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# Metal-Organic Frameworks for fingermark detection – A feasibility study

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## Highlights

- MOFs can be used to detect fingermarks
- Detection with MOFs is inferior to current detection methods
- MOFs may be promising as an alternative to powder suspension techniques

## Abstract

Metal-Organic Frameworks (MOFs) are porous crystalline structures, currently used as sensors, separators in membranes, and as catalysts. Due to their physicochemical and optical properties, they have been recently proposed for fingermark detection. This study further explored their potential for fingermark detection. Natural fingermarks, as well as charged and protein-enriched marks, were used to test the efficiency of the technique. Various parameters, such as precursor concentration, pH, immersion time and detection protocols, were investigated and optimised. The performance of the optimised MOF-based method was then compared to that of routinely used techniques.

The results obtained indicated that MOFs can effectively detect fingermarks, especially protein-rich marks such as marks contaminated with body fluids. However, after comparison and evaluation against benchmark techniques, results were judged to be inferior to those from currently employed detection methods. However, with further research and optimisation MOFs may be promising as an alternative to current powder suspension techniques.

## 1. Introduction

The field of fingermark detection is in constant need of improved detection techniques to lower detection thresholds and allow for more fingermarks to be detected with an improved quality. Techniques need to be quick to apply, reasonably inexpensive, and user-friendly. Additionally, when applied in sequence, they need to be compatible with the other techniques used routinely and allow for the exploitation of other types of traces such as DNA.

Many of the current techniques routinely used in forensic laboratories worldwide have been adapted from methods employed in other disciplines. Commonly cited examples are ninhydrin [1] used in biochemistry to detect amino acids, physical developer [2, 3] adapted from a photographic development solution, and vacuum metal deposition [4] originally used in industry to manufacture mirrors. Other promising methods have been derived from new technologies such as nanotechnology [5, 6] and immunodetection [7, 8]. In the same vein, a recent publication in the field of material sciences focused on the directed growth of Metal-Organic Frameworks (MOFs) on proteins printed on a substrate [9]. This group further explored the process to target the proteins found in fingermark secretions and presented successful fingermark detection using MOFs.

MOF is an umbrella term for crystalline structures that combine an organic ligand and a metal ion or a metal ion cluster [10]. The combination of a large variety of organic linkers and metal ions can result in diverse MOF structures with tuneable physicochemical properties. The crystalline structure of MOFs is very porous and they have a massive internal surface area. These characteristics make them especially useful for applications such as gas separation, gas storage and catalysis [11]. MOFs can also be used as thin films that can be applied to many different substrates, and be used as sensors and separation membranes [12].

Liang and co-workers [9] described the production of thin-film luminescent MOFs using proteins such as bovine serum albumin (BSA) to concentrate lanthanide ions in the desired pattern for MOF formation. The BSA was applied to a flexible polymer substrate using a stamp. A solution of the MOF components was then pipetted on top of the stamped pattern.

The high concentration of ligands and metal ions around the BSA initiated the crystallisation and formed a thin film selectively on the BSA pattern. This quick process can be performed in aqueous conditions at room temperature, and the use of either terbium or europium ions with terephthalate ligands induces luminescent properties in the resulting MOF. As a proof of concept, the authors applied their process to fingermark detection under the assumption that the protein found in fingermark secretions would initiate the MOF formation in a similar manner as the BSA. The authors successfully detected fingermarks on a silicon wafer with a 30-second immersion in the ligand and ion ($Tb^{3+}$ or $Eu^{3+}$) precursor solution. After being washed in deionised water, the results showed a strong green ($Tb^{3+}$) or red ($Eu^{3+}$) luminescence emission under UV (254 nm). Fingermarks were detected on plastic, glass and metallic substrates following the same procedure.

This is an interesting and promising application of MOFs for fingermark detection, with a quick and easy process that produces luminescent marks. However, the efficiency of the technique remains difficult to assess based on the preliminary study; very little information was provided on application parameters. The number of donors used as well as the type and age of fingermarks is unknown. Therefore, the goal of the present study was to further investigate the application of MOFs to fingermark detection following an established Phase 1 testing protocol as described in the guidelines published by the International Fingerprint Research Group (IFRG) [13]. The application mode was studied and further optimised. The technique's efficiency was evaluated on fingermarks of different types and ages from various donors, with a comparison against benchmark techniques on various substrates, in order to provide an evaluation of its potential as a novel fingermark detection method.

## 2. Materials and methods

### 2.1 Fingermark specimens and substrates

Natural, charged and protein-enriched marks were collected from a pool of eight donors. The former were collected from donors who had not washed their hands, intentionally touched their face or worn gloves within the previous hour. Charged fingermarks were

prepared by the donor rubbing their fingers on their forehead before deposition. The donors were instructed to deposit the marks by lightly pressing the finger onto the surface of the substrate. Single fingermarks and a depletion series (of up to 3 depletions) were collected. To further investigate the components targeted by MOFs, four protein-enriched fingermark types were also collected. Aqueous solutions of 0.1% w/v bovine serum albumin (BSA) and 0.1% w/v lysozyme were prepared. Fingermarks were obtained by smearing 20 µl of solution onto the donor's thumb. The finger was then left to dry for 2 minutes before depositing three depletions. Blood fingermarks were obtained by pricking the donor's finger with a blood lancet and smearing the blood onto another finger before depositing three depletions. Lastly, semen-contaminated fingermarks were made using a fingermark stamp. Undiluted, 10 and 100 times water-diluted semen solutions were applied to the stamp using a cotton swab. The stamp was left to dry for 2 minutes before being used to make three depletions on a substrate. Fingermarks were left to age in the dark at room temperature for 24 hours, one week and one month. The MOF-based technique was first optimised on glass, and then further tested on the substrates listed in Table 1.

## 2.2    MOF formation and optical characterisation

Terephthalic acid disodium salt (>99%, Tokyo Chemical Industry Co., Ltd) and terbium trichloride hexahydrate (99.9%, ACROS Organics) were used as the MOF precursors. Aqueous solutions of various concentrations were prepared using deionised water and were mixed immediately before fingermark detection.

Photoluminescence excitation and emission spectra of the MOF suspension were measured at room temperature using a Shimadzu RF-6000 fluorescence spectrophotometer. 1 mL of each precursor solution was mixed together 10 minutes prior to luminescence measurement to allow for complete MOF formation. The resulting MOF suspension was diluted by a factor of 10 before measurement.

### 2.3 Fingermark detection protocols

#### 2.3.1 Liang et al. original method

The method published by Liang et al. was applied as described without modification to assess its effectiveness at detecting latent fingermarks. Aqueous solutions of 20 mM terephthalic acid disodium salt and 20 mM terbium trichloride hexahydrate were mixed and pipetted straight onto the fingermarks until a visible mark could be seen. The solution was then rinsed off with deionised water to prevent further deposition and to remove unattached MOFs (Figure 1a). To try to improve the technique, various immersion times, pH of the terephthalic acid disodium salt solution, and solution concentrations were investigated (Table 2). A pH Cube benchtop pH meter (TPS Pty Ltd) was used to measure the pH of the various solutions.

#### 2.3.2 Sequential solution application

When mixed, the two precursor solutions lead to rapid MOF formation and precipitation. Therefore, to provide better control over detection and to minimise solution waste, the sequential application of one solution after the other was tested. The procedure consisted of immersing the fingermarks in the first solution (terbium trichloride), followed by a brief rinsing step in deionised water, and then immersing the marks in the second solution (terephthalic acid disodium salt solution), again followed by a rinsing step (Figure 1b). This process was further tested by varying the number of immersion cycles, duration of the cycles, and solution concentration (Table 3).

#### 2.3.3 Alternative application method

Aqueous solutions of 25 mM terephthalic acid disodium salt and 25 mM terbium trichloride hexahydrate were mixed until MOF formation, as indicated by the presence of a white precipitate. Kodak Photoflo 200 was then added at a concentration of 7.5 µL per 20 mL of MOF solution. The fingermarks were either immersed in the MOF solution for 30 seconds or sprayed with the MOF solution using a nebuliser (EcoSpray), and then rinsed with

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deionised water (Figure 1c). This detection protocol was directly inspired by powder suspension methods [14, 15] where the suspended MOFs act as a luminescent powder.

### 2.4    Imaging, comparison and evaluation

Detected fingermarks were recorded using a Poliview IV imaging system and a Polilight PL550XL forensic light source from Rofin Australia Pty Ltd. Appropriate excitation and visualisation filters were employed as determined by the MOF characterisation described above.

For comparison purposes and to assess the technique's efficiency against benchmark techniques, fingermarks were split in halves and each half processed separately. Natural fingermarks detected with MOFs were compared to cyanoacrylate fuming and rhodamine 6G staining (CA+R6G). Blood fingermark enhancement was assessed against acid yellow 7 (AY7) treatment. The alternative MOF application method was compared to the use of a luminescent small particle reagent (SPR; Sirchie SPR400UV).

CA fuming was performed in a MVC1000 cabinet (Foster and Freeman Ltd.) with 0.5 g of Cyanobloom (Foster and Freeman Ltd.) per fuming cycle. The marks were fumed for 20 minutes or until a result was visible. The staining step with rhodamine 6G occurred 24 hours after CA treatment. The formulation and application of the staining solution was as described in [16]. The blood fingermarks were fixed with a 2% w/v 5-sulfosalicylic acid solution prior to immersion in either the MOF or AY7 solution [16]. Marks were immersed in the AY7 solution for 4 minutes, rinsed to remove the stain, and then air-dried.

The luminescent SPR was applied using a hand-held spray bottle. This was compared to the MOF suspension, which was applied either via immersion of the fingermarks in the pre-formed MOF or using an EcoSpray. With both techniques, the fingermark was treated with the MOF suspension for 30 seconds and then the surfaces were rinsed with deionised water.

Due to the generally poor results obtained using MOFs throughout the study, a visual comparison was judged sufficient to assess the results. Therefore, no formal quantitative evaluations were performed and no assessment scales were employed. When comparing MOFs to CA+R6G and AY7, each technique was imaged under its own optimal visualisation conditions (Table 4) and then the images combined, without digital enhancement.

## 3. Results and discussion

### 3.1 Optical characterisation of the MOFs

The recorded excitation and emission spectra are shown in Figure 2. There is a wide excitation band in the UV region of the spectrum, from about 250 to 340 nm, with a maximum at 310 nm. The emission is characteristic of a terbium complex, with several narrow peaks from 485 to 635 nm, with the strongest emission peak centred at 547 nm.

Result observation was performed using the available forensic light source. UV light was produced using the 350 nm filter provided on the Polilight PL550XL. A band centred at 310 nm would be more appropriate regarding the excitation spectrum, but the 350 nm setting was judged suitable since the bandwidth of the 350 nm filter is wide enough to provide adequate excitation at 310 nm. The observation was made using a 555-nm bandpass interference filter tilted to provide a 545-nm band that fits the stronger emission peak.

### 3.2 Liang et al. original method

The original method published by Liang et al. was applied to both natural and charged fingermarks. The two solutions were mixed and pipetted directly onto the marks and left for a duration of 60 seconds. This was double the time reported in the published protocol as there were no visible results after the recommended treatment (30 seconds). A white precipitate formed on the marks and the excess was then rinsed off the substrate with deionised water. Representative results for both types of fingermarks on glass are depicted in

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Figure 3. Good results were generally obtained for sebaceous-rich marks; however, for natural impressions, weakly luminescent and poor-quality results were consistently obtained. As shown in Figure 3a, charged fingermarks can be overdeveloped, indicating that immersion time is a parameter that needs to be closely controlled with this technique.

The fact that charged marks can be detected with a reasonable quality shows that the current method does target fingermark residue, but it lacks sensitivity for natural marks. Therefore, several application parameters were modified in order to improve general sensitivity. Immersion time, pH of the terephthalic acid disodium salt solution, and concentration of the precursor solutions were varied (Table 2). It was hypothesised that leaving the MOF solution in contact with the fingermark residue for an extended duration would allow for the complete formation and growth of the MOFs. However, since the MOFs tended to form quickly, as indicated by the appearance of a white precipitate, longer contact time did not improve the results but only increased the background development. Increasing the precursor concentration was another way to potentially improve sensitivity; however, an immediate precipitation occurred when precursor solution concentrations were above 20 mM. A decreased concentration was also evaluated in order to slow down the reaction. Both 10 and 1 mM solutions did not improve the fingermark detection quality. The last parameter studied was the pH of the terephthalic acid disodium salt solution. It was hypothesised that the non-charged form of terephthalic acid would be better adsorbed by the non-polar components of the fingermarks. A diluted solution of hydrochloric acid was used to adjust the pH of the terephthalic acid disodium salt solution to 5.5, 5.0 and 4.5. A pH of 4.5 led to some improvements in terms of sensitivity; however, it also increased the background staining, diminishing the quality of the results.

None of these modifications brought significant improvements to the original Liang et al. method. Moreover, the technique suffered from several issues, such as a lack of sensitivity and high background staining. The technique could only detect charged, sebaceous-rich fingermarks, which are not a realistic representation of the marks found in operational casework. The white MOF precipitate also tended to deposit on both the fingermark and the background, indicating a lack of selectivity. The application method also needed to be

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revisited; pipetting the solution onto the mark implies that the location of the mark should be known beforehand, which is not the situation in casework. The MOF working solution is stable for just a few minutes, so immersing an item the solution would lead to large waste of solution and high cost.

### 3.3 Sequential solution application

For the reasons expressed above, it appeared that mixing the two solutions prior to detection was not the ideal way to apply the technique. Therefore, keeping the two reactive solutions in two separated baths and successively immersing the marks in one solution then in the other with a rinsing bath in-between was found to be a viable alternative and a more efficient application mode. This multi-step process could help with reducing unwanted MOF formation on the background, improving detection sensitivity by promoting the growth of more MOFs, and decreasing solution waste.

It is hypothesised that a small amount of $Tb^{3+}$ ions from the terbium chloride solution would be adsorbed or absorbed by the secretions and would then trigger MOF formation when immersed in the terephthalic acid disodium salt solution. The process would allow for better control over the reaction and the detection of marks. Development can be checked at each cycle, and additional cycles can be performed to reinforce detection. Additionally, the concentration of each bath can be increased without the risk of precipitation since the two solutions are kept separate.

As depicted in Table 3, several solution concentrations, immersion times and cycle repetitions were tested. A concentration of 200 mM for each solution, an immersion time of 5 min in each bath, and 5 cycles was found to be optimal. The sequential application process allowed for fingermarks to be detected (Figure 4). These results showed a significant improvement compared to the original method. Marks depicted in Figure 4 are natural marks that could not be developed using the original method. However, even if the quality of the mark was relatively good, uneven background staining became visible after several cycles. To further test the sensitivity of the method, three-month-old natural marks on glass from a weak donor were processed and imaged after both 3 and 5 additional cycles. The marks

shown in Figure 5 are a first and second depletion, meaning that the substrate was touched twice in succession. The effect of additional cycles is clearly illustrated in Figure 5. The second depletion was barely visible after 3 cycles but became visible after 5 additional cycles. More cycles lead to an increase in sensitivity but was also associated with an increase in background development. The technique was also characterised by a lack of reproducibility.

In order to assess the efficiency of the sequential application procedure, the results were compared to those obtained using cyanoacrylate fuming followed by rhodamine 6G staining. As illustrated in Figure 6, both techniques led to fingermark detection; however, CA+R6G produced more homogeneous ridge detail and more intense luminescence. As observed before, the MOF-based method produced background staining. It is hypothesised that this background was due to some dissolution of water-soluble proteins and amino acids present in the fingermark residue, leading to MOF formation on the substrate.

The sequential application method offered some improvements over the protocol published by Liang and co-workers, with increased sensitivity and better control over fingermark development. However, the technique lacked reproducibility with variable background staining and no results obtained on substrates other that glass (Figure 7). Based on the results obtained, it was concluded that CA+R6G performed better than the MOF-based method.

### 3.4 Protein-enriched fingermarks

As described by Liang et al., proteins such as BSA can trigger the formation of MOFs. In regard to fingermark residue, the poor results obtained can be explained by very low protein concentrations, or by the presence of other components in the residue that hinder MOF

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formation. That may lead to poor binding of the MOFs to the proteins in the fingermarks. Therefore, even if the proposed MOF-based method does not provide enough sensitivity for natural fingermarks, the technique may be adequate on protein-rich marks such as marks contaminated with blood or semen.

To test this proposition, fingermarks artificially contaminated with BSA and lysozyme were used as a control to confirm that the MOFs actually form on proteins. Marks in blood and semen were then deposited on glass, aged and treated with the sequential solution application method. As illustrated in Figure 8, artificially enriched fingermarks were efficiently detected by the MOF process. The uneven background staining was still present, but the marks were highly luminescent. Both blood and semen contaminated marks were also successfully detected but, again, similar background staining was observed.

To further evaluate the potential of MOFs as a blood enhancement reagent, marks in blood of three different ages were assessed in comparison with AY7 treatment, a benchmark luminescent technique for fingermarks in blood. Figure 9 illustrates the resulting comparison and indicates that MOFs can detect blood marks up to at least one month of age. The age of the blood marks seems to have little to no effect on the MOF enhancement achieved. However, despite the positive results obtained using MOFs, the benchmark AY7 technique enhanced the marks more efficiently, with better ridge definition, more intense luminescence and less background staining.

### 3.5    Alternative application

While using the sequential solution application method, it was observed that good results were obtained when the marks were rinsed in a water bath between each reactive bath (terbium ions and ligand). However, when the marks were rinsed with running deionised water (clean water for each rinse), no results could be obtained. This observation suggested that contamination of the solutions occurred through the processing cycle, leading to the formation of some MOFs in the various solutions. It can then be hypothesised that the MOFs

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formed in solution are physically adhering to the fingermark residue in a manner similar to powder suspensions. When the terbium salt and ligand solutions are mixed, a white precipitate (MOFs) is formed within a few minutes. This luminescent and non-water-soluble precipitate has a very fine structure that could interact with the fingermark secretion as is the case with Small Particle Reagent (SPR).

To test that hypothesis, two precursor solutions were mixed and left aside a few minutes to allow for MOF formation and precipitation to occur. A surfactant, Kodak Photoflo 200 (7.5 µL/20 mL), was added and fingermarks immersed in the suspension for 30 seconds and then rinsed with deionised water. Figure 10a shows the result of this SPR-like application. The technique can detect natural fingermarks on glass with limited background staining. Since there is no chemical reaction involved and the MOFs are already formed, the suspension can be reused multiple times. Immersing the mark for longer did not improve the detection but produced more background development. Figure 10b illustrates the comparison between the sequential solution application and the SPR-like application. A luminescent mark can be seen for the sequential application; however, since the two halves were imaged together and the SPR-like half was much more luminescent, the right side was underexposed. It is clear that the SPR-like application outperforms the sequential application method in terms of luminescence intensity, ridge clarity, and process simplicity.

To assess the performance of this application mode, the MOF SPR was compared with a commercial luminescent SPR (Sirchie SPR400UV). Results are illustrated in Figure 11. The commercial SPR had a stronger luminescence and offered a more homogeneous detection compared to the MOFs. Using the EcoSpray applicator tends to give slightly better results in terms of ridge luminescence, however, there is some background staining.

## 4. General discussion

### 4.1 Interaction mechanism

In the original paper, Liang et al. [9] promoted MOF formation on various substrates by stamping pure protein solutions such as BSA. It was demonstrated that MOF growth was chemically triggered by the presence of proteins. Transposing this process to fingermark

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residue, however, is not as straightforward. While proteins and amino acids are found in fingermark secretions, they are present in very small quantities within a complex mixture of many other compounds.

Results obtained during this study show that fingermark residue can trigger MOF formation and lead to fingermark detection; however, this was only true for charged and protein-enriched fingermarks. In addition to the chemical interaction between the proteins in the fingermarks and the MOF precursors, it was found that a pre-formed MOF suspension can also interact with the residue. This physical interaction was shown to be stronger than the chemical one, easier to replicate and simpler to apply.

Further research is needed to investigate the precise detection mechanism but, as evidenced by the results presented here, it can be hypothesised that, while chemical interaction does play a role in the detection mechanism, the detection is mainly driven by physical interaction between pre-formed MOFs and the fingermark residue. This interaction is the same as that observed with powder suspensions in general (e.g., commercial SPR formulations).

## 4.2    IFRG guidelines and viability of the technique

In the Liang and co-workers study [9], MOFs were shown to be a very promising technique for fingermark detection. The publication and the related press releases attracted much attention from the forensic community. However, unfamiliar with the forensic science field, the authors did not perform any optimisation of the method or extensive evaluation against a benchmark technique. It was therefore difficult to assess the technique's potential. The IFRG published best-practice guidelines for evaluating new detection techniques [13]. When used appropriately, these guidelines are particularly useful, especially for research groups outside the forensic field.

In regard to the general assessment of MOFs for fingermark detection, it was shown in this study that MOFs can effectively detect fingermarks, especially protein-rich marks such as marks contaminated with body fluids. However, even with the optimised application method, the results were judged inferior to what can be achieved with currently available

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techniques. Further optimisation is still required to improve the reproducibility of the technique and more research needs be conducted on MOFs to further investigate crystalline structure, luminescence properties, and the choice of ligand and metal ion. It is interesting to note that MOFs are not the first reported use of lanthanide in the field. Various forms of terbium and europium were used to detect fingermarks. Europium chelates, applied as a lipid reagent [17] gave good results with fresh fingermarks on both porous and non-porous substrates. Europium chelates were also used as a luminescent cyanoacrylate dye with satisfactory results [18, 19]. Finally, europium long emission lifetimes were exploited for time-resolved imaging to get rid of background interference [20].

## 5. Conclusions

This paper focused on the use of Metal-Organic Frameworks (MOFs), specifically terbium terephthalate MOFs for fingermark detection, and further investigated three application modes. Good results were obtained with the original application method [9] when applied on sebaceous-rich fingermarks; however, the method led to poor-quality results for natural marks and uneven background staining. Immersion time, pH of the solutions, precursor solution concentration, as well as application mode were then optimised to increase sensitivity and ease of application. The two MOFs precursor solutions were kept separated and the fingermarks were successively immersed in one solution and then the other, with rinsing baths in-between. Good results were obtained with this optimised sequential solution application, but comparison with cyanoacrylate fuming followed by rhodamine 6G staining showed that MOFs were not sensitive enough and were not a valid replacement for existing techniques. Protein-enriched fingermarks (BSA, lysozyme, blood and semen) were also processed. The technique showed some promises for blood marks; however, more intense luminescence, better ridge definition and less background staining was obtained with acid yellow 7.

The last application mode was the most promising. The two MOFs precursor solutions were mixed prior to fingermark detection, and MOFs were allowed to form for a few minutes. After adding a surfactant, the marks were then immersed in the MOF suspension for 30

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seconds. This SPR-like application was able to detect natural fingermarks with limited background staining.

Overall, MOFs provided luminescent fingermarks under UV, but with inconsistent results and unwanted background staining. MOFs did not provide satisfactory results on natural fingermarks when compared to benchmark detection techniques. However, if further optimisation is undertaken to improve reproducibility, MOFs could become a viable alternative to current SPR or wet powder techniques.

# CRediT author statement

| Term | Definition | Author's initials |
|---|---|---|
| Conceptualization | Ideas; formulation or evolution of overarching research goals and aims | SM, CL, CR, XS |
| Methodology | Development or design of methodology; creation of models | ES, AB |
| Validation | Verification, whether as a part of the activity or separate, of the overall replication/ reproducibility of results/experiments and other research outputs | ES, AB |
| Investigation | Conducting a research and investigation process, specifically performing the experiments, or data/evidence collection | ES, AB |
| Resources | Provision of study materials, reagents, materials, patients, laboratory samples, animals, instrumentation, computing resources, or other analysis tools | SM, KL, XS |
| Writing – Original Draft | Preparation, creation and/or presentation of the published work, specifically writing the initial draft (including substantive translation) | SM, ES |
| Writing – Review & Editing | Preparation, creation and/or presentation of the published work by those from the original research group, specifically critical review, commentary or revision – including pre-or postpublication stages | SM, ES, AB, KL, CL, CR, XS |
| Visualization | Preparation, creation and/or presentation of the published work, specifically visualization/ data presentation | SM, ES, AB, XS |
| Supervision | Oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team | SM, KL, CL, CR, XS |

| Term | Definition | Author's initials |
|------|-----------|-------------------|
| Project Administration | Management and coordination responsibility for the research activity planning and execution | CL, CR |

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        560-571.
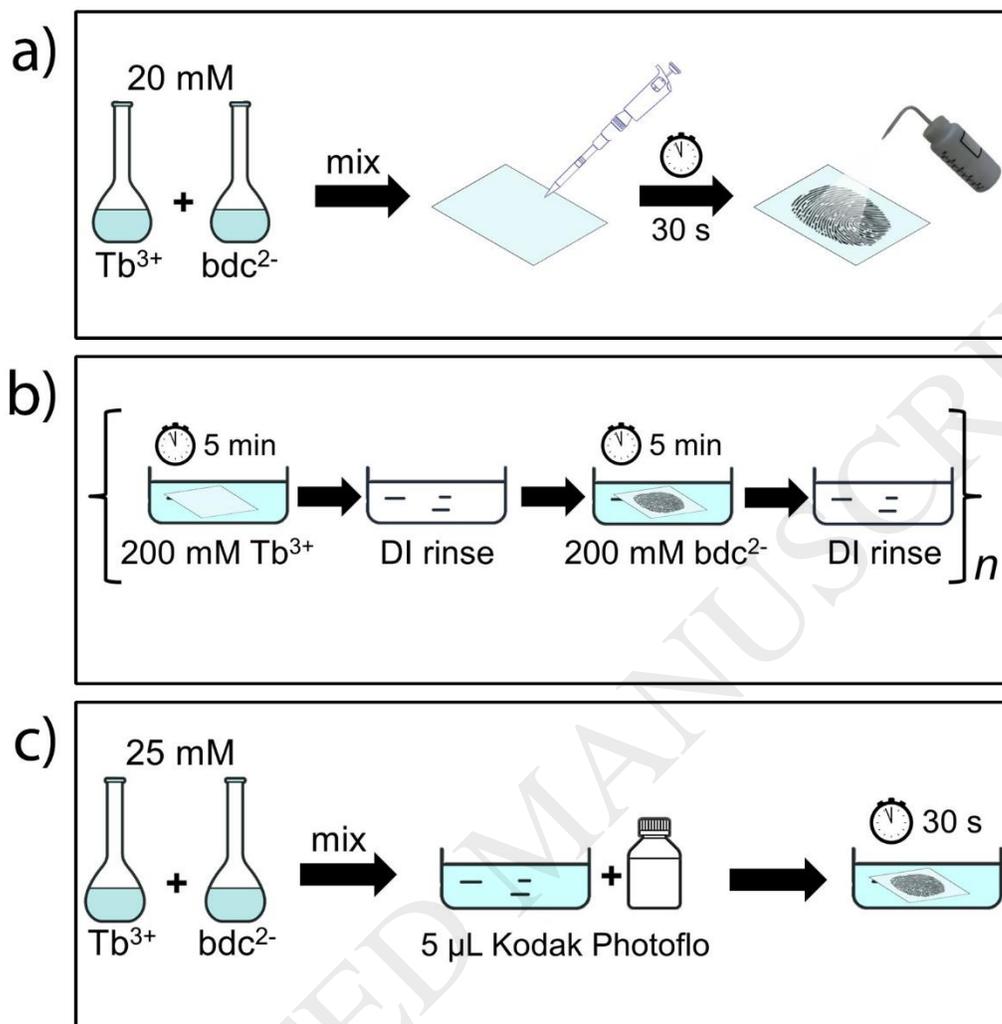
**Figure 1**: Illustration of the three application modes: (a) Liang et al. original method; (b) sequential solution application where the process can be repeated *n* times; and (c) alternative application method.
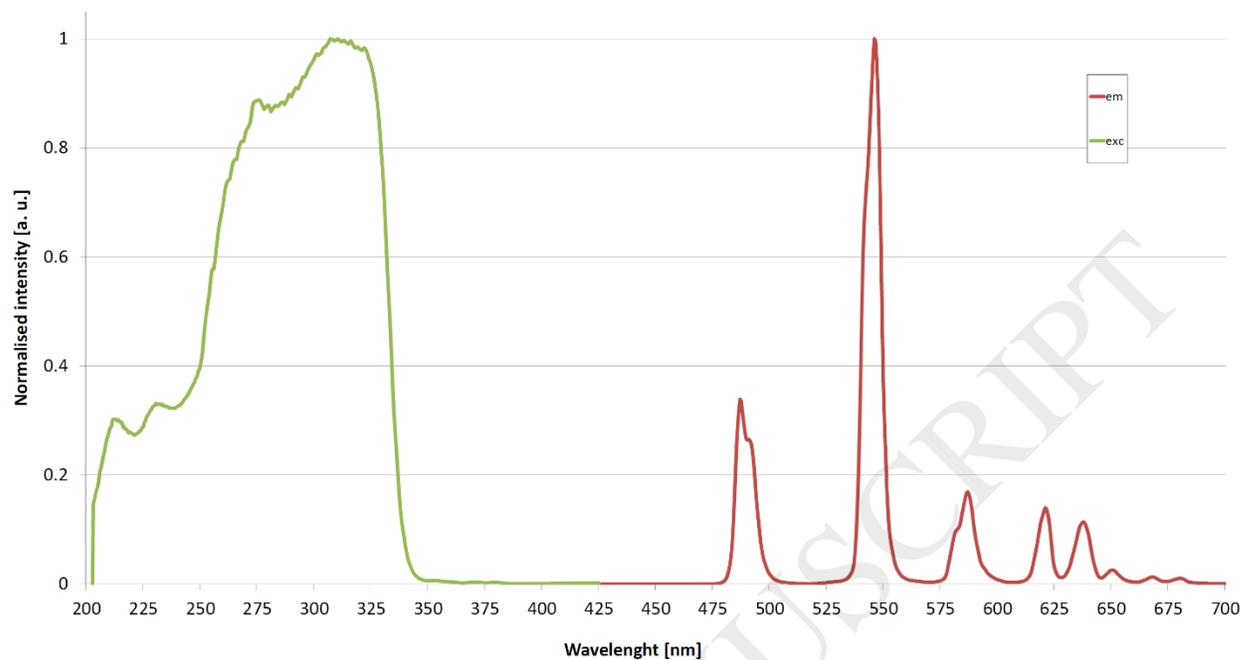
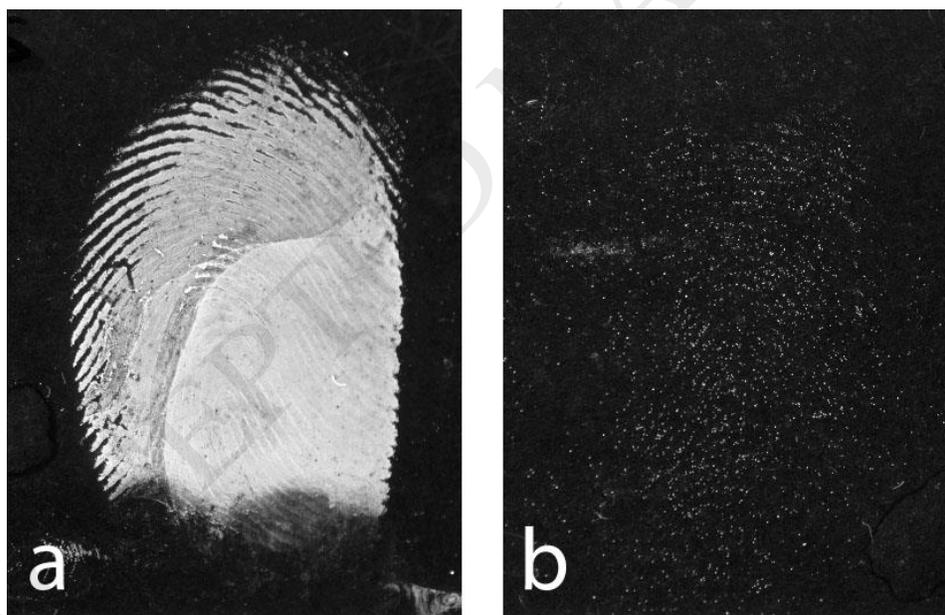**Figure 2**: Excitation and emission spectra of the MOF suspension.



**Figure 3**: Results obtained with the Liang et al. method on glass after 60-sec immersion in the MOF solution: (a) 1-day old sebaceous mark; and (b) 1-day old natural mark (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).
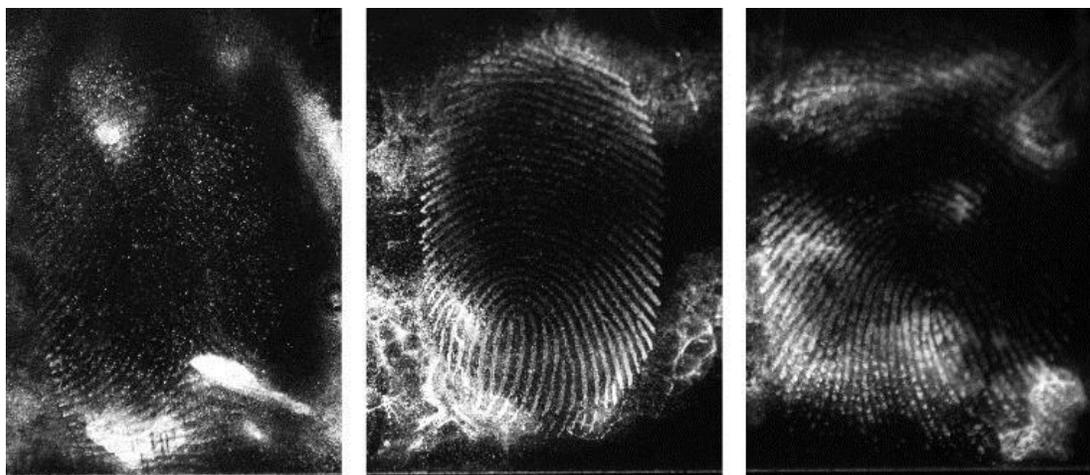
**Figure 4**: Results obtained with one-week-old natural fingermarks on glass from three different donors with the sequential application method (200 mM precursor solutions with 5 rounds of 5 min each; results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).
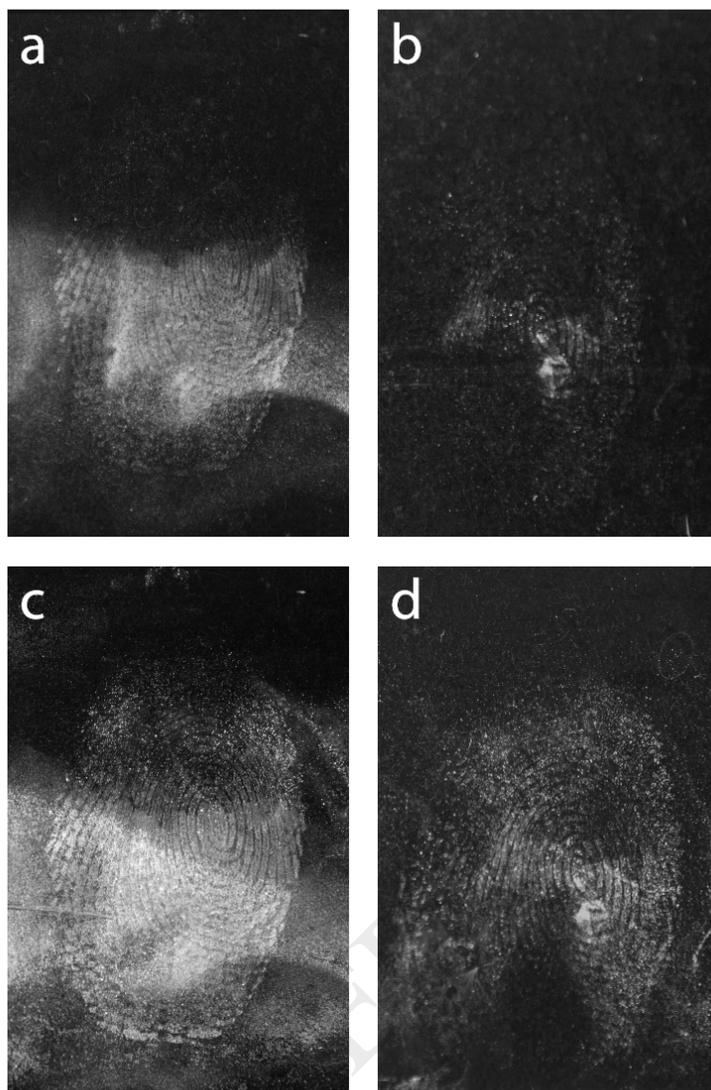
**Figure 5**: Results obtained with three-month-old natural marks on glass from a weak donor using the sequential application method. Images on the left are from a first depletion (a and c) and on the right (b and d) from a second depletion. Top images show the results obtained after 3 cycles and bottom after 5 additional cycles (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).
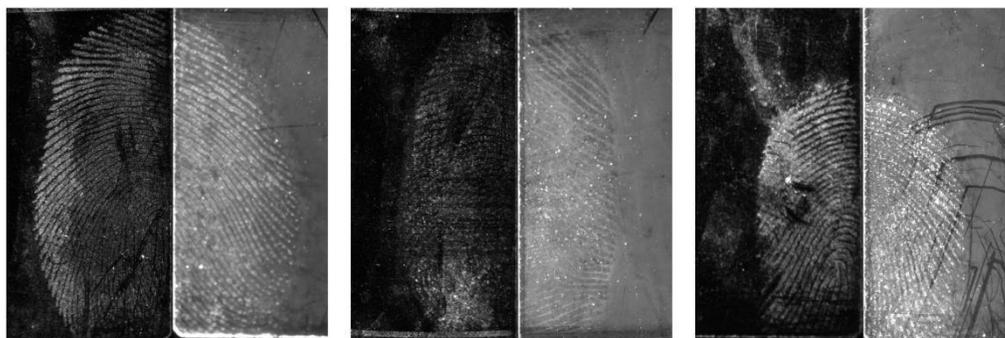
**Figure 6**: Results obtained with one-week-old natural fingermarks on glass from three different donors. Left halves: MOF sequential application method (200 mM precursor solutions with 5 rounds of 5 min each). Right halves: cyanoacrylate fuming followed by rhodamine 6G staining. (Both halves recorded simultaneously in the luminescence mode, with excitation at 350 nm and observation at 545 nm.)
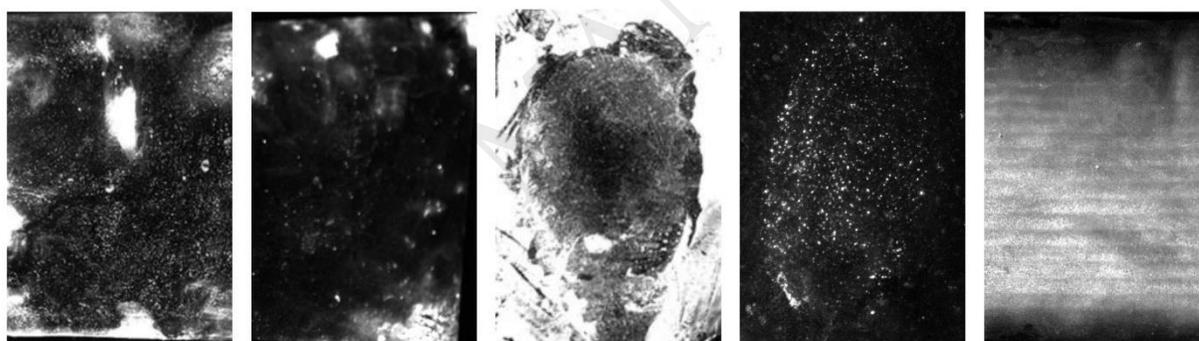


**Figure 7**: Results obtained using the sequential application method (200 mM precursor solutions with 5 rounds of 5 min each) with 24-hour-old natural fingermarks on: (a) clear plastic ziplock bag; (b) black polyethylene garbage bag; (c) aluminium foil; (d) hard plastic; and (e) duct tape (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).
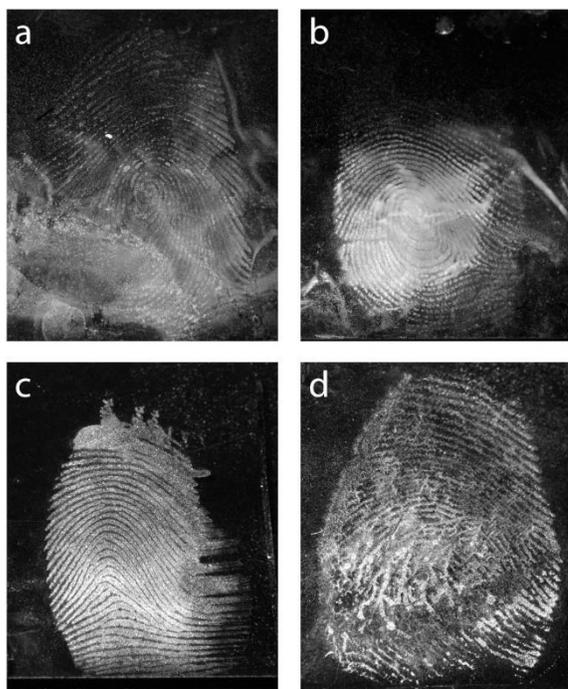
**Figure 8**: One-month-old (a) BSA and (b) lysozyme enriched mark on glass, and 1-month-old (c) blood and (d) semen contaminated marks on glass, detected using the sequential solution method (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).
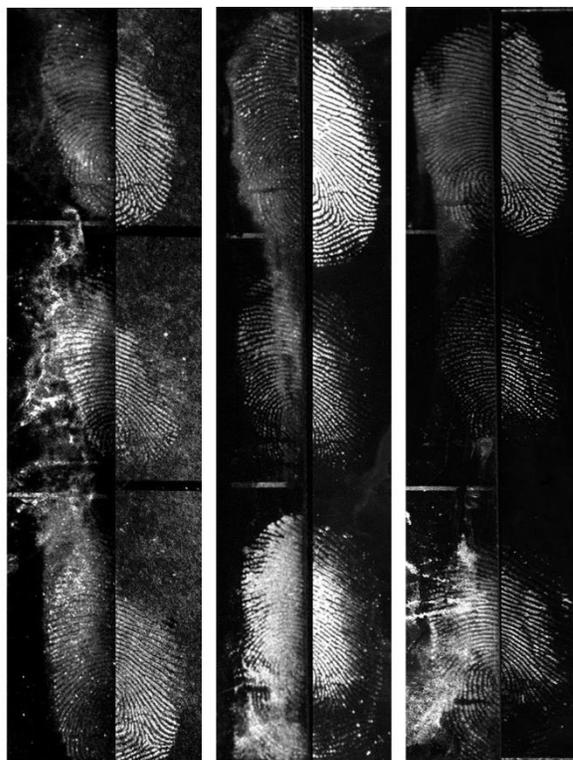
**Figure 9**: Blood mark on glass aged for 24 hours (left column), one week (middle column) and one month (right column) enhanced using the MOF sequential application method (left halves) and acid yellow 7 (right halves) (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm for the MOF treatment and excitation at 440 nm and observation at 515 nm for the AY7 treatment).



**Figure 10**: (a) 1-day-old natural fingermark on glass detected after immersion for 30 seconds in a suspension of pre-formed MOFs containing 7.5 µL/20 mL of Photoflo; and (b)

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1-day-old natural fingermark detected under the same conditions as (a) for the left half, and with the sequential application method for the right half (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).
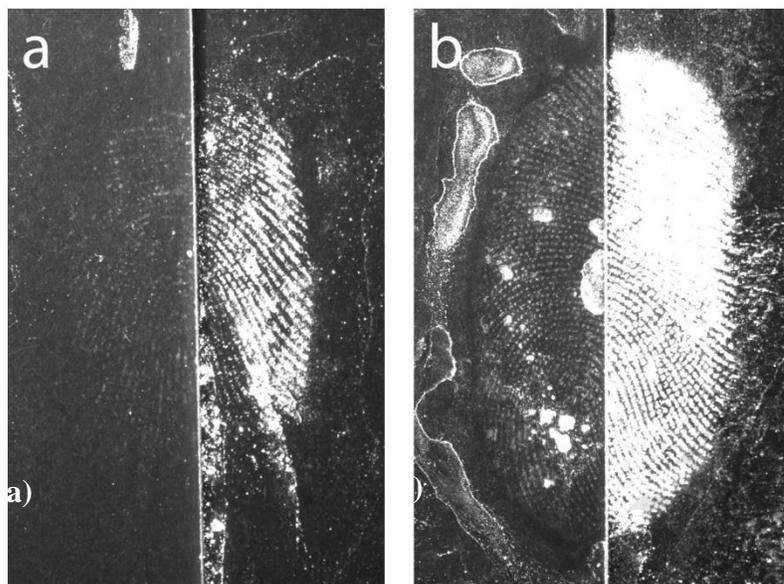


**Figure 11**: One-day-old natural fingermarks on glass with right halves detected with commercial luminescent SPR (Sirchie SPR400UV) and left halves detected with the MOF SPR: (a) with 30-second immersion in the suspension; and (b) with application using an Ecospray (results recorded in the luminescence mode, with excitation at 350 nm and observation at 545 nm).

**Table 1 – Substrates used in this study.**

| Substrate | Manufacturer |
|---|---|
| **Glass microscope slides** | Livingstone International Pty Ltd |
| **Resealable sandwich bags** | Powerbrands |
| **Black garbage bags** | Multix |
| **Aluminium foil** | Cast Away Food Packaging |
| **Silver duct tape** | Cling Adhesive Products |

**Table 2 – Summary of the tested detection conditions and precursor solution properties.**

| Tested parameter | Values | | |
|---|---|---|---|
| Immersion time [min] | 1 | 2 | 5 |
| pH of the terephthalic acid disodium salt solution | 4.5 | 5 | 5.5 |
| Precursor solution concentration [mM] | 1 | 10 | 20 |

**Table 3 – Summary of the tested detection conditions and precursor solution properties.**

| Tested parameter | Values | | | | | |
|---|---|---|---|---|---|---|
| Number of immersion cycles | 1 | | 3 | 5 | | 8 |
| Immersion time [min] | 1 | 2 | 5 | 15 | 30 | 55 |
| Precursor solution concentration [mM] | 50 | | | 100 | | 200 |

**Table 4 – Summary of the visualisation conditions used to image the results.**

| Technique | Excitation | Observation |
|---|---|---|
| MOFs | 350 nm | tilted 555-nm bandpass interference filter (545 nm) |
| CA + R6G | 530 nm | 610 nm bandpass interference filter |
| Acid Yellow 7 | 440 nm | tilted 530-nm bandpass interference filter (515 nm) |
| UV SPR | 350 nm | tilted 555-nm bandpass interference filter (545 nm) |