The ability to confine functional materials in controlled locations has enabled technological progress in miniaturizing devices for sensing, catalysis, luminescence, diagnosis, and biomedicine. Metal-Organic Frameworks (MOFs), also known as porous coordination polymers, are an emerging class of multifunctional porous materials arising from the vast combination of metal atoms and polydentate bridging ligands. MOFs have recently attracted increasing scientific interest due to their structural modularity (e.g., use of different metals, reticular chemistry, post-synthetic modifications) and exceptionally controlled porosity, making them an ideal platform material for a broad scope of applications. Within the different emerging applications, MOF thin films and patterns containing functional biomacromolecules, such as proteins, hold promise for the generation of biomedical diagnostic tools or lab-on-a-chip devices. To date, the fabrication of MOF biocomposite thin films and patterns has only been achieved by first engineering and spatially controlling...
the MOF, with the incorporation of the biomolecules as a secondary functionalization step unrelated to the actual MOF growth and patterning.\[6\] As a result, the current fabrication methods are often complex, time consuming and involve multistep procedures.\[7\] Recently, we discovered that a wide range of biomacromolecules have the ability to attract several metal ions and organic ligands, resulting in the rapid, biomimetic crystallization of MOFs in aqueous solution (biomimetic MOF mineralization).\[8\] On the other hand, no MOF particles were formed in the absence of proteins due to the lack of ability to locally concentrate the precursors necessary for MOF particle formation.\[8\] Herein, we demonstrate that this new concept can offer a rapid route for fabricating MOF thin films and patterns directly from surface bound proteins, to replicate the pattern of the proteins with micrometer-scale resolution (Scheme 1). Essentially a pattern of proteins, which can be easily created using various lithographic techniques such as contact printing, tip-based nanolithography or photolithography,\[9\] can be used to promote the spatially controlled growth of MOF biocomposites. Furthermore, functional MOF biocomposite patterns can be rapidly formed on a flexible polymer film, allowing for the patterned functionality to be retained even during bending. We further exploit the potential of this technique by demonstrating that luminescent patterned MOFs can be generated within 30 s from the latent proteins remaining from fingerprint residues. The protein induced biomimetic crystallization of MOF patterns is simple, rapid and effective, and should accelerate the exploitation of MOF-biomacromolecule based systems for applications ranging from biomedical devices to forensic science.

To ascertain the biomimetic mineralization on protein films, bovine serum albumin (BSA) was tested as promoting agent for the Zeolitic Imidazolate Framework-8 (ZIF-8) formation. BSA was selected as a model protein because it is abundant, extensively investigated and characterized; additionally, BSA has been shown to rapidly accumulate metal cations and organic ligands in solution, leading to efficient biomimetic mineralization for several
MOFs.\textsuperscript{[8]} ZIF-8 is composed of zinc ions coordinated by four imidazolate rings, which closely resembles the framework of zeolites,\textsuperscript{[10]} and has previously been used to test different fabrication protocols.\textsuperscript{[6b, 11]} More importantly, ZIF-8 can be prepared in biologically friendly conditions (i.e. aqueous solutions at room temperature),\textsuperscript{[12]} which are compatible for biomolecules.\textsuperscript{[8]} The film was prepared by drop-casting an aqueous solution of BSA onto silicon wafers. Subsequently, aqueous precursor solutions containing 2-methylimidazole and zinc acetate were mixed and immediately added on top of the drop-cast proteins and left to incubate for 12 h. After rinsing and drying, a homogenous film was visually detected, however no crystals were formed in the absence of BSA. An SEM investigation confirmed the complete coverage of fused crystalline films with a thickness of ca. 2 \( \mu m \) (Figure 1a and e). Powder X-ray diffraction (XRD) pattern revealed that the film displayed typical ZIF-8 crystalline characteristics; the difference between the peak intensity of the collected diffraction patterns and the simulated one by randomly oriented crystals can be explained by a model that take into account a partial preferential orientation of ZIF-8 mainly in the [100] direction (Figure 1b and Figure S1, Supporting Information), which is similar to ZIF-8 films grown using liquid phase epitaxy techniques.\textsuperscript{[11e]} Moreover, the thickness of the MOF films can be tuned by additional re-growth method by adding fresh MOF precursors (Figure S2, Supporting Information). Additionally, in the presence of EDTA, the MOF biocomposite film could be dissolved, as a result, the embedded biomacromolecules could be selectively released (Figure S3-S5, Supporting Information), demonstrating its potential for therapeutic delivery and integration into biomedical devices.

Luminescent MOFs were employed to verify the ability of the proposed method for generating functional MOF coatings. Luminescent MOF films and patterns hold significant promise for applications such as electroluminescence, integrated optics, and biological labeling.\textsuperscript{[4i, 5c, 13]} Similar to the previous experiment, BSA was drop-cast on a silicon wafer
and aqueous solutions of various lanthanide ions (Ln\(^{3+}\), i.e. Tb\(^{3+}\), Eu\(^{3+}\), or Ce\(^{3+}\)) and terephthalate ligand (bdc\(^{2-}\)) were mixed and immediately transferred onto the BSA film. Within 30 s, a white film was observed on the wafer. SEM revealed that the films were composed of microcrystals with complete surface coverage of c.a. 5 µm thickness (Figure 1c, f). XRD measurement showed the crystalline characteristics well aligned to Ln\(_2\)(bdc)\(_3\) MOFs (Figure 1d).\(^{[14]}\) Interestingly, super-resolution fluorescence microscopy revealed that the BSA was embedded within the ZIF-8 film as was obvious by the homogenous fluorescence (Figure 1g), while in contrast, the BSA appeared to be under the Ln\(_2\)(bdc)\(_3\) film as was apparent from the stratification of the fluorescence emissions(Figure 1h and S6, Supporting Information). This could be due to the more rapid formation of the luminescent MOF films deposited onto BSA, which would prevent the dissolution of BSA into the MOF precursor solution. FTIR measurements showed that 62% of the originally deposited BSA remained after the MOF growth (Figure S7, Supporting Information). The resultant MOF films inherited the luminescent nature of the Ln\(_2\)(bdc)\(_3\) crystals, showing bright fluorescence under exposure to UV light (254 nm). Importantly, by tuning the ratio of the composition of lanthanide ions in the precursor solution, MOF films with tunable luminescence were successfully formed on top of BSA (Figure 1i and S8, Supporting Information). The defects in the luminescent films probably resulted from the non-uniform drop-casting of the BSA layers. With the aid of spin coating techniques, more homogeneous luminescent MOF films were achieved (Figure S9, Supporting Information).

Having demonstrated the bulk formation of MOF films using drop-cast proteins, we further explored the use of this chemistry as a means of generating patterned MOF films. A commercial stamp was employed and dipped into a “protein ink” composed of aqueous solutions of BSA. The BSA was then stamped onto silicon wafer and a protein pattern was formed after air drying (Figure 2a). Aqueous solutions of Ln ions and bdc ligands were then
mixed and immediately transferred over the protein patterns. Within 30 s, MOF crystals were observed growing specifically on the stamped BSA pattern, thereby replicating the pattern of the proteins (Figure 2b). As a result, fluorescent MOF patterns could be constructed with different emission profiles under UV light (Figure 2c). To extend the versatility of this technique, BSA solution was stamped on PET polymer films, and the replicated MOF patterns could be bent without affecting the integrity of the patterns (Figure 2d).

To reduce the size of the MOF patterns, we employed a serial lithographic technique like microfluidic-pen lithography (MPL) to deposit arrays of BSA dots with various sizes. MPL utilizes a microfluidic based patterning tool as a pen to deposit materials at the sub-µm scale upon contact with a surface. Arrays of BSA dots with various diameters from 5 to 30 µm were deposited and dried on a piece of silicon wafer (Figure 2e and S10, Supporting Information). These dot array patterns were then used as templates for the production of MOF patterns. Examples of Tb$_2$(bdc)$_3$ dot array patterns after 30 s of reaction time are shown in Figure 2f, g. From these images, it is clear that features of the BSA arrays were transferred to the replicated MOF patterns even though the proteins are able to diffuse into the MOF precursor solution. Interestingly, on each 5 µm diameter BSA dot the Tb$_2$(bdc)$_3$ crystals appeared to assemble into spherical superstructures (Figure 2f-g); on the other hand, the 30 µm diameter BSA dots resulted in Tb$_2$(bdc)$_3$ crystals that mostly grew around the dot, displaying a coffee stain effect (Figure S11, Supporting Information). This could be due to the Marangoni effect where more proteins accumulate at the border of the droplet upon drying, hence leading to a more rapid MOF formation at the border of the protein droplet. The resultant MOF dot arrays displayed strong fluorescence upon exposure to UV light (Figure 2h, and Figure S12, Supporting Information).
To further illustrate the potential of this biomimetic replication technique for MOF patterning, we demonstrate the recognition of fingerprints using luminescent MOFs. Fingerprint residues are primarily composed of proteins, peptides, fatty acids, and inorganic salts, and serve as one of the primary methods for identifying individuals at crime scenes.[17] For an initial test, fingerprints from unwashed hands were deposited on a silicon wafer by lightly pressing the thumb against the wafer (Figure 3a). The replication of fingerprints with MOFs was carried out by immersing the wafer into MOF precursor solution containing Ln ions and bdc ligands for 30 s followed by washing in deionised water. Under the exposure of UV light, the MOF fingerprint patterns displayed strong luminescence using both Eu and Tb as the Ln ions without any loss of the friction ridge details from the fingerprint patterns (Figure 3b-h). Moreover, luminescent MOF fingerprint patterns were successfully replicated from fingerprint marks deposited on various surfaces including plastic, metal, and glass (Figure 3i-p). Additionally, luminescent MOF fingerprint patterns were also successfully generated without noticeable loss of resolution using fingerprint residues more than two-month old (Figure S13, Supporting Information), demonstrating the versatility of this technique for cold case analysis. Compared with current commonly employed fingerprint detection methods including cyanoacrylate (CA) fuming, vacuum metal deposition (VMD), 1,8-diaza-9-fluorenone (DFO) and ninhydrin staining,[18] the demonstrated MOF patterning technique does not require temperature and/or vacuum treatment and typically reveals the fingerprints with comparable resolution within 30 s using a simple UV light.

In summary, we demonstrated that ZIF-8 and Ln$_2$(bdc)$_3$ crystalline thin films and patterns can be formed as a result of biomimetic replication directly from protein patterns on various surfaces. This rapid process was performed in aqueous conditions at room temperature with a resolution in the micrometer range. We also highlighted the capability of this technique to form MOF patterns from fingerprint residues on various surfaces with high resolution.
Although we performed the rapid biomimetic replication of MOF patterns using BSA and proteins from fingerprint residue, other therapeutic biomolecules such as enzymes and antibodies could potentially be used. This technique is expected to facilitate the production of MOF based biosensors and biomedical devices, and potentially aid in crime scene investigation.

**Experimental Section**

*Materials:* information on reagents and materials is reported in the Supporting Information.

*Formation of macroscopic BSA patterns:* Aqueous BSA solutions (50 mg mL\(^{-1}\)) were prepared. A clean and dry ink pad was soaked in the BSA solution and removed. This BSA-containing pad was used as an ink pad for the stamps. A commercial stamp was lightly pressed against the ink pad, and then pressed on the substrate to transfer the proteins patterns. The protein patterns were then left to dry under ambient conditions.

*Spin-coating of BSA films:* reported in the Supporting Information.

*Formation of microscopic BSA patterns:* BSA solution (50 mg mL\(^{-1}\)) was prepared by dissolving BSA in a mixture solution containing 20% glycerol and 80% water (v/v). Next, a surface patterning tool (SPT10, BioForce USA) was loaded by adding 1 µL droplet of the filtered BSA solution into the reservoir. The tip was then brought into contact with a SiO\(_2\) surface to fabricate arrays of droplets of the BSA solution and upon air-drying, the BSA patterns were formed. Full details are reported in the Supporting Information.

*MOF formation:* For the formation of ZIF-8 thin films and patterns, separate stock solutions of zinc acetate dihydrate (40 mM, 1 mL) and 2-methylimidazole (160 mM, 1mL) were prepared in deionised water. These two solutions were mixed and immediately transferred onto the BSA patterns. After 12 h, the formed ZIF-8 patterns were washed 3 times in ethanol and dried under a stream of N\(_2\). For the formation of Ln\(_2\)(bdc)\(_3\) thin films and patterns, separate stock solutions of LnCl\(_3\) hydrate (e.g. TbCl\(_3\)·6H\(_2\)O, EuCl\(_3\)·6H\(_2\)O, and CeCl\(_3\)·7H\(_2\)O,
20 mM, 1 mL) and terephthalic acid disodium salt (Na2(bdc), 20 mM, 1mL) were prepared in deionised water. These two solutions were mixed and immediately transferred onto the BSA patterns. After 30 s, the formed luminescent MOF patterns were washed 3 times in deionised water and dried under a stream of N2. For spin-coating the MOF films, please refer to the Supporting Information.

Characterization: reported in the Supporting Information.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1. Schematic showing the biomimetic replication of MOF patterns using a protein pattern. (a-c) Protein patterns were created using a stamp to transfer protein solutions onto a substrate. (d-e) MOF precursor solution containing metal ions and ligands were dropped on top of the protein patterns. (f-h) MOF crystals only form at the location of the proteins, replicating the protein patterns.

Figure 1. (a) SEM image and (b) XRD spectrum of biomimetically replicated ZIF-8 thin films using BSA deposited on silica. (c) SEM image and (d) XRD spectra of biomimetically replicated Ln$_2$(bdc)$_3$ thin films using BSA deposited on silica. Perspective SEM images of (e) ZIF-8 and (f) Ln$_2$(bdc)$_3$ thin films. (g) 3D view of super-resolution microscopy images of ZIF-8 thin films (grey) on BSA (green). (h) 3D view of super-resolution microscopy images of Eu$_2$(bdc)$_3$ thin films (red) on BSA (green). (i) Photograph under the exposure of UV light.
Various colors were observed by mixing the Eu, Tb, and Ce ions in the precursor solution at different ratios. From left to right (Eu%:Tb%:Ce): 0:0:100; 10:10:80; 25:20:55; 10:50:40; 60:15:25; 90:5:5; 2.5:93.5:4; 0:100:0; and 100:0:0.

Figure 2. (a) Photograph of a stamped BSA pattern on a silicon wafer. (b) SEM image of the biomimetically replicated Ln$_2$(bdc)$_3$ patterns. (c) Photograph under UV light of Eu$_2$(bdc)$_3$ (red), Tb$_2$(bdc)$_3$ (green), and mixed Ln$_2$(bdc)$_3$ (yellow) patterns. (d) Photograph of the Tb$_2$(bdc)$_3$ pattern on a PET film. (e) DIC microscopy image of BSA dot microarrays deposited by DPN. (f-g) SEM images of Tb$_2$(bdc)$_3$ dot microarrays. (h) Fluorescence microscopy image of Tb$_2$(bdc)$_3$ dot microarrays under UV irradiation.

Figure 3. (a) Photographs of Eu$_2$(bdc)$_3$ (left) and Tb$_2$(bdc)$_3$ (right) patterns grown from fingerprint residue, and (b) under UV light. (c-h) SEM and EDS measurement of Eu$_2$(bdc)$_3$
patterns. (i-l) Photographs of Tb$_2$(bdc)$_3$ patterns grown from fingerprint residues, and (m-p) under UV light.
We demonstrate that metal-organic frameworks (MOFs) can be replicated in a biomimetic fashion from protein patterns. Bendable, fluorescent MOF patterns are formed with micrometer resolution under ambient conditions. Furthermore, this technique is used to grow MOF patterns from fingerprint residue in 30 s with high fidelity. This technique is not only relevant for crime scene investigation, but also for biomedical applications.

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