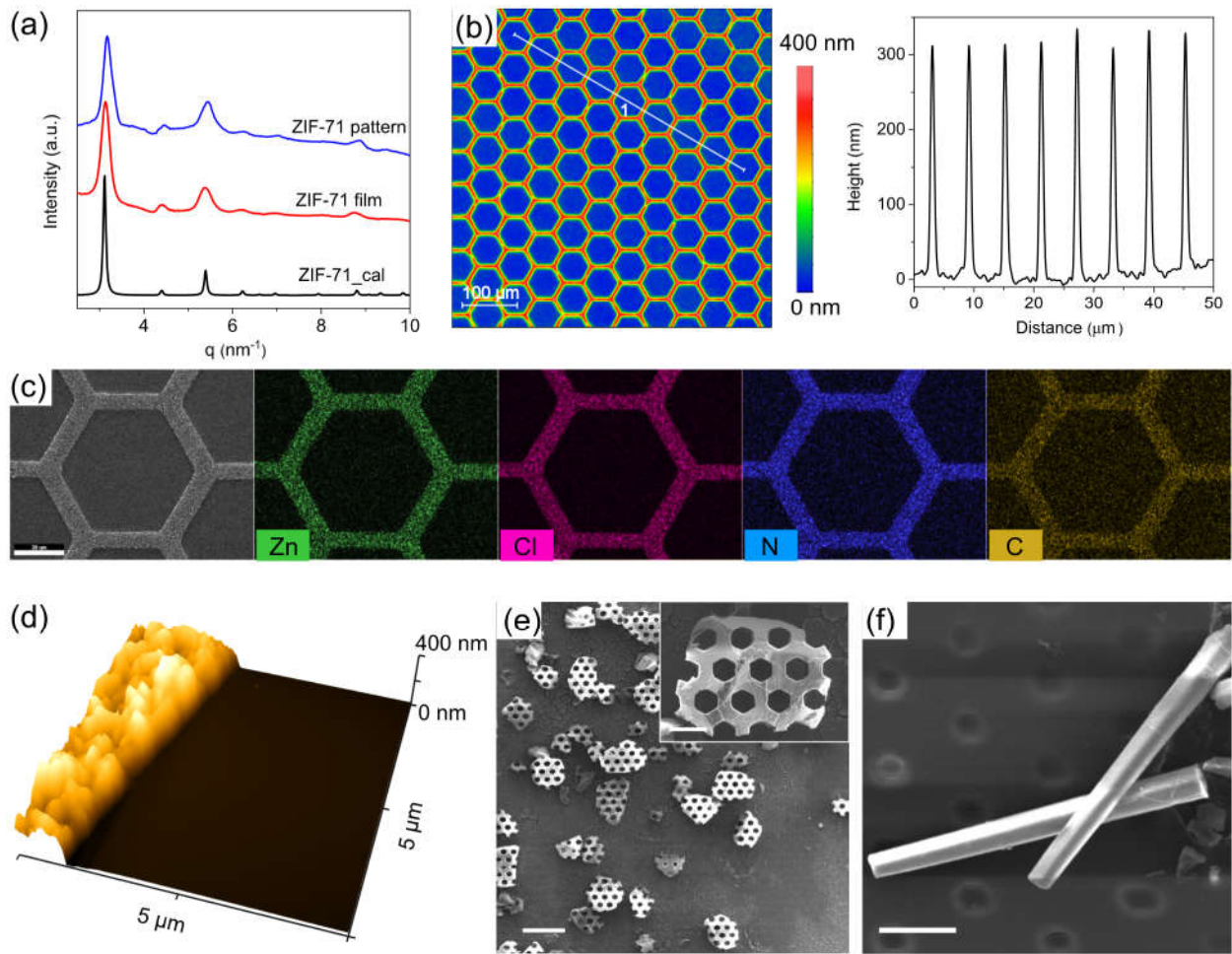


Figure 2. Characterisation of halogenated ZIFs after XRL patterning. (a) Synchrotron GISAXS patterns of 300 nm thick ZIF-71 films before and after XRL, in comparison with the calculated ZIF-71 PXRD pattern. (b) Optical profilometry of the patterned ZIF-71 film and the line profile extracted from this image. (c) SEM-EDX mapping (Zn, Cl, N and C) of the patterned ZIF-71 film. (d) AFM image of the edge of the ZIF-71 pattern. (e-f) SEM images of  $\sim 100 \mu\text{m}$  ZIF-8\_dclm single crystals after XRL patterning with a positive and negative hexagonal grid mask, respectively. The resulting particles retain their single-crystalline nature. Scale bars: (b) 100  $\mu\text{m}$ ; (c) 20  $\mu\text{m}$ ; (e) 200  $\mu\text{m}$  and 50  $\mu\text{m}$  for inset; (f) 20  $\mu\text{m}$ .



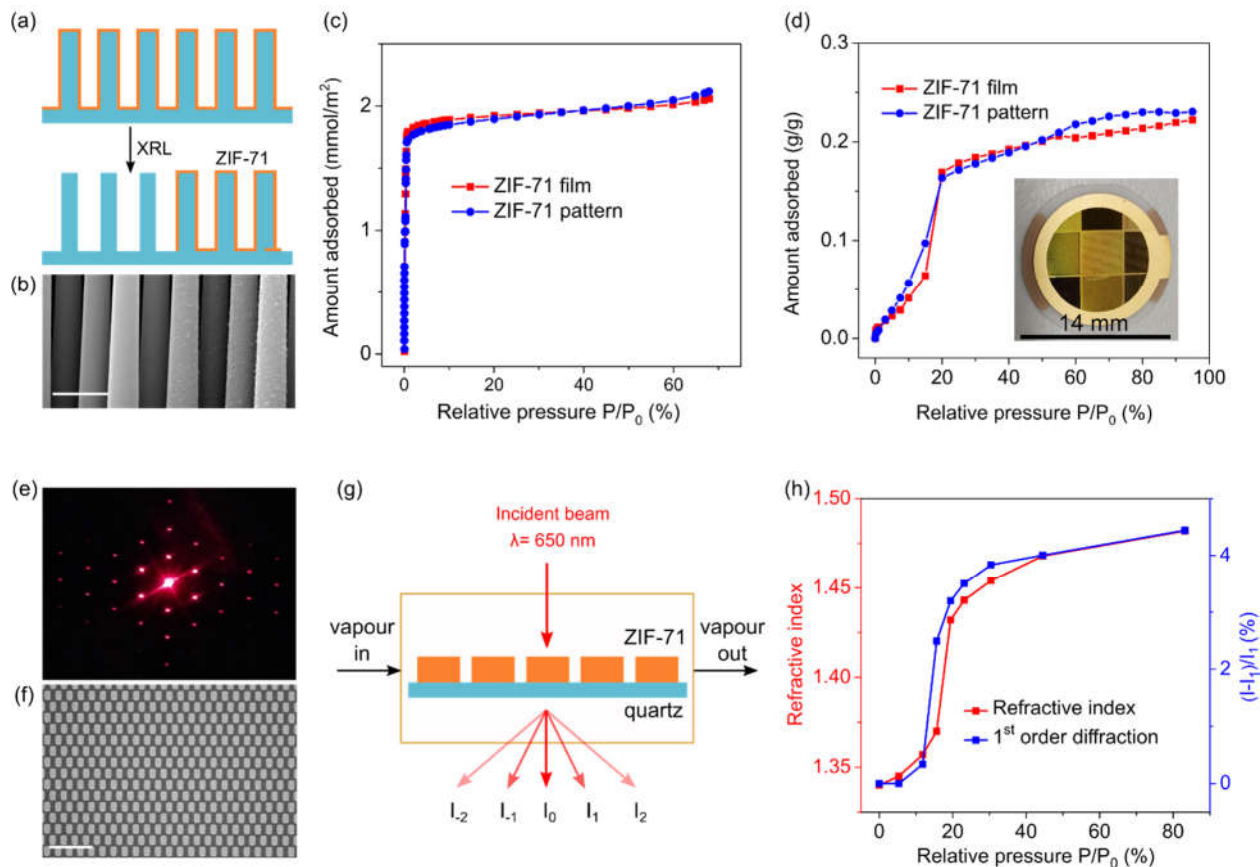


Figure 3. Porosity characterisation and sensing application of patterned ZIF-71 films. (a) Scheme of XRL patterning of a ZIF-71-coated Si pillar array for Kr physisorption. (b) Cross-section SEM image of a Si pillar array after removal of the ZIF-71 film in the left half. Scale bar: 5  $\mu\text{m}$ . (c) Kr adsorption isotherms of ZIF-71-coated Si pillar arrays before and after XRL. The uptake values, per square metre of MOF, are plotted by only considering the MOF-covered area for the patterned pillar array. (d) Methanol adsorption isotherms of ZIF-71-coated QCM substrates before and after XRL. Specific uptake values, per gram of MOF, are plotted by only taking the MOF-covered area into account for the patterned film. Inset: photograph of the ZIF-71 pattern on a QCM substrate. Each of the squares consists of different geometries. (e) Picture of the diffraction pattern resulting from illuminating a ZIF-71 pattern on quartz with a red laser pointer. (f) Optical microscopy image of the corresponding patterned ZIF-71 film acting as a diffraction grating. Scale bar: 100  $\mu\text{m}$ . (g) Scheme of the evaluation of ZIF-71 patterns as diffraction grating vapour sensors. (h) Evolution of the refractive index of a ZIF-71 film measured by ellipsometry (red) and the normalized intensity of the 1<sup>st</sup> order diffraction spot ( $I_1$ ) of the ZIF-71 grating (blue) as a function of methanol vapour pressure.

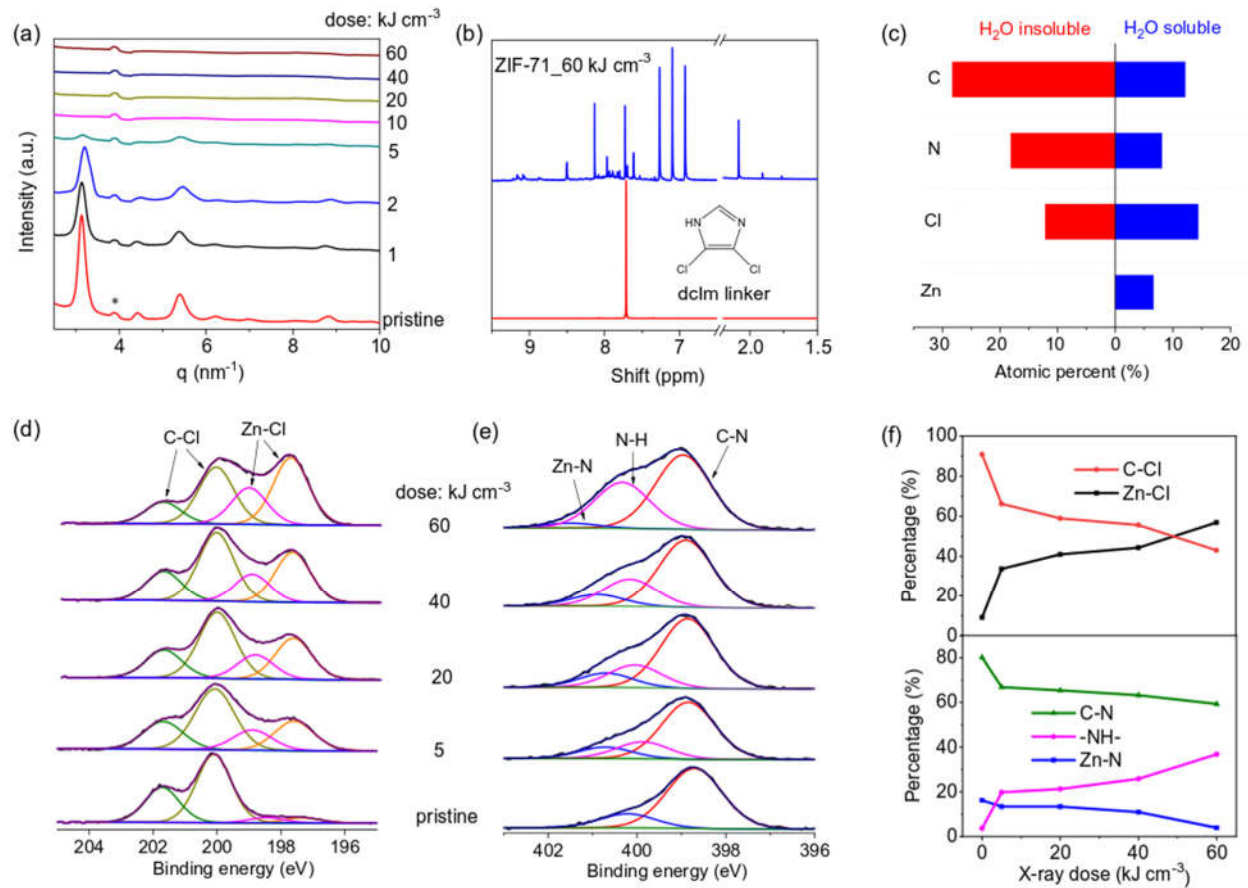


Figure 4. Mechanistic investigation of the X-ray dose effect on ZIF-71. (a) *Ex situ* synchrotron GISAXS patterns of a ZIF-71 film as a function of X-ray dose. The asterisk represents a detector artefact. (b) Solution  $^1\text{H}$  NMR spectra of dclm linker (red) and X-ray irradiated ZIF-71 powder ( $60 \text{ kJ cm}^{-3}$ , blue) in  $\text{DMSO}_d6$ . (c) Elemental analysis of the water-soluble and -insoluble fractions of ZIF-71 powder after X-ray exposure ( $60 \text{ kJ cm}^{-3}$ ). XPS Cl 2p (d) and N 1s (e) spectra of a 200 nm ZIF-71 film as a function of X-ray dose. (f) The proportion of Cl bonds (C-Cl and Zn-Cl, top) and N bonds (C-N, N-H, and Zn-N, bottom) as a function of X-ray dose, calculated from the XPS spectra.

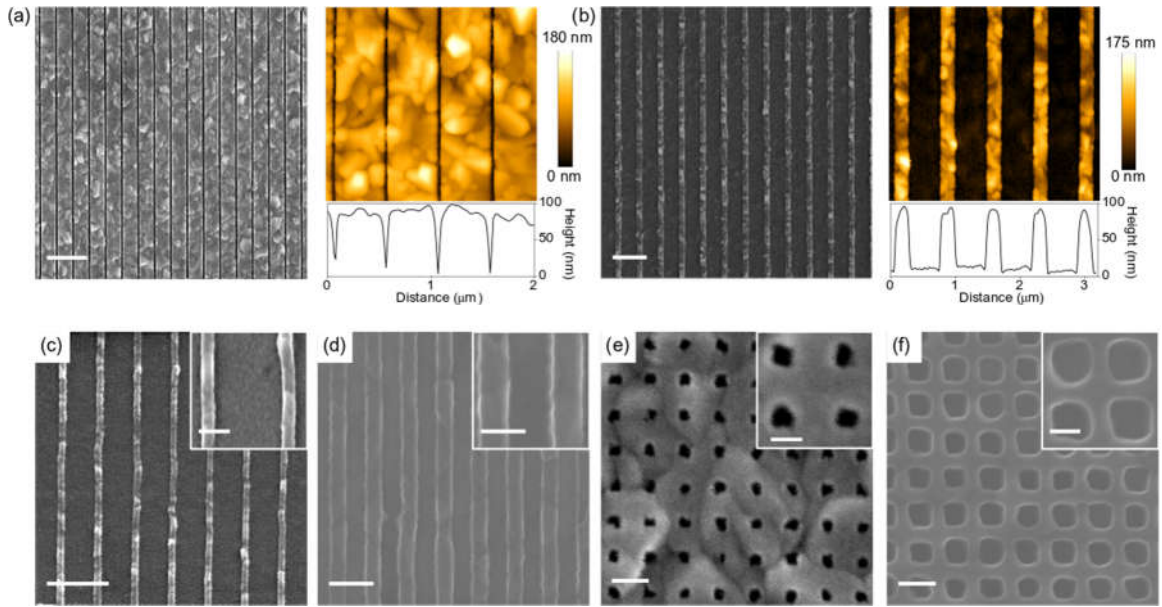


Figure 5. High-resolution EBL patterning of 100 nm thick ZIF-71 films. (a) SEM and AFM images of 50 nm trenches etched into the ZIF-71 film. (b) SEM and AFM images of 200 nm lines. (c-d) SEM images of 100 nm and 60 nm lines, respectively. (e-f) 40 nm holes and grid with a 30 nm line width etched in the ZIF-71 film. Scale bars: (a) and (b) 1  $\mu\text{m}$ ; (c) 1  $\mu\text{m}$  and 200 nm for inset; (d) 200 nm and 100 nm for inset; (e) and (f) 100 nm and 50 nm for inset.

## Methods

### MOF thin film deposition

Single-side polished and back-etched Si wafers were used. Si pillar arrays with a diameter and height of 2 and 50  $\mu\text{m}$ , respectively, were produced by deep reactive ion etching (Bosch process). The MOF film deposition consists of two steps: 1) ZnO precursor layer deposited by atomic layer deposition (ALD); 2) vapour solid conversion of ZnO layer in an organic linker atmosphere. The ZnO films were deposited using a Savannah S-200 thermal ALD reactor (Veeco Instruments, Inc.) with deionized water and diethylzinc as precursors. The pulse and purge durations for the ALD precursors were set to 0.015 s and 5 s, respectively. The reactor base pressure was  $\sim 0.4$  mbar at an  $\text{N}_2$  gas flow of 20 sccm. This process resulted in a ZnO growth rate of 1.7  $\text{\AA}/\text{cycle}$  on Si substrates at 120  $^\circ\text{C}$ . In the case of ZIF-71 deposition, ZnO film, 50 mg of 4,5-dichloroimidazole (dclm) powder and a small quantity of DMF (50  $\mu\text{L}$ ) were placed separately in a 250 mL schlenk tube. After heating in a convection oven at 110  $^\circ\text{C}$  for 1 day, ZIF-71 film was obtained. ZIF-8\_Cl and ZIF-8\_Br were deposited by the same method using 2-chloroimidazole (Cl-Im) and 2-bromoimidazole (Br-Im), respectively. The ZIF-72 film was deposited at 150  $^\circ\text{C}$  without the addition of DMF. The obtained MOF films were activated by heating at 150  $^\circ\text{C}$  under dynamic vacuum (0.1 mbar) for 1 day.

### X-ray lithography

XRL was performed at the XRL beamline of Elettra synchrotron (Trieste, Italy).<sup>57</sup> A scheme of the filter chamber and of the XRL scanner is shown in Figure S1. Samples can be directly exposed to the X-ray beam, or a mask containing patterns can be placed in front of the sample. The X-ray beam is composed of different energies (2-30 keV) with a characteristic wavelength of 3.22 keV. The two main setups are the one for films deposited on flat substrates and the one for holding powders. The film sample holder is the standard one available in every XRL beamline. The powder sample holder consists of a 200  $\mu\text{m}$  trench machined in a stainless steel block. The patterning of ZIF-8\_dclm single crystals was performed in the film patterning mode by spreading out the crystals on double-side Kapton tape. The mask employed for the patterning of the film, contains arrays of dots and holes with different shape (squares, circles, hexagon, lines) with different dimensions (5-150  $\mu\text{m}$ ) and spacing (5.5-150  $\mu\text{m}$ ). A picture of the mask is shown in Figure S1. In XRL, the dose is commonly expressed as energy per unit volume absorbed at the bottom of the exposed material (traditionally expressed as  $\text{kJ cm}^{-3}$ ). It takes into account the thickness of the material and its attenuation length (in the energy range of the X-ray beam spectrum). The typical X-ray doses for the patterning of ZIF-71, ZIF-8\_Cl, ZIF-8\_Br and ZIF-72 are 60, 80, 80 and 100  $\text{kJ cm}^{-3}$ , respectively.

### Electron beam lithography

The EBL of MOF films was performed on a nanofabrication system from Raith GmbH. The working distance was set to 10 mm. The typical acceleration voltage was 20 kV. The beam current, measured by a Faraday cup, was in the range of 300-350 pA. The step sizes of the area and line doses were set to 10 nC/ $\text{cm}^2$  and 1000 pC/cm, respectively. The patterns were written in a concentric and clockwise mode.

### Small-angle X-ray scattering

SAXS data were collected on the SAXS beamline at the ELETTRA synchrotron light source (Trieste, Italy) using a photon energy of 8 keV.<sup>58</sup> Images were recorded using the Pilatus3 1M detector (DECTRIS Ltd., Baden-Daettwil, Switzerland). The powder samples were recorded in capillary mode. The beamline setup was adjusted to a sample-to-detector distance of 757 mm to result in an available  $q$  range between 0.1 and 9.8  $\text{nm}^{-1}$ . In the case of GISAXS, the beamline setup was adjusted to a sample-to-detector distance of 286 mm. A secondary vertical beamstop was used to safeguard the detector, resulting in an anisotropic  $q$  range of 0.1-25  $\text{nm}^{-1}$ . All measurements were done at an incidence angle of 0.36 $^\circ$ . The calibration and the calculation of the vertical slices were conducted using the FIT2D software package.<sup>59</sup>

### Single-crystal X-ray diffraction

SCXRD data was collected for pristine and patterned ZIF-8\_dclm crystals on a Bruker APEX II diffractometer with an Incoatec microfocus Mo K $\alpha$  tube ( $\lambda = 0.71073 \text{ \AA}$ ) and a CCD area detector. Empirical absorption corrections were applied using SADABS or TWINABS.<sup>60</sup> The structures were solved with the use of the intrinsic phasing option in SHELXT and refined by the full-matrix least-squares procedures in SHELXL.<sup>61</sup> The space group assignments and structural solutions were evaluated using PLATON.<sup>62</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions corresponding to standard bond lengths and angles and refined using a riding model. Atomic positions in the framework were evaluated by using the “squeeze” option available in the PLATON program suite.<sup>63</sup>

### Scanning electron microscopy

SEM images were recorded using a FEI XL30FEG instrument after sputter-coating the samples with 5 nm Pt. EDX mapping was recorded by an EDAX detector with a resolution of  $512 \times 512$  pixels.

### Atomic force microscopy

AFM topography images ( $512 \times 512$  pixels) were recorded in intermittent contact mode using an Asylum Research Cypher ES AFM instrument at ambient conditions using Si cantilevers (OLYMPUS, AC160TS-R3). Data analysis was performed using Gwyddion 2.44.<sup>64</sup>

### Optical profilometry

Optical profilometry images were recorded on a Sensofar 3D optical profilometer at ambient conditions. Data analysis was performed using Gwyddion 2.44 software.<sup>64</sup>

### Porosity study

Both N<sub>2</sub> and Kr sorption isotherms were measured at 77 K using a Micromeritics 3Flex physisorption instrument. The samples were degassed before measurements at 423 K under dynamic vacuum ( $10^{-2}$  mbar) for 12 h. The BET method was applied in the region between 0.005 and 0.05 P/P<sub>0</sub>, according to the consistency criteria for microporous materials. Methanol adsorption isotherms on ZIF-71-coated QCM substrates were measured using a BEL-QCM instrument at 298K.<sup>65</sup> The equilibrium time was set to 5 min.

### Ellipsometry

The optical properties of the deposited layers were measured using an M-2000x spectroscopic ellipsometer (J. A. Woollam Co. Inc.,  $\lambda = 246\text{--}1000$  nm). A two-layer optical model was used, consisting of a native oxide layer and a MOF layer to be analysed. For MOF films, the Cauchy model was used with variable thickness and optical constants. The bare Si substrates were measured to determine the thickness of the native oxide before every experiment. The ellipsometric parameters of the Si substrate and the native oxide were taken from literature<sup>66</sup> and kept fixed for all measurements. *In situ* ellipsometry porosimetry measurements were performed on a custom-built tool featuring a vacuum chamber, spectroscopic ellipsometer (Sentech SE801, 350–850 nm wavelength), and a programmable adsorbate dosing platform. The isotherms were recorded at room temperature. The equilibration time at each pressure point was set to 5 min.

### Diffraction grating vapour sensing

In the configuration of Figure 3g, a phase difference ( $\varphi$ ) is created when light passes through a MOF pattern deposited on a transparent substrate (equation 1).

$$\varphi = \frac{2\pi d(n_{MOF} - n_{air})}{\lambda} \quad (1)$$

In which  $\varphi$  is the phase difference,  $d$  is the MOF film thickness,  $n_{MOF}$  and  $n_{air}$  are the refractive indices of the MOF and the surrounding atmosphere, respectively, and  $\lambda$  is the wavelength of the incident beam.

When guest molecules are adsorbed in the MOF pores, the resulting refractive index increase of the MOF layer causes a larger phase difference. Thus, guest adsorption can be transduced through monitoring the intensity changes of the first-order diffraction spots (equation 2).<sup>43</sup>

$$I_1 = \frac{2(1-\cos\varphi)}{\pi^2} \quad (2)$$

In which  $I_1$  is the first-order diffraction intensity, and  $\varphi$  is phase difference of the grating.

Vapour sensing was performed by illuminating MOF patterns on quartz substrates, horizontally positioned in a sealed enclosure (Linkam stage) which is connected to a vapour generating system. A 650 nm laser (Picotronic, modulated with adjustable focus) is used as light source. The diffraction pattern are directly captured with a CMOS camera (Flir Chameleon 3, 2048x1536 pixel, monochrome, typ. grating-sensor distance ca. 10 cm). During dosing of methanol vapours, the intensity of a first-order diffraction spot was monitored every 2 s by integrating the CMOS response over 136x136 pixel around the spot (PySpin). To adjust the incoming laser intensity, PWM and a polarizer are used.

### **Nuclear magnetic resonance spectroscopy**

Solution <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer. DMSO-d<sub>6</sub> was used as a solvent to dissolve dclm linker and X-ray irradiated ZIF-71 powder samples.

### **Elemental analysis**

Elemental analyses for C, H and N were carried out on a Hekatech EuroEA Elemental Analyser. Zn content was determined by atomic absorption spectroscopy after decomposing the sample in a mixture of sulfuric acid and nitric acid in a microwave. Cl content was determined by potentiometric titration using an Agilent technologies 200 series AA.

### **X-ray Photoelectron Spectroscopy**

XPS data for X-ray irradiated ZIF-71 films were collected using a PHI5600 Versaprobe II (Physical Electronics) utilizing a Al K $\alpha$  monochromatic X-ray source (1486.71 eV photon energy) with a beam irradiation power of 25 W. The kinetic energy of the photoelectrons was measured with a take-off angle of 45° and a spot diameter of 100  $\mu$ m to measure surface compositions up to ~5 nm in depth. The analysis and fitting were performed using CasaXPS software (Casa Software, Ltd.) employing a mixed Gaussian-Lorentzian peak shape and a Shirley-type background.

### **Infrared spectroscopy**

Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) spectra were recorded on a Varian 670 FTIR spectrometer equipped with a VeeMAXTM III accessory (PikeTech). The spectra were collected with a Ge ATR crystal at an incidence angle of 60°. 64 scans were accumulated by either a DLaTGS or MCT detector with a resolution of 4 cm<sup>-1</sup>.

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### Author contributions

M.T. and R.A. conceived and designed the experiments. M.T. carried out and analysed film deposition, patterning and characterisation experiments. M.T., B.X., D.K., M.V., A.T.G and P.F. carried out bulk MOF synthesis and characterisation. M.T., B.X., D.K. and B.M. carried out the XRL patterning. M.T., B.X., D.K. and H.A. carried out SAXS measurements. A.J.C and T.F. conducted the XPS measurements. M.T., J. T. and S.D.F contributed to the AFM measurements. M.L.Z. designed and conducted the diffraction grating sensing. Z.W. and R.A.F. conducted QCM measurement. The manuscript was written by M.T. and R.A., with the input of all authors.

### Competing interests

The authors declare no competing financial interests.

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