Fluorescent metal organic frameworks for the visual enhancement of latent fingermarks

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Fluorescent Metal Organic Frameworks for the visual enhancement of latent fingermarks

Dedicated to the loving memory of Antonio (Tony) A. Cantu, who passed away on June 29 2018.

Abstract

Lanthanide-based (Eu and Tb) metal organic frameworks (MOFs) synthesized in this work are highly fluorescent crystalline structures that form through a self-assembly process in an aqueous environment. Various bio-organic molecules, including proteins and amino acids, can act as inducing agents for this process. The fact that these components are present in fingermark secretions, in combination with the excellent luminescent properties of the MOFs, create a visualisation method for (latent) fingermarks. The aqueous MOF precursor solutions are not ideal for the visualisation of latent fingermarks on non-porous surfaces, such as aluminium foil and glass. However, they offer a simple, non-toxic, long-lasting and effective approach for the visibility enhancement of fingermarks treated with cyanoacrylate fuming on aluminium foil and glass and latent fingermarks on the adhesive side of a transparent tape. The luminescent properties of MOF-treated fingermarks persevered for at least 12 months, providing great alternative for commonly used organic dyes such as Basic Yellow 40 and Gentian Violet. In this communication we evaluate the applicability of the proposed method for the forensic fingermark workflow.

1. Introduction

Fingermark evidence plays a dominant role in forensic investigations.[1] Often, fingermarks found on crime scenes are not visible (latent) and thus require a visibility enhancement. Over the years, many methods for this visualization have been developed.[2] One recently explored fingermark visualization method makes use of lanthanide-based metal-organic frameworks (MOFs).[3] MOFs are a class of porous materials that consist of metal coordination centres linked by organic ligands.[4] The MOF-building units have the ability to spontaneously self-assemble and crystallize in aqueous solution. In 2015 and 2017 Liang *et al.* found that bio-macromolecules can act as inducing agents (that is, they speed up the MOF-formation by concentrating the MOF-precursors, in which they are encapsulated by the MOF) in the MOF self-assembly.[5-6] Therefore, they can be used to visualize latent fingermarks, which generally contain substantial amounts of amino acids and proteins.[7] Liang *et al.* [3] explored this application using lanthanide based (Eu^{3+}, Tb^{3+} and Ce^{3+}), terephthalate MOFs, which display a strong luminescence in the visible region upon irradiation with UV-light.[8] Fluorescence of fingermarks in the visible region results in increased contrast between the fingermark and the substrate which can be seen with the naked eye.

In this communication, we further explore the method reported by Liang *et al.*[3] to enhance (latent) fingermarks on aluminium foil, glass and transparent adhesive tape. We will primarily focus on Eu-based MOFs. Liang *et al*. described the direct application of the aqueous MOF precursor solutions to a (freshly) deposited fingermark. [3] This approach is surprising, as the amino acids and proteins are

generally water-soluble, and would be washed away when applying the aqueous solution to the mark.[2] We have therefore improved this methodology by treating freshly-deposited fingermarks with cyanoacrylate fumes (during this process, a white polymeric network is formed on the fingermark ridges) prior to the addition of MOF precursor aqueous solutions. We also compared the cyanoacrylate/MOF treated fingermarks to cyanoacrylate/Basic Yellow 40 treated marks (on aluminium foil and glass). In addition, we explored the use of the MOF visualisation method on fresh fingermarks found on the adhesive side of transparent tape and compared the method to Gentian Violet treated marks on the same substrate. Both Basic Yellow 40 and Gentian Violet are commonly used dyes in fingermark development. Fluorescent fingermark dyes for the visualisation of fingermarks on adhesive tapes are currently lacking. Although, recently a new fluorescent dye for the visualisation of latent fingermarks on the sticky side of tapes has been reported.[9] It also must me noted that Gentian Violet displays a fluorescence in the deep red/NIR region under influence of green light.[10] Our results clearly suggest that MOF precursors may be a valuable addition (or even replacement) to the currently existing forensic process when looking for (latent) fingermarks. However, we would like to state beforehand that comparative experiments will have to be carried out to determine the scope and applicability of the employed reagents in relation to existing methods in casework. These studies will have to be carried out according to worldwide accepted guidelines.[11-12]

2. Experimental section

2.1 Chemicals. $EuCl_3 \cdot 6H_2O$; $TbCl_3 \cdot 6H_2O$ (99.9% trace metal basis); terephthalic acid (para-benzenedicarboxylate, bdc) (98%) and NaOH (≥98%) where purchased from Sigma Aldrich and were used without further purification. Basic yellow 40 (=Panacryl Brilliant Flavine 10GFF, BVDA, Haarlem, the Netherlands) solution was prepared using 1 L ethanol and 1 g Basic Yellow powder. Gentian Violet solution contains methyl violet (Gentian Violet (≥85%, Merck (Darmstadt, Germany), phenol (≥99%, Sigma Aldrich), ethanol (≥99%, Sigma-Aldrich), and deionized water). Cyanoacrylate was purchased from BVDA (Haarlem, the Netherlands). Na_2(bdc) was prepared using reported methodology, with a few minor alterations. [5, 13-14] 1 equiv. of terephthalic acid and 2 equiv. of NaOH were fully dissolved in deionized water at room temperature, where after ethanol was added until precipitation started to occur. Then the solution was refluxed for 6 h at 90°C. After cooling, ethanol was added to precipitate the Na_2(bdc). After filtering, the white powder was dried at room temperature on glass in ambient conditions. The chemical structure of the collected white crystals was confirmed to be Na_2(bdc) using FT-IR.

An amino acid solution (containing glycine, alanine, serine, proline, valine, threonine, cysteine, hydroxy-proline, isoleucine, leucine, asparagine, ornithine, aspartic acid, glutamine, lysine, glutamic acid, methionine, histidine, phenylalanine, arginine, tyrosine, tryptophan and cystine) in deionized water was used.

2.2 Working solutions and mark development. The procedure was adapted from Liang *et al*.[3] Separate stock solutions of 0.02 M Na_2(bdc) and 0.02 M $LnCl_3$ hydrates were prepared in deionized water. The solutions were mixed (1:1 v/v) in a polypropylene Eppendorf 1.5 mL tube, and immediately transferred onto the substrate containing the fingermark, allowing the crystals to form on the fingermark and not in solution. After 30-60 s the substrates were washed using deionized water and then dried in air.

Basic yellow 40 solution was sprayed onto the substrate (using a spray bottle) containing the cyanoacrylate treated fingermark and immediately washed with deionized water followed by air drying.

Gentian Violet solution was applied by submerging the substrate containing the fingermark into the Gentian Violet solutions. The substrate was then washed with deionized water and air-dried.

2.3 Instrumentation. A FEI Quanta 3D FEG 600 scanning electron microscope equipped with an Oxford EDS detector and Omniprobe 200 nanomanipulator, was used to acquire SEM-images. A Hyperion, Bruker Vertex FT-

IR spectroscopy instrument was used. Measurements were carried out on a KBr-tablet. X-ray diffraction (XRD) and X-ray fluorescence (XRF) measurements were carried out with a Panalytical XPERT^3 Powder XRD system and EDAX Orbis Micro-XRF system by Ametek®. A Polylight light source was operated at wavelength 350 nm for the MOF treated marks and 415 nm for the Basic Yellow 40 treated marks. Cyanoacrylate fuming was carried out with a CAptureBT Fuming System, Labconco Corporation, Kansas City. The instrument was operated at 80% relative humidity using approximately 1 gram of cyanoacrylate, which is a typical amount for the specific fuming cabinet.

2.4 Sample collection. As this is a Phase 1 study, according to IFRG guidelines, a small pool of donors was used for fingermark collection. [9] In an initial experiment, fingermarks from 6 donors (3 male and 3 female, ages 20-26 y.o.) were collected on aluminium foil and glass microscopic slides in a set of 10 depletions, without any specific instructions. The first and last depletion from each set was used for development. The marks were treated directly with the MOF-precursor solutions as described in section 2.2.

In a second experiment, fingermarks from 6 donors were collected on aluminium foil, glass microscopic slides and the adhesive side of the transparent tape, in a set of 10 depletions. The first and last depletion from each set was used for development. The aluminium and glass substrates were all treated with cyanoacrylate fuming. They were divided into two halves after which one half was treated with the MOF-precursor solutions, as described in section 2.2. In some cases, subsequent treatment with the MOF-precursors was necessary for adequate development. The other half was treated with Basic Yellow 40, as described in section 2.2. Gentian violet and MOF-treated marks were visualized and photographed under UV-light (350 nm), without a camera filter. Basic Yellow 40 treated marks were photographed under 415 nm light using a 510 nm longpass filter. The marks on adhesive tape were divided into two halves. Note that they were not treated with cyanoacrylate fuming. One half was treated directly with the MOF-precursor solutions while the other half was treated with Gentian Violet, as described in section 2.2.

3. Results

3.1. Eu- MOFs characterisation

The Eu-terephthalate MOFs prepared in aqueous environment exhibit excellent red luminescent properties under the influence of UV-light. This is the case for MOFs prepared in the presence of 23 different amino acids (at 1 μgmL^{-1}) and in absence of any additional reagents. XRD and XRF (see supporting information figure S3-S6) measurement show that these crystals hold the crystalline characteristics of Europium 1,4-benzenedicarboxylate tetrahydrate. SEM images reveal that the MOF crystals formed in the presence of amino acids are significantly larger (approximate diameter of 18-23 µm) and more spherically shaped (Figure 1b) than those formed in the absence of amino acids (Figure 1a). In addition, the crystals we found are visually similar to the crystal found by Liang *et al.* on printed protein patterns. [3] These findings confirm that amino acids play a role in the self-assembled MOF formation. Possibly through intermolecular hydrogen bonding and hydrophobic interactions, during which the amino acids are encapsulated in the crystal structure.[15]

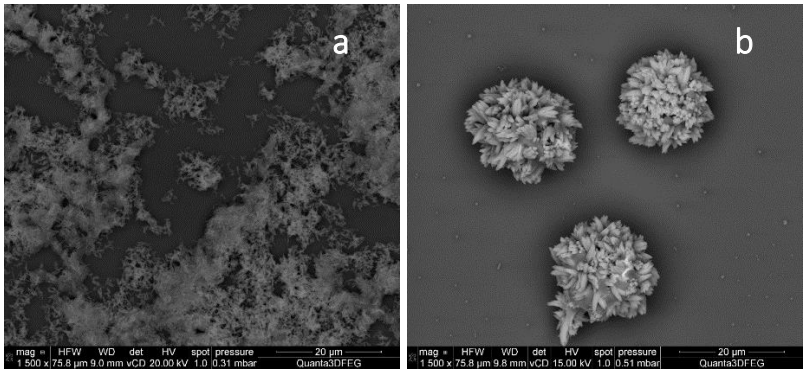

Figure 1: SEM image of Eu-based MOFs prepared, on a glass slide, in water as follows: (a) 500 µL of a 0.02 M Na_2(bdc) solution was mixed with 500 µL of 0.02 M of $EuCl_3 \cdot 6H_2O$ (both prepared in deionized water) in a polypropylene tube. (b) 500 µL of a 0.02 M Na_2(bdc) solution was mixed with 500 µL of 0.02 M of $EuCl_3 \cdot 6H_2O$ and 10 µL of a 100 ngmL $^{-1}$ amino acid solution (all in deionized water).

3.2 Development of fresh fingermarks and fingermarks pre-treated with cyanoacrylate fuming

Fingermarks on aluminium and glass substrates have been visualized by direct application of the MOF precursor solutions. It was found that the aluminium foil is a poor substrate for developing fingermarks using MOFs, because the crystals adhere to the metal surface even in the absence of a fingermark. This results in a significant amount of background staining which displays, in most cases, a stronger luminescence than the fingermark itself (Figure S2a,b). When the MOF solutions were applied to fingermarks on glass substrates, no development was observed. SEM images reveal that no MOFs are present on these substrates and that spherical MOFs with an approximate diameter of 15 µm are present in the washed off solution (Figure S1). Most likely, the hydrophilic fingermark components are washed off the surface upon application of the aqueous MOF-precursor solutions.

Fingermarks on aluminium and glass substrates have successfully been visualized by subsequent treatment with cyanoacrylate fuming followed by MOFs deposition. The MOFs do not adhere to the aluminium surface (as we have seen when applying the solutions to an untreated fingermark) after cyanoacrylate fuming. Presumably, a thin layer of cyanoacrylate is deposited on the entire surface, which inhibits the adherence of the MOFs. SEM images of the cyanoacrylate and MOF developed fingermarks reveal that MOF crystals with an approximate diameter of 7-10 µm are present on the fingermark ridges (Figure 2a,b,c). Their spherical shape is comparable to MOFs formed in the presence of amino acids and to the MOFs found by Liang *et al.* on printed protein patterns. [3] This, together with the finding that there is very limited background staining, indicates that the MOFs indeed form on the fingermark components itself. The fact that the MOFs are solely present on the fingermark ridges, indicates that the polymeric network prevents the fingermark components from being washed away from the fingermark. What is of great interest is that the 'noodle like' structure of cyanoacrylate is not present in these SEM images. Further investigations will be undertaken to generate more information on this phenomenon.

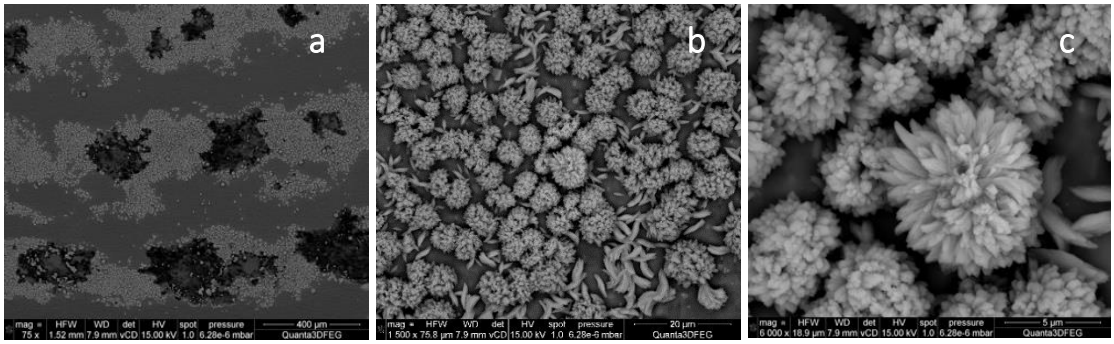

Figure 2: SEM images of a fingermark on an aluminium substrate treated subsequently with cyanoacrylate fuming and Eu-MOF precursor solutions. Magnifications (a,b,c) 75x; 1500x; 6000x

Finally, we compared the cyanoacrylate and MOF treated fingermarks to cyanoacrylate and Basic Yellow 40 treated fingermarks on aluminium foil and to Gentian Violet treated fingermarks on the adhesive side of transparent tape. For this purpose, we used both Eu- and Tb-based MOFs for the fingermark development. The luminescent properties of the MOF treated fingermarks (Figure 3a,c,e,g) are comparable to that of Basic Yellow 40 (Figure 3b,d,f,h).

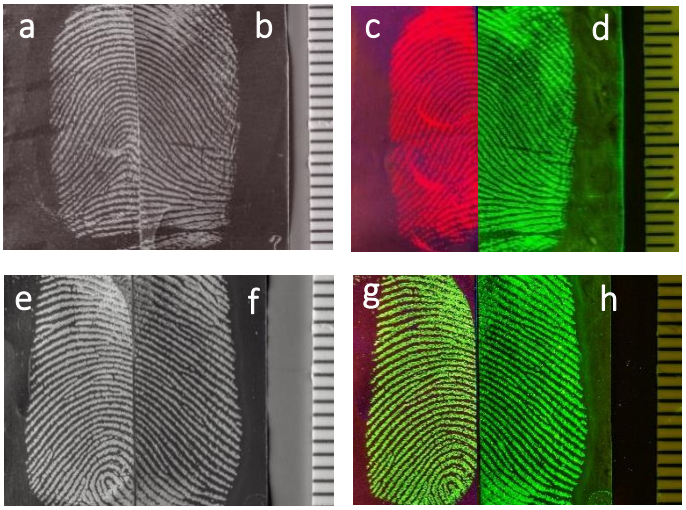

Figure 3: Fingermarks treated with cyanoacrylate fuming and MOF precursor solutions or Basic Yellow 40 on aluminium foil. Mark treated with cyanoacrylate and MOF (a: Eu-MOF under white light, e: Tb-MOF under white light, c: Eu-MOF under UV-light, g: Tb-MOF under UV-light). Marks treated with cyanoacrylate and Basic Yellow 40 (b and f: Under white light, d and h: under 415 nm, 510 long pass filter respectively). Original images can be found in the Supporting information Figure S7.

Marks on the adhesive side of the transparent tape were successfully developed using the MOF precursor solutions (Figure 4a and c). The marks displayed a strong luminescence with no significant background development (Figure 4c). The results were compared to fingermarks treated with Gentian Violet, a commonly used reagent to visualize fingermarks on adhesive tapes (Figure 4b and d). We found that development using the MOF precursors results (i) in the strong luminescence of a fingermark generated by the MOFs that clearly contributes to mark visibility; (ii) much better contrast between mark and substrate compared to Gentian Violet stained marks; (iii) reduced toxicity of the approach which is an issue when using Gentian Violet, as it contains phenol, and finally (iv) significantly improved stability of the staining which is preserved for at least 12 months (Gentian Violet developed marks fade after a few days).

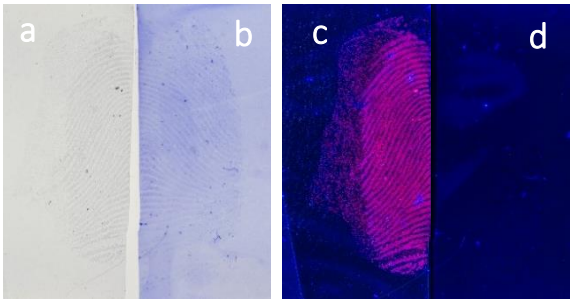

Figure 4: Fingermarks treated with Eu-MOF precursor solutions (a and c) or Gentian Violet (b and d) on the adhesive side of the transparent tape. (a and b: under white light using light box; c and d: under UV-light). Original images can be found in the Supporting Information Figure S8.

These preliminary findings show that the cyanoacrylate fuming followed by luminescent MOF deposition gives good contrast and long-lasting stability of stained fingermarks. Due to these unique characteristics, our (cyanoacrylate)/MOFs based method is a potential alternative, or even replacement, for Basic Yellow 40 (on non-porous surfaces) and Gentian Violet (on adhesive tapes) dyes. However, a more extensive study should be carried out to compare sensitivities, effect on DNA and applicability of MOFs deposits on various substrates.

4. Conclusion

We have shown that the direct application of the aqueous MOF precursor solutions on non-porous substrates (aluminium foil and glass) is not ideal for the visualization of latent fingermarks, as the hydrophilic fingermark components are washed off the surface upon application of the aqueous phase. In most cases, this leads to insufficient fingermark visualization. When fingermarks are treated with cyanoacrylate fuming prior to treatment with the MOF solutions, successful visualization is achieved. This is also the case when the MOF solutions are applied to fingermarks on the adhesive side of transparent tape. The MOF deposits offer a simple, non-toxic, long-lasting and effective approach for the visibility enhancement of fingermarks treated with cyanoacrylate fuming on aluminium foil and glass and latent fingermarks on the adhesive side of a transparent tape. In an extensive study we are now exploring the full scope and applicability of the MOFs as an alternative for Basic Yellow 40 (after development with cyanoacrylate fuming on non-porous surfaces) and Gentian Violet (on adhesive tape).

References

1. Champod, C.; Lennard, C.; Stoilovic, M.; Margot, P., *Fingerprints and other ridge skin impressions*. CRC Press: Boca Raton, FL, 2004; p 285.
2. Ramotowski, R. S., *Lee and Gaensslen's advances in fingerprint technology*. 3rd ed.; CRC Press: Boca Raton, FL, 2013.
3. Liang, K.; Carbonell, C.; Styles, M. J.; Ricco, R.; Cui, J.; Richardson, J. J.; Maspoch, D.; Caruso, F.; Falcaro, P., Biomimetic Replication of Microscopic Metal–Organic Framework Patterns Using Printed Protein Patterns. *Adv. Mater.* **2015,** *27* (45), 7293-7298.
4. Cook, T. R.; Zheng, Y. R.; Stang, P. J., Metal-organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design, synthesis, and functionality of metal-organic materials. *Chem Rev* **2013,** *113* (1), 734-77.
5. Liang, K.; Ricco, R.; Doherty, C. M.; Styles, M. J.; Bell, M.; Kirby, N.; Mudie, S.; Haylock, D.; Hill, A. J.; Doonan, C. J.; Falcaro, P., Biomimetic mineralization of metal-organic frameworks as protective coatings for biomacromolecules. *Nature Communications* **2015,** *6*, 7240.
6. Liang, K.; Wang, R.; Boutter, M.; Doherty, C. M.; Mulet, X.; Richardson, J. J., Biomimetic mineralization of metal-organic frameworks around polysaccharides. *Chem Commun (Camb)* **2017,** *53* (7), 1249-1252.
7. Girod, A.; Ramotowski, R.; Weyermann, C., Composition of fingermark residue: A qualitative and quantitative review. *Forensic Science International* **2012,** *223*, 10-24.
8. Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J., Luminescent metal-organic frameworks. *Chem Soc Rev* **2009,** *38* (5), 1330-52.
9. Barros, H. L.; Stefani, V., A new methodology for the visualization of latent fingermarks on the sticky side of adhesive tapes using novel fluorescent dyes. *Forensic Sci Int* **2016,** *263*, 83-91.
10. Bramble, S. K.; Cantu, A. A.; Ramotowski, R. S.; Brennan, J. S., Deep Red to Near Infrared (NIR) Fluorescence of Gentian Violet-treated Latent Prints. *J. For. Ident.* **2000,** *50* (1), 33.
11. Almog, J.; Cantu, A. A.; Champod, C.; Kent, T.; Lennard, C., Guidelines for the assessment of fingermark detection techniques. *Journal of Forensic Identification* **2014,** *64* (2), 174.
12. Sears, V. G.; Bleay, S. M.; Bandey, H. L.; Bowman, V. J., A methodology for finger mark research. *Sci Justice* **2012,** *52* (3), 145-60.
13. Daiguebonne, C.; Kerbellec, N.; Guillou, O.; Bunzli, J. C.; Gumy, F.; Catala, L.; Mallah, T.; Audebrand, N.; Gerault, Y.; Bernot, K.; Calvez, G., Structural and luminescent properties of micro- and nanosized particles of lanthanide terephthalate coordination polymers. *Inorg Chem* **2008,** *47* (9), 3700-8.
14. Park, Y.; Shin, D. S.; Woo, S. H.; Choi, N. S.; Shin, K. H.; Oh, S. M.; Lee, K. T.; Hong, S. Y., Sodium terephthalate as an organic anode material for sodium ion batteries. *Adv. Mater.* **2012,** *24* (26), 3562-7.
15. Xu, J. F.; Niu, L. Y.; Chen, Y. Z.; Wu, L. Z.; Tung, C. H.; Yang, Q. Z., Hydrogen bonding directed self-assembly of small-molecule amphiphiles in water. *Org Lett* **2014,** *16* (15), 4016-9.