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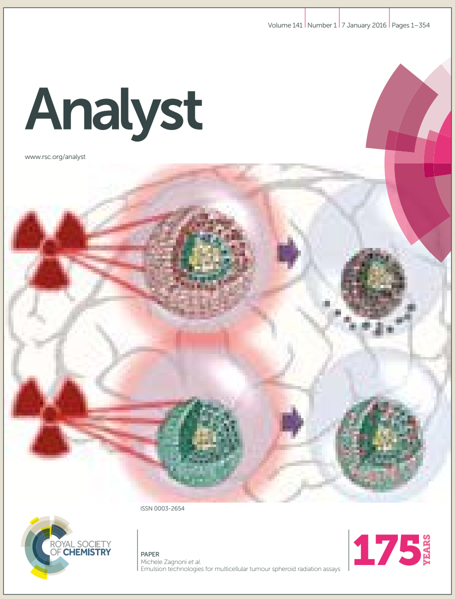

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# Harnessing volatile luminescent lanthanide complexes to visualise latent fingermarks on nonporous surfaces

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**Two commercially-available terbium and europium complexes, EuFOD and TbTMHD, provide luminescent visualisation of latent fingermarks placed on non-porous surfaces via sublimation. This is demonstrated using UV radiation from a forensic light source. The method was optimised on metal foil, with other archetypal nonporous surfaces (i.e. glass, ceramic) also suited to this method.**

Latent fingermarks (*i.e.* invisible fingerprints) are an important class of evidence evaluated by law-enforcement agencies to assist with the identification of individuals.[1] Given the plethora of surfaces on which fingermarks may be placed new techniques and reagents are needed to enable visualisation across this range of scenarios. Different surface types will possess unique degrees of porosity, emissivity, and reactivity, complicating this endeavour. Recent innovations to address this challenge include adoption of nanoparticle materials,[2] harnessing near-IR emission for highly emissive surfaces,[3] targeting new biological components,[4] and new chemical treatments for challenging surfaces like bullet casings.[5]

Vacuum metal deposition (VMD) is a commonly used technique for visualising latent fingermarks owing to its high sensitivity, and applicability to a wide range of surfaces. It works by depositing metal films (*e.g.* silver, gold, chromium, zinc) under high vacuum conditions. Surface contamination caused by latent fingermarks hinders the deposition of these metallic films, thereby producing visible contrast. A typical procedure begins with the surface being coated in a thin layer of gold, followed by a second layer of zinc. This typically produces a ‘negative’ image, wherein metal coating is observed everywhere but for where ridge patterns of the fingermark are present.[6] Surface effects may influence the behaviour of metal deposition, with some polymeric surfaces shown to produce reversed metal deposition, (*i.e.* within the fingermark residues themselves) under certain VMD conditions.[7] This represents the benchmark for new volatile treatments using VMD-like conditions. A new state-of-the-art in VMD could be achieved by deposition of luminescent materials. This is because the current approaches require additional treatments, such as cyanoacrylate (CA) fuming or staining with a dye such as Basic Yellow 40,[8] to improve visualisation, which complicates and lengthens the VMD process.

Harnessing lanthanide luminescence to improve fingermark visualisation has recently seen a surge in interest,[9] particularly centred on upconversion nanoparticles (UCNPs).[10] UCNPs are capable of producing visible and near-IR radiation by absorbing multiple lower-energy photons as a result of the long excited-state lifetimes produced upon interaction with a photon. One such UCNP material harnessed a DNA aptamer to target the lysosome component of fingermark residues to visualise the ridge patterns,[11] while another benefitting from simpler synthetic protocols produces upconverted green luminescence upon excitation at a wavelength of 980 nm.[12] These materials avoid generating background autofluorescence that can be an issue when higher excitation wavelengths are applied to surfaces bearing fingermarks.

Fingermark residues are made up of a complex mixture of polar (*e.g.* amino acids) and nonpolar (*e.g.* lipids) components. This provides two distinct targets for a new fingermark visualising treatment. The nonpolar, lipid fraction is the more attractive of the two targets, given that it persists for long periods of time (in the order of years) on surfaces.[1] The nonpolar components are also more resistant to environmental degradation such as surface wetting. The creation of new VMD treatments with an affinity for the nonpolar components of fingermark residues will thus offer improved visualisation strategies for forensic practitioners.

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Electronic Supplementary Information (ESI) available: TGA and DSC traces of EuFOD and TbTMHD. Example experimental setup and expanded discussion of fingermark grading scheme. See DOI: 10.1039/x0xx00000x



 

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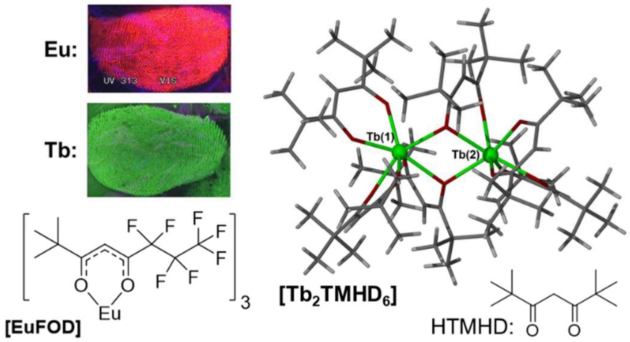


**Fig. 1** The two volatile phosphorescent lanthanide complexes employed in this study: EuFOD (lower-left) and TbTMHD (right). Both reagents are common and can be sourced commercially. Examples of the luminescent behaviour provided by these species is shown in the top-left.

This work targets this aim by exploring two established, commercially available lanthanide complexes with known lipophilicity. The first, europium(III)-tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate), EuFOD, (Fig. 1, bottom-left) has a long history of application as an NMR shift reagent,[13] coupled with well-characterised volatility.[14] In addition, EuFOD emits strong red luminescent emission, primarily from $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0–6) transitions.[15] Additionally, this complex is furnished with multiple ligand-bound perfluorinated chains that boost its lipophilicity and thus affinity towards nonpolar fingermark residues. The second complex investigated in this study, terbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), $Tb(TMHD)_3$, (Fig. 1, right) is actually a dimeric species with the composition $[Tb_2(TMHD)_6]$. Like EuFOD, the volatile nature of TbTMHD is well-characterised and the complex possesses a lipophilic ligand shroud that is capable of providing an affinity for nonpolar fingermark residues.[16] The primary emissive transitions for the terbium species are $^5D_4 \rightarrow {}^7F_J$ ($J$ = 6–0), which give strong green emission.[15] Luminescent lanthanide complexes have seen extensive use across a range of applications,[13,17] including solution-state studies involving latent fingermarks,[18] however this work constitutes the first application that harnesses the volatility of lanthanide complexes to visualise latent fingermarks, circumventing issues such as excessive background surface development, and degradation of fragile fingermarks, while generating improved phosphorescent visualisation.

Of the two compounds studied, EuFOD was obtained commercially and used as received, whereas TbTMHD was synthesised according to a literature procedure.[16] Both complexes yielded luminescent profiles consistent with prior reports.[19,20] The volatile behaviour of each reagent was characterised using thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) (Figures S1 & S2, ESI). The TGA data of both complexes matched that reported in the literature,[14,16] with mass loss commencing for EuFOD at *ca* 180 °C, and occurring in a single step without degradation that concluded with complete mass loss at *ca* 280 °C. The terbium dimer $[Tb_2(TMHD)_6]$ initially showed similar behaviour, with 90% of mass loss occurring between *ca* 180 °C and 300 °C, however a second step was observed for the final 10% of the mass loss, with concomitant signs of degradation by DSC. The DSC data showed further unique behaviour for the terbium complex to distinguish it from EuFOD. EuFOD showed a single melting/sublimation event without any obvious signs of degradation, consistent with the TGA trace. In contrast, the TbTMHD DSC trace shows additional features: a melting curve at *ca* 160 °C, which triggers a second event between 180–200 °C that precedes the main mass loss event. This second endothermic curve is posited to be a transition from $[Tb_2(TMHD)_6] \rightarrow 2[Tb(TMHD)_3]$ that is only free to occur post-melt. The monomeric complex would be expected to have higher volatility than the dimer, behaving analogously to EuFOD. This monomerisation occurs simultaneously with the commencement of the mass loss event in the TG trace, and a third endothermic curve in the DSC that commences at *ca* 200 °C and is attributed to boiling/sublimation of TbTMHD. This third endothermic event concludes with evidence of degradation in the DSC trace.

Armed with this interpretation of the thermal behaviour of both lanthanide complexes, a study was next undertaken to identify the optimal conditions for transference of each luminescent complex into fingermark residues. Fingermarks were placed on a nonporous metal surface, aluminium foil, for this optimisation trial. Evaluation of these samples involved transferring a small amount (20 mg) of lanthanide complex into sealable vials and partitioned that material with a plug of cotton wool (Figure S3, ESI). The vials were then placed under reduced pressure ($4.0 \times 10^{-1}$ mbar) to depress the boiling point of the lanthanide complex, and then subjected to varying temperatures and time durations. The results of these studies for both EuFOD and TbTMHD are summarised in Table 1. Further discussion of the grading scheme can be found in the ESI. This chosen level of vacuum is mild compared to that attainable by traditional VMD equipment, however it was selected to allow rapid screening of new visualisation reagents using common laboratory equipment. Under real-world VMD conditions (e.g. $5.0 \times 10^{-4}$ mbar) the boiling points of the lanthanide complexes would be considerably further depressed. Interestingly, the boiling point of EuFOD was readily depressed by application of vacuum to well below that determined by the TGA at ambient pressure, however the TbTMHD complex did not. This finding supports the assertion that a thermal $[Tb_2(TMHD)_6] \rightarrow 2[Tb(TMHD)_3]$ transition is required which is largely independent of the influence of reduced pressure.

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**Table 1.** Optimisation of lanthanide complex uptake by fingermark residues placed on aluminium foil at $4.0 \times 10^{-1}$ mbar. Variables investigated were temperature and heating duration.

**EuFOD**

| Time (minutes) \ Temperature (°C) | 100 | 110 | 120 | 130 | 140 | 150 | 175 | 185 | 200 |
|---|---|---|---|---|---|---|---|---|---|
| 10 | No | No | No | No | Partial | Partial | Good | Good | Good |
| 30 | No | No | No | Partial | Partial | Partial | Good | Good | Good |
| 50 | No | No | No | Partial | Partial | Good | Good | Good | Good |
| 90 | No | No | Partial | Partial | Partial | Good | Good | Good | Good |
| 120 | No | No | Partial | Good | Good | Good | No | No | No |
| 180 | No | Partial | Partial | Good | Good | Good | No | No | No |

**TbTMHD**

| Time (minutes) \ Temperature (°C) | 160 | 170 | 180 | 190 | 200 |
|---|---|---|---|---|---|
| 10 | No | No | No | No | Partial |
| 30 | No | No | No | No | Partial |
| 50 | No | No | No | Partial | Good |
| 90 | No | No | No | Good | Good |
| 120 | No | No | Partial | Good | Good |
| 180 | No | Partial | Good | Good | Good |

No visualisation / degradation
Partial visualisation
Good visualisation

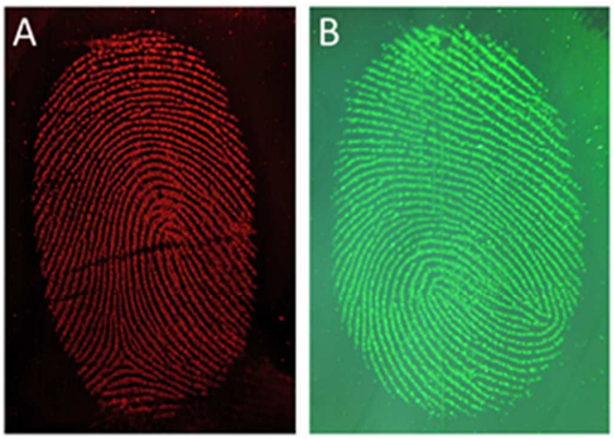


**Fig. 2** Visualised latent fingermarks placed on aluminium foil using volatile lanthanide reagents and UV radiation. A) EuFOD volatilised at 175 °C under reduced pressure ($4.0 \times 10^{-1}$ mbar) and with a heating time of 10 minutes in a sealed vessel. The fingermark was photographed using a brightred longpass filter. B) TbTMHD volatilised at 200 °C under reduced pressure ($4.0 \times 10^{-1}$ mbar) and heated for 60 minutes in a sealed vessel. The fingermark was photographed using a yellow-m longpass filter.

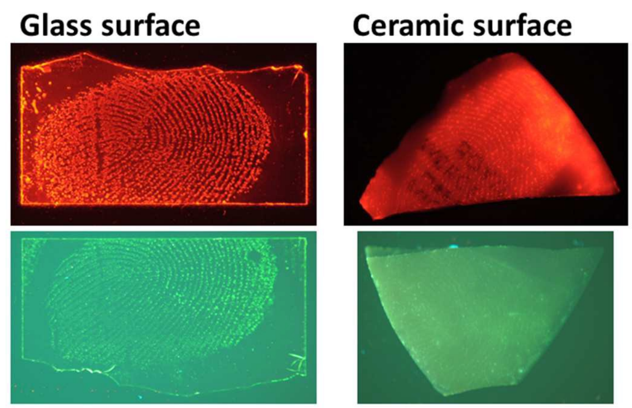


**Fig. 3** Applying volatile lanthanide complexes to fingermarks placed on other types of nonporous surfaces. Left: Fingermarks visualised on glass cover slides using EuFOD (top) and TbTMHD (bottom). Right: Fingermarks visualised on porcelain using EuFOD (top) and TbTMHD (bottom). Treatment conditions for these materials were identical to those optimised for aluminium foil, as were the visualisation and photographic setup.

These results show that under reduced pressure EuFOD is capable of effecting visualisation of fingermarks at temperatures as low as 110 °C, and can rapidly produce high-quality visualisation of fingermarks (Fig. 2, Left) above 150 °C. The visualisation in Figure 2 was achieved by heating for 10 minutes at 175 °C under reduced pressure. Third level ridge details, *e.g.* pores within the ridges, were evident after treatment using the EuFOD complex (Figures S4 & S5, ESI). Visualisation of the fingermark was performed with illumination using a LUMATEC Superlite S04 portable forensic light source set to the UVA wavelength range of 320–400 nm. The fingermark was viewed through a spectral magnifier combined with a light diffuser attachment of the Superlite light guide. Reflected UV light wavelengths were filtered out using a 'brightred' long-pass filter attached to a Nikon D300 camera coupled with an AF-S DX Micro NIKKOR 40mm Lens. Full details of equipment used and camera settings are provided in the ESI. This use of forensic equipment highlights the applicability of these common reagents to real-world forensic practitioners.

Higher temperatures and longer heating times were required to achieve visualisation of fingermark residues using TbTMHD. Heating at 200 °C for 60 minutes produced characteristic green terbium luminescence localised within the ridge deposits on the aluminium foil surface. This Tb luminescence was photographed in an identical manner as for the europium emission, albeit using a 'yellow-m' long-pass filter attachment for the Nikon D300 camera.

These preliminary results showcase the exceptional promise of applying volatile luminescent lanthanide complexes to VMD. To expand upon these results, two other archetypal nonporous surfaces were next evaluated: glass and a ceramic material (porcelain).

The glass surface consisted of a thin glass slide cover slip that was broken lengthways to accommodate the vacuum vessel. Two fingermarks were placed on separate halved glass cover slides and subjected to the optimised conditions determined for metal foil, using either EuFOD, or TbTMHD. After 10 minutes for the former, and 60 minutes for the latter, visualisation of the fingermarks was seen to occur (Fig. 3, top-left and bottom-left). These results were imaged as described

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above for metal foil. Given the ubiquity of broken glass to many crime scenes, this finding is of great relevance to forensic practitioners.

Porcelain proved to be a more challenging nonporous surface for the terbium reagent, with only weak visualisation seen on this surface (Fig. 3 bottom-right). Better visualisation was obtained using EuFOD (Fig. 3 top-right), however stronger background emission was observed than for the previous two surface types. This may be the influence of surface polishing during the manufacture of porcelain, which alters the morphology of the surface by opening pores that may trap and accumulate the volatilised luminescent complexes.[21]

The application of elevated temperatures to forensic evidence will not always be feasible, particularly for items containing materials prone to thermal degradation such as polymers, however as a rapid screening tool for identifying new coating candidates for VMD and showing their behaviour in the presence of fingermarks we believe this simple methodology offers considerable benefit. Once suitable candidates are identified further work optimising the protocols for the thermal evaporative process of forensic VMD systems can be implemented. This aspect of the work is ongoing.

## Conclusions

This preliminary study demonstrates the promise of applying volatile luminescent lanthanide complexes to visualise latent fingermarks placed on common, archetypal nonporous surfaces using simulated VMD conditions. Both lanthanide complexes used in this study are common, commercially available and affordable,[22] which will enable of the rapid and widespread adoption of this innovation to crime laboratories world-wide. Further work is needed to integrate this work with current VMD technology, however these early results show clear advantages in terms of delivering a single-step, phosphorescent development of fingermark residues.

## Conflicts of interest

There are no conflicts to declare.

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22 As of 20/04/18 EuFOD can be purchased for £32.10/g, TbTMHD for ca £80.50/g. Supplier: Sigma Aldrich.

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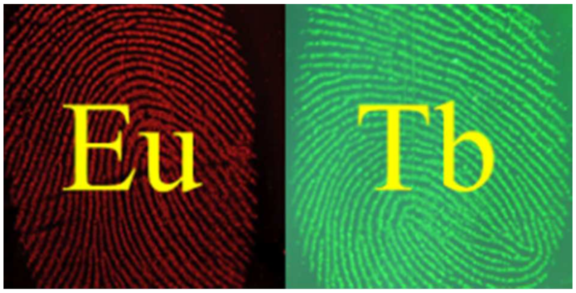


Sublimation of luminescent lanthanide complexes is shown here to be a facile means of visualising latent fingerprints on nonporous surfaces.