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Luminescent Visualization of Latent Fingerprints by Direct Reaction with a Lanthanide Shift Reagent

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ABSTRACT: The utilization of the lanthanide shift reagent tris (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium (III) [Eu(fod)$_3$] as a simple one-step reagent for the luminescent visualization of latent fingerprints has been investigated. UV excitation of Eu(fod)$_3$-treated prints, achieved by using a handheld UV lamp or a Polilight®, results in an orange emission at 614 nm. Time-resolved imaging is not required for visualization. Visualization of latent fingerprints on paper under the conditions used, although good, was found to be inferior to that obtained by standard DFO (1,8-diazafluoren-9-one) treatment, whereas visualization of prints obtained on aluminum drink cans and galvanized iron proved superior to that obtained by Superglue/panacryl treatment. Eu(fod)$_3$ treatment can also be used first without compromising subsequent ninhydrin or DFO treatment, making it a "nothing-to-lose" reagent.

KEYWORDS: forensic science, europium, fingerprints, fluorescence, luminescence, nuclear magnetic resonance, shift reagents

The lanthanide metal europium is large enough that it comfortably provides space for coordination of nine monodentate ligands. In this respect it differs from most familiar transition metals, which commonly show a maximum coordination number of six. However, europium's usual preference is eight or nine, and in this paper we refer to europium with all available sites occupied as being in a coordinatively-saturated state. Correspondingly, we also refer to europium ligand complexes with any less than nine sites occupied as being coordinatively-unsaturated. In this category, six-coordinate europium complexes are well known, relatively stable, and commercially available. Six-coordinate europium complexes are also quite reactive, because three further ligands can be readily accommodated around the metal.

In this work we assessed the potential of such a reactive coordinatively-unsaturated (six-coordinate) europium complex as a reagent for the direct visualization of latent fingerprints, on both porous and nonporous surfaces.

Lanthanide metals, in particular europium and terbium, have enjoyed the attention of a select number of fingerprint researchers in the past. The feature that makes these metals attractive as fingerprint visualization aids is the strong luminescence they exhibit, when appropriately complexed. Previous research with these metals in the fingerprints area includes an examination of the emission characteristics of the complexes they form with Ruhemann's Purple (1,2), and use of coordinatively-saturated europium complexes as luminescent dyes to enhance fingerprints developed by Superglue (cyanoacrylate ester) fuming (3–5).

In the former category, the europium-Ruhemann's Purple complex examined by Menzel and Mitchell (1) exhibited Eu^{3+} luminescence at 615 nm with a lifetime of 0.4 ms. The analogous terbium complex showed Tb^{3+} luminescence at 545 nm with a lifetime of 1.3 ms (2). These relatively lengthy lifetimes imply that the europium and terbium luminescence observed is best described as phosphorescence rather than fluorescence, although this difference becomes academic in the absence of time-resolved imaging apparatus. Coordinatively-saturated europium complexes assessed in terms of their potential as luminescent dyes to enhance Superglue-fumed prints include thenoyl europium chelate (TEC) and its analogues (3–5). These complexes were also reported to exhibit characteristic Eu^{3+} luminescence at 614 nm.

Luminescence of europium complexes is strongly related to the type of ligands that are coordinated to the metal. Substantial enhancement of the luminescence can result when an optically absorptive ligand's excited triplet state overlaps the excited state of europium in energy (6). Under these conditions, much of the energy absorbed by the ligand on excitation (with a laser or similar source) can be transferred to the metal, which then rereleases it as light of a longer wavelength. For this reason, attempts have also been made to develop latent prints using a two-step approach, whereby the fingerprint is first treated with a reactive ligand capable of binding to either lipids or amino acid components in the print. On subsequent treatment with an Eu^{3+} solution, the metal cation coordinates to the print-bound ligand, causing substantive luminescence to develop. These approaches are discussed by Menzel (7).

A one-step variation of this approach involves direct treatment of prints with an aqueous solution of ortho-phenanthroline complexed $EuCl_3$ in the presence of acacia. This method has also been outlined by Menzel (7), where it was suggested the europium complex binds to the acacia, which in turn binds to the lipid components of the prints. Interestingly, this approach has recently been observed to work just as well without acacia (8), implying that the aqueous europium ortho-phenanthroline complex is naturally attracted to the lipid matrix of the prints. Once the complex is absorbed by the lipids, luminescence develops, presumably as a result of displacement of water molecules from the coordination-sphere of europium, caused by the attachment of various lipid-based ligands.

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To date, however, there have been no studies on the potential for coordinatively-unsaturated europium complexes to work as fingerprint reagents in their own right.

In terms of their spectroscopy, complexes of europium (and also of terbium, samarium, and dysprosium) possess optical properties that make them a good choice for visualization of fingerprints. Under the right conditions they show intense luminescence, and their emission spectra are characterized by sharp lines with very large Stoke's shifts (over 200 nm) and unusually long lifetimes (1 μs to over 1 ms) (9). By itself, the intense luminescence means that such complexes can be visualized in the same way as standard fluorescent reagents. The large Stoke's shift (distance between the excitation and emission wavelengths) adds the additional prospect that background fluorescence can be more readily removed by use of simple optical filters. The long lifetime of the luminescence adds a further dimension, in that such reagents are also amenable to time-resolved imaging (10) as an alternative means of removing background fluorescence.

Six-coordinate europium complexes differ from those currently in use as cyanoacrylate dyes in that they are likely to be reactive toward a number of functional groups present in latent fingerprints. There is good evidence that this should be the case. In the past, such complexes have been widely employed as lanthanide shift reagents, a class of additives used in NMR Spectroscopy (11). Such reagents are all derived by tris-complexation of the lanthanide metal ion with enolic β-dicarbonyl compounds, and work by virtue of the fact that six-coordinate europium has space available to form a complex with the molecule being analyzed, provided this molecule contains a suitable functional group. Association of an electropositive lanthanide metal to an organic molecule has the effect of shifting the latter's NMR proton peak positions to varying degrees, depending on the proximity of each carbon atom to the metal; in this way lanthanide shift reagents were used to improve the NMR peak resolution. In this role they are most effective with molecules belonging to such functional classes as amines, alcohols, ethers, aldehydes, ketones, esters, nitriles, and epoxides (12). Progressive increases in the magnetic field strengths of NMR instruments have resulted in a steady decline in the use of six-coordinate europium complexes as shift reagents, but they are still readily available.

In this work we investigated the coordinatively-unsaturated europium complex tris (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium (III). This is more conveniently known as [Eu(fod)$_3$], and its structure is provided in Fig. 1. Eu(fod)$_3$ was first synthesized by Springer et al. (13) and has since seen extensive use as an NMR shift reagent for the structural analysis of various organic compounds (11,14–19). It is a covalent charge-neutral compound, soluble in nonpolar solvents such as aliphatic hydrocarbons.

Eu(fod)$_3$ is likely to be reactive toward a broad variety of functional groups. Direct experimental evidence (obtained using NMR) has been published, which establishes that Eu(fod)$_3$ reacts with alcohols, ketones, and carboxylic acids (14,15), and similar compounds have been previously found to react with amine groups (12). Eu(fod)$_3$ should therefore be quite reactive toward many of the functional constituents found in latent fingerprints, the most significant of which would be alcohols, carboxylic acids, and amino acids.

In the context of europium's excellent optical properties, the high reactivity of Eu(fod)$_3$ with functional groups known to be present in latent fingerprints suggests that such complexes have definite potential as reagents for direct single-step visualization of latent fingerprints.

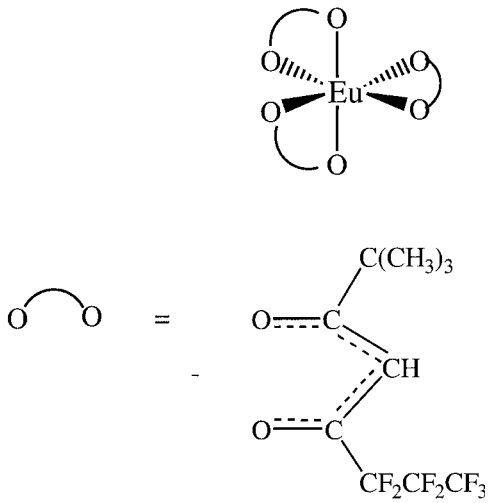

FIG. 1—*Structure of Eu(fod)$_3$.*

Methodology

Chemicals

Eu(fod)$_3$ (Resolve-Al™ EuFOD, 99%) and ninhydrin (ACS reagent) were both purchased from Aldrich Chemical Company Ltd. DFO (1,8-diazafluoren-9-one) was obtained from Lumichem Ltd.

Toluene, dichloromethane, chloroform, and hexane were bought from R.P. Normanpur™ (AR); petroleum spirits (b.p. 40 to 60°C) (AR), and petroleum spirits (b.p. 80 to 100°C) (AR), glycine (AR), methanol (AR), ethanol (AR) glacial acetic acid (AR), propionic acid (LR), and N,N-dimethylformamide (GPR), were all obtained from BDH; ethyl acetate (AR), urea (AR), and triethylamine (LR) from Ajax Chemicals; octanoic acid (AR) from Aldrich Chemical Company Ltd; and D-(+)-glucose from May and Baker Laboratory Chemicals. Freon (1:1:2 trichlorotrifluoroethane) was originally sourced from E.I. Dupont de Nemours and Company.

Instrumentation and Equipment

A Perkin Elmer Luminescence Spectrometer LS 50B was used for collection of all luminescence data; this utilizes a xenon-lamp source. A Mineralight® hand-held UV lamp (model UV GL-58) was used with two wavelength settings of 254 and 366 nm for initial visualization of treated fingerprints. When images were required, use was made of an operational Polilight® (model PL10A) owned by the New Zealand Police; the 320 nm filter was used in conjunction with a CCD camera and thermal printer. A Spectra Physics 164 argon-ion laser (1 W) in combination with a 265 Exciter was used for visualization of DFO-treated fingerprints. A Fisons VG Platform II Electrospray Mass Spectrometer was used to look for evidence of particular substrates binding to Eu(fod)$_3$. White paper (A4, 80 gsm) was obtained from Copyright (Australian Paper Ltd.).

Excitation-Emission Spectra of Eu(fod)$_3$

A preliminary investigation indicated that Eu(fod)$_3$ readily dissolves in petroleum spirits (b.p. 40 to 60°C) which was therefore, unless otherwise specified, used as the general reagent for fingerprint trials. Solvents containing significant quantities of water are generally not suitable, because direct coordination of water

molecules to the europium center tends to quench the luminescence (9).

Emission and excitation spectra of $Eu(fod)_3$ in petroleum spirits (b.p. 40 to 60°C and b.p. 80 to 100°C) were obtained using a luminescence spectrometer. Solutions were prepared by dissolving 10 mg $Eu(fod)_3$ in 20 mL petroleum spirits. Slit widths for both excitation and emission were set at 10 nm, with solutions being held in a 10 mm quartz cuvette. Data for a three dimensional spectrum of $Eu(fod)_3$ luminescence in petroleum spirits (b.p. 40 to 60°C) were collected by exciting at 200 nm, running a full emission scan, and then repeating the process but with the excitation wavelength increased by 10 nm each time, in progressive increments up to 500 nm.

Fingerprint Trials

For the initial trials, unless otherwise specified, latent fingerprints were placed on strips of white paper and then cut bilaterally down the center so that each half could be treated in a different way, and accurate comparisons thus be made. In order to deposit the fingerprints on a given surface, the finger or thumb was rubbed across the forehead and then pressed firmly down on to the surface being investigated. Again, unless otherwise stated, treatment consisted of a short dip or immersion in a 6.67 g/L petroleum spirits (b.p. 40 to 60°C) solution of $Eu(fod)_3$ using a 20 s dipping time. Visualization of the $Eu(fod)_3$-treated fingerprints was obtained using a Mineralight® hand-held UV lamp (Model UV GL-58). This has a mercury vapor source, with two wavelength settings of 254 and 366 nm, and it was found that the 254 nm setting gave the best visualization. Orange goggles were necessary for successful viewing of the prints in order to filter out background fluorescence from the paper. For photographic purposes a Polilight® was used to induce luminescence (using the 320 nm wavelength filter), and an orange filter was placed over the camera lens.

A number of different aspects of reagent performance were examined. These are outlined below.

Preliminary trials were carried out to determine the dipping times and reagent concentrations that gave best print development. Dipping times ranging from 10 s to 5 min were compared at a standard solution concentration of 3.333 g $Eu(fod)_3$/L. $Eu(fod)_3$ concentrations ranging from 0.133 g/L to 6.67 g/L were also compared at a standard 20 s dipping time.

In an attempt to get a relative measure of the degree of luminescence obtainable from $Eu(fod)_3$-treatment, standard DFO treatment was used for comparison. DFO is considered to be one of the most effective fluorescent reagents currently in use (20). In this trial, fifty prints were deposited on paper and then cut down the center into halves; half of each print was treated with $Eu(fod)_3$, and the other half with DFO. After development, DFO-treated prints were excited at 514.5 nm, and $Eu(fod)_3$-treated prints were excited at 254 nm.

A trial was carried out to establish the stability of developed prints in air after treatment. Print halves deposited on paper were used to compare stability of treatment from 1 to 72 h after dipping (this trial was carried out in triplicate). To test the possibility that moisture in the air was reacting with europium in the treated print, a print deposited on paper was treated and then cut bilaterally down the center. One half was placed in an oxygen- and moisture-free dry nitrogen atmosphere (dry-box) for four days, while the other half was left in a normal atmosphere for four days, before both halves were compared.

Loss of material from a fingerprint with age is known to progressively compromise the performance of most reagents. A trial was carried out on prints up to three days old in order to establish whether the age of the latent print influenced the final development obtainable with $Eu(fod)_3$ over this term. In this trial, prints were deposited on paper and then cut in two; one half of each print was left for 10 min before being treated with $Eu(fod)_3$ while the other half of each print was left over ranges of time from 1 min to 72 h before being treated. After each half print was treated, it was placed in a nitrogen atmosphere to prevent further deterioration that might occur due to exposure to moisture while it awaited comparison with its corresponding print half. This trial was carried out in duplicate.

Reagent stability is also an issue with a number of formulations. In theory, solutions of $Eu(fod)_3$ in petroleum spirits should be stable for long periods of time. Short-term reagent stability was tested experimentally by subjecting halves of the same print to treatment with a one week old $Eu(fod)_3$ solution and a fresh solution at the same time.

Most chemical reactions occur more readily as the temperature is raised. In order to test the effect of heat treatment on $Eu(fod)_3$ development, one print was treated for 20 s and then cut in two, with one half being left to dry in air, and the other half left in an oven at 100°C for 2 min (this was repeated in triplicate). A second print was then cut in two, with one half being left in an oven at 100°C for 2 min before both halves were treated with $Eu(fod)_3$ (this trial was also repeated in triplicate).

In some cases, steps can be taken post-treatment to enhance luminescence. Two different methods for possible enhancement of the luminescence after $Eu(fod)_3$ treatment were investigated. First, liquid nitrogen was used to cool a $Eu(fod)_3$-treated latent fingerprint on paper that was being subjected to UV excitation. This method is often used for the enhancement of ninhydrin/$ZnCl_2$-treated fingerprints and is based on the idea that (in many systems) fluorescence becomes more likely as vibrational modes are frozen out (21). Second, a $Eu(fod)_3$-treated fingerprint deposited on paper was also treated in a second step, by soaking it in a solution of 75 mg 1,10-phenanthroline in 40 mL methanol and 10 mL acetone. This method has been used in the enhancement of lanthanide fluorescence (5) and is based on the known ability of a coordinated bidentate ligand to cause enhanced europium luminescence, when compared with that obtained when two monodentate ligands occupy the same space (22).

Various solvents were compared for use with $Eu(fod)_3$ treatment in order to establish whether there is a best one to use. Also, different solvents were tested on different surfaces in order to establish which solvent works best for which surface. Up to this point, petroleum spirits had been used as the solvent in all trials involving use of $Eu(fod)_3$. The selection of this was based mainly on the nonpolar nature of $Eu(fod)_3$ and the desirability of excluding water. The possibility existed that other solvents might result in better development of prints, and for this reason, a range of formulations were tested on a selection of surfaces. All solutions were prepared using a $Eu(fod)_3$ concentration of 6.67 g/L.

The compatibility of $Eu(fod)_3$ treatment with two commonly-used reagents for the visualization of latent fingerprints on porous surfaces was also examined. The two reagents were ninhydrin and DFO (1,8-diazafluoren-9-one), both of which react with the amino acid component of the print. Ninhydrin reacts to yield the colored compound Ruhemann's Purple, whereas DFO forms a compound that emits in the yellow (550 nm) region when excited at 514.5 nm. An argon laser (1 W) was used to produce the excitation of DFO-treated prints. Ninhydrin and DFO were both prepared in freon/acetic acid/ethanol solutions (20,23).

The efficiency of $Eu(fod)_3$ on nonporous surfaces was gaged by comparison with the Superglue fuming/dye-staining method. Ten prints were deposited equally over ten pairs of galvanized iron strips and three prints were deposited equally over three pairs of aluminum Coke® can strips. One set of half prints were treated with $Eu(fod)_3$/ethyl acetate while the other corresponding set of half prints were treated with Superglue, allowed to harden, then stained with Panacryl (23).

Simple tests were also performed to ascertain whether the $Eu(fod)_3$ was reacting primarily with the water-soluble component of the latent prints, or the lipid component. Twenty prints were deposited on strips of paper and then cut down the center. One set of halves were immersed for 1 min in distilled water, to selectively remove the water-soluble components, and then left to air-dry, leaving lipid-only prints. Both sets of halves were then treated with $Eu(fod)_3$ in petroleum spirits. In addition, four unconventional prints were deposited on paper using Fernleaf semisoft butter as a "lipid mimic." The prints were then treated with $Eu(fod)_3$.

Chemistry of the $Eu(fod)_3$ Reaction with Components of Latent Fingerprints

The following work was carried out in order to determine what types of fingerprint components $Eu(fod)_3$ is likely to be reacting with.

Water-Soluble Fingerprint Components—Of the water-soluble components of latent fingerprints, it is possible that $Eu(fod)_3$ could react with amino acids, amines, monosaccharides, urea, and lactic acid, all of which are nonlipids and are found in latent fingerprints.

Preliminary evidence for the reactivity of $Eu(fod)_3$ with glycine (an amino acid), triethylamine (an amine), glucose (a monosaccharide), and urea was obtained by using a pasteur pipette to place a small spot of an aqueous solution of the substance under investigation on white paper. The paper was dried at 100°C for 2 min in an oven and then treated with $Eu(fod)_3$ solution (6.67 g/L, petroleum spirits) and examined under the hand-held UV lamp.

More definitive evidence for the reactivity of $Eu(fod)_3$ with glycine, triethylamine, urea, and acetic acid and propionic acid (both of which contain the carboxylic acid group of amino acids), was obtained by adding each potential ligand into a solution containing the lanthanide chelate and analyzing ions formed using Electrospray Mass Spectrometry (ES-MS). ES-MS spectra were recorded on a Fisons VG Platform II instrument. The sample was injected into the spectrometer via a Rheodyne injector fitted with a 10 μL sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source at a flow rate of 0.01 mL min^{-1} and nitrogen was employed both as a drying and nebulizing gas. The cone voltage was set at 20 V.

ES-MS has previously been used to monitor ligand exchange processes involving acetate ions and the coordinatively-unsaturated lanthanide 2,2,6,6-tetramethyl-3,5-heptanedione (dpm) complexes $Eu(dpm)_3$, $Gd(dpm)_3$, and $Yb(dpm)_3$ (24,25). The following experimental methods are based on this work.

Acetic acid is the simplest of the water-soluble carboxylic acids likely to be found in the latent fingerprint. To test the reactivity of acetic acid with $Eu(fod)_3$, a 10 mg amount of $Eu(fod)_3$ was added to 20 mL of carrier solution. The carrier solution was prepared from 95 mL methanol, 95 mL water (1:1 ratio), and 10 mL acetic acid.

Propionic acid is the next simplest water-soluble carboxylic acid after acetic acid. In this case, a 10 mg amount of $Eu(fod)_3$ was added to 20 mL of carrier solution. The carrier solution was prepared from a 1:1 methanol/water solution plus 13 mL propionic acid (200 mL total).

Glycine (NH_2CH_2COOH) is the simplest of the water-soluble amino acids likely to be found in latent fingerprints. Here a 10 mg amount of $Eu(fod)_3$ and 2.17 mg (3 mole excess) of glycine was added to 20 mL of carrier solution. The carrier solution (200 mL total) was prepared from a 1:1 methanol/water solution plus 10 mL acetic acid (acetic acid was required in this instance to help dissolve the $Eu(fod)_3$).

Urea is also likely to be available in a latent fingerprint for reaction with $Eu(fod)_3$. Its reactivity was tested by adding a 10 mg amount of $Eu(fod)_3$ and 4.7 mg (large excess) of urea to 20 mL of carrier solution. The carrier solution (200 mL total) was prepared from a 1:1 methanol/water solution plus 1% propionic acid (propionic acid was required to dissolve $Eu(fod)_3$).

Triethylamine ($(CH_3CH_2)_3N$) is an example of a water-soluble amine. A 10 mg amount of $Eu(fod)_3$ and 50 μL (large excess) of triethylamine was added to 20 mL of carrier solution. The carrier solution (200 mL total) was prepared from a 1:1 methanol/water solution plus 10 mL acetic acid (required to help dissolve the $Eu(fod)_3$).

Lipid Fingerprint Components—The lipid component of latent fingerprints mainly comprises triglycerides (triacylglycerols) and free fatty acids (26). Evidence of hexanoic acid binding to $Eu(fod)_3$ has been published by Shoffner (15). Hexanoic acid seems to be on the boundary between what is considered a fatty acid and what is considered to be a water-soluble carboxylic acid. In this work, it was decided that octanoic acid should be used as a representative free fatty acid. Unfortunately, aspiration of $Eu(fod)_3$ dissolved in petroleum spirits, along with some octanoic acid, would have induced terminal complications throughout the length of the Electrospray Mass Spectrometer (usual solvents are water and acetonitrile), so this method was not available for direct observation of octanoic acid binding.

Indirect evidence of octanoic acid binding to (or closely associating with) $Eu(fod)_3$ was obtained by monitoring its effect on the emission spectrum of a 0.5 g/L $Eu(fod)_3$ solution in petroleum spirits (b.p. 40 to 60°C). The spectrum was recorded before and after addition of a large molar excess (10 μL) of octanoic acid to 2 mL of the solution. Slit widths for both excitation and emission were set at 15 nm, with solutions being held in a 10 mm quartz cuvette. An analogous experiment was carried out where the UV-visible absorbance was measured instead of emission. In this case, the absorbance spectrum was recorded before and after addition of 10 μL of octanoic acid to 0.02 g/L solution of $Eu(fod)_3$ in petroleum spirits.

Results and Discussion

Excitation-Emission Spectra of $Eu(fod)_3$

The complete three-dimensional excitation-emission spectrum of $Eu(fod)_3$ dissolved in petroleum spirits (b.p. 40 to 60°C) is presented in Fig. 2, and essential features of this are summarized in Tables 1 and 2. A number of illumination sources in use (UV lamps, most lasers) only operate at fixed wavelengths, and it was felt that the three-dimensional spectrum would be useful for checking the emission bands expected when exciting at a given wavelength.

The most prominent feature of this spectrum is the sharp europium emission line produced at 614 nm (visibly this is orange), which reaches a maximum intensity when excited at 340 nm (ultraviolet). This emission line is the one most likely to be of use in fin-

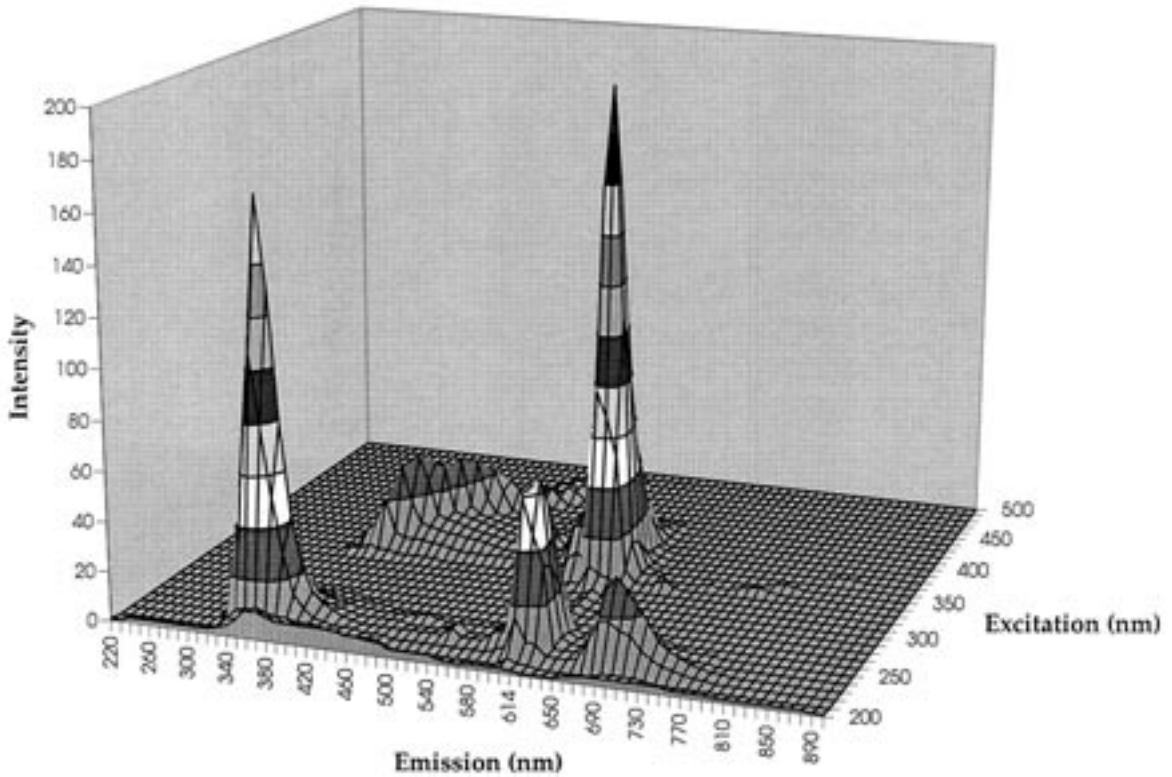

FIG. 2—*Three dimensional excitation-emission spectrum of Eu(fod)$_3$ in petroleum spirits (b.p. 40 to 60°C).*

TABLE 1—*Main emission wavelength maxima and intensities for Eu(fod)$_3$ dissolved in petroleum spirits.*

Excitation at 340 nm		Excitation at 225 nm	
Max Emission λ (nm)	Relative Intensity	Max Emission λ (nm)	Relative Intensity
614.0	198	613.5	54
592.0	25	592.5	7
537.5	14	537.0	5
379.5	20	350.5	212

TABLE 2—*Peak excitation wavelengths resulting in the 614 nm and 351 nm emission lines from Eu(fod)$_3$ dissolved in petroleum spirits.*

614 nm Emission		351 nm Emission	
Peak Excitation λ (nm)	Relative Intensity	Peak Excitation λ (nm)	Relative Intensity
340.0	199	225.5	227
238.0	68		
228.5	67		

gerprint visualization, and is further toward the red end of the spectrum than is the case for most fluorescent fingerprint reagents. The large Stoke's shift of 274 nm has the practical advantage that the main fingerprint emission will always be well removed from almost all background fluorescence expected for typical objects excited at 340 nm. Background emission can be removed by use of filters with a wavelength cutoff right up to about 600 nm. In this work, we found orange goggles (and camera filters) to be ideal. (Obviously, if the orange glass or plastic is too red, it may also start filtering out the 614 nm emission itself, so some experimentation may be necessary.) The optimum excitation wavelength of 340 nm is also within the range of standard tuneable print illumination sources, such as the xenon-lamp powered Polilight®.

Use of a higher-boiling fraction petroleum spirits (b.p. 80 to 100°C) produced poorly-defined luminescence spectra with very broad and overlapping peaks. This was probably due to fluorescent contributions from higher molecular weight aromatic hydrocarbons in the solvent. Experiments with this higher-boiling range solvent were discontinued.

In moving from solution studies to those of Eu(fod)$_3$-treated fingerprints on surfaces, a standard hand-held UV lamp was used. This has a mercury vapor source, with two wavelength settings, nominally of 254 nm and 365 nm. Here it was found that the 254 nm setting gave the best visualization. These results contrast with the emission/excitation results obtained for Eu(fod)$_3$ in solution (Fig. 2), where the 614 nm emission was found to be twice as intense when excited at 365 nm than when excited at 254 nm. The likely reason for the difference between solution and surface results is in the nature of the excitation source. In the case of the UV lamp, the 254 nm mercury line is simply more intense than the line at 365 nm. This is borne out by the fact that for mercury detection by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), the 253.652 nm line possesses a signal-to-background ratio which is 17 times higher than that of the 365.015 nm line.

Fingerprint Trials

Successful visualization of prints was obtained on white photocopy paper (though some background luminescence from the

reagent itself is also observed), aluminum drink cans, and galvanized iron. Examples of luminescent prints developed on paper and an aluminum Coke® can are presented in Fig. 3. It is assumed that on initial treatment, $Eu(fod)_3$ does react with up to two functional groups containing oxygen (e.g., carboxylate) in the lipid or nonlipid component of the prints, to form an 8-coordinate europium complex. Prints are not directly visible to the eye, but are easily seen by luminescence.

Optimization of Treatment Time and Reagent Concentration—The best dipping time at a solution concentration of 3.333 g $Eu(fod)_3$/L was found to be 20 s. Times tested ranged from 10 s to 5 min. Using this 20 s dipping time, print development was found to get steadily better as the $Eu(fod)_3$ concentration was raised from 0.133 g/L (no prints visible) to 6.653 g/L (very good prints). It was decided that a 20 s dipping time in a solution of 6.653 g/L $Eu(fod)_3$ would be used for further work.

It is important to note that when using this reagent, dipping times longer than 20 s result in poorer outcomes. This effect was examined using iodine fuming, and found to be related to dissolution of the lipid fraction of the fingerprints in the petroleum spirits. There may well be a better (possibly mixed) solvent system that would allow dissolution, infusion, and reaction of the europium complex with the latent fingerprint, without also causing the lipid fraction of the print to slowly dissolve, or introducing extra water. Further research in this area could be quite profitable, because longer soaking times than 20 s may lead to yet better results.

Comparison of $Eu(fod)_3$ Treatment with DFO Treatment on Porous Surfaces—In the comparison of $Eu(fod)_3$ with DFO on paper, all 50 prints were visible by both treatment methods. In all cases, the DFO-treated prints were significantly brighter than the $Eu(fod)_3$-treated prints, but in some cases the detail of the developed ridges was clearer and more continuous for $Eu(fod)_3$. DFO tended to produce more blotchy, noncontinuous ridge development than $Eu(fod)_3$.

It remains unclear from the results of this trial whether the DFO treated prints are intrinsically more luminescent than those treated with $Eu(fod)_3$, because the former were excited using an argon-ion laser and the latter using a UV-lamp. The laser was likely to have been a more intense excitation source than the lamp, and the two sources also operate at different preset wavelengths (514 nm for DFO and 254 nm for $Eu(fod)_3$). Such preset wavelengths themselves represent compromises relative to the best excitation wavelengths possible.

However, under standard conditions as they are currently employed for DFO, it would appear that DFO would still be the reagent of choice for obtaining strongly fluorescent prints on porous surfaces. Use of $Eu(fod)_3$ before DFO might also be of value, given that the former appears capable of resolving more detail in some cases, and doesn't inhibit use of the latter (see below).

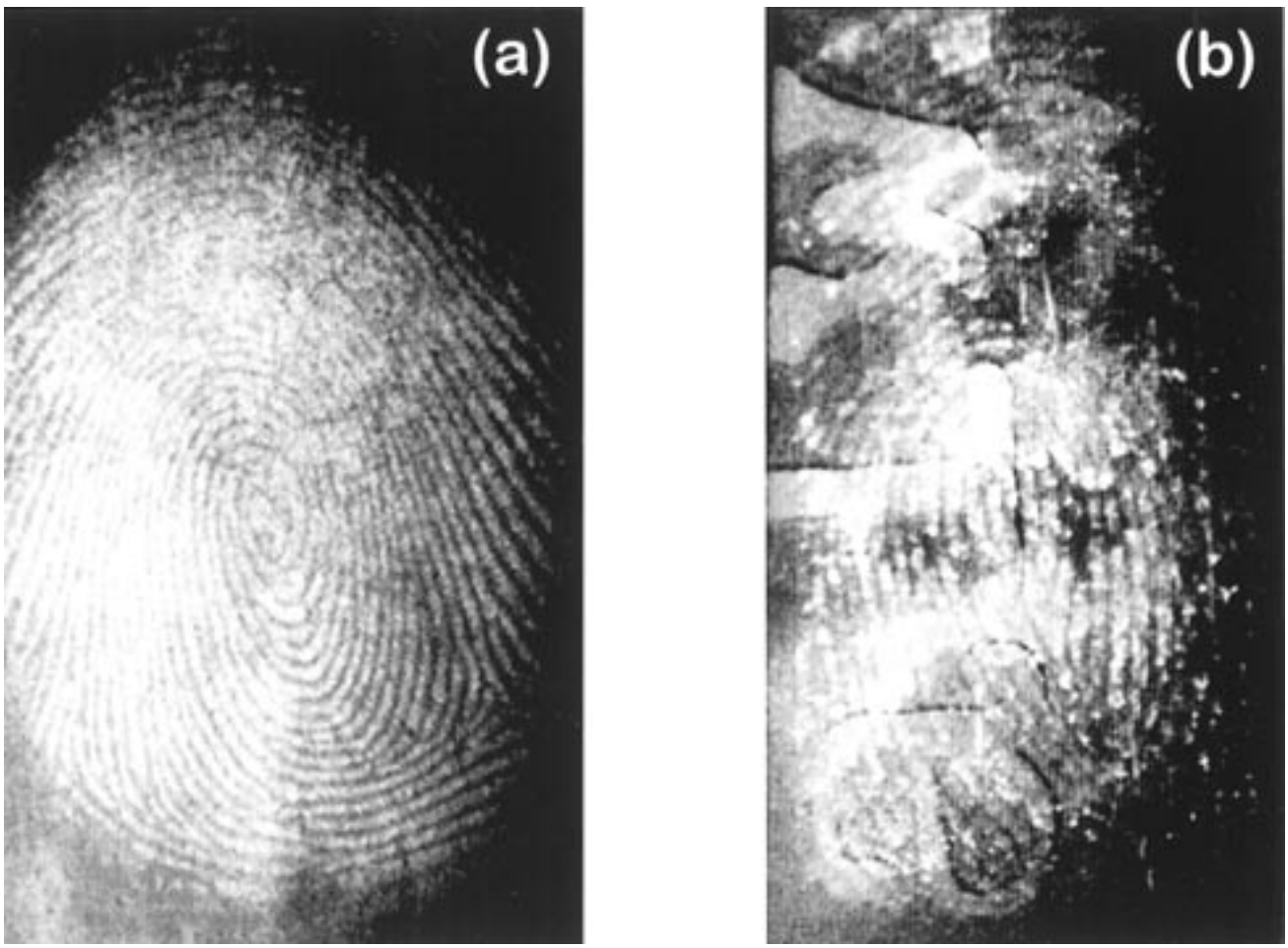

FIG. 3—*Visualization of a $Eu(fod)_3$ treated print on white paper and a Coke® can (excited at 340 nm, and viewed through an orange filter).*

Given the simplicity of the $Eu(fod)_3$ treatment used in this preliminary assessment (a 20 s dip), these early results are certainly encouraging. The DFO method is already optimized, but there should be scope for further improvement in the performance of coordinatively-unsaturated lanthanide reagents.

Stability of Prints in Air After Treatment—At times of up to 8 h after treatment, prints were still as luminescent as when they were freshly treated. However, after 24 h, some fading was evident, and after 72 h, only the outer parts of the print were visible.

The probable reason for this effect is that moisture in the air can further react with the europium complex once it is in the fingerprint. Support for this idea was provided by the results of the nitrogen atmosphere dry-box trial. After four days, the half-print left in a dry nitrogen atmosphere was still fully visible, while the other half left in the air (under the same lighting conditions) was only partially visible. Mechanistically, the gradual deterioration of the treated prints in air is likely to be caused by progressive entry of H_2O from the air into the inner coordination sphere around europium, and displacement of other ligands, a process that is known to quench lanthanide fluorescence (9).

Performance of $Eu(fod)_3$ on Older Prints—The trial was carried out in duplicate and the same results were obtained for both sets of prints. These are presented in Table 3. The effectiveness of $Eu(fod)_3$ was the same for day-old prints as it was for fresh prints. However, by the time the print had aged for two days, visualization obtained with $Eu(fod)_3$ was noticeably poorer (Table 3). Like many reagents, $Eu(fod)_3$ will work best on prints on paper that are somewhere less than 48 h old (relatively fresh).

TABLE 3—*Effect of print age on the subsequent ability of $Eu(fod)_3$ to visualize it.*

Print*	Age of Print Half in the Pair Being Compared	Visualization Achieved
1	10 min and	Good
	1 min	Good
2	10 min and	Good
	1 h	Good
3	10 min and	Good
	4 h	Good
4	10 min and	Good
	8 h	Good
5	10 min and	Good
	24 h	Good
6	10 min and	Good
	48 h	Poor
7	10 min and	Good
	4 days	Poor

* NOTE: trial was carried out in duplicate or each print, with identical results.

Effect of Solution Age Over the Short Term—The working solution of $Eu(fod)_3$ in petroleum spirits (b.p. 40 to 60°C) is easily prepared, and in this work use was made of reasonably fresh solutions, but it would be operationally convenient to be able to use working solutions stored in the laboratory refrigerator. Although we only tested for possible degradation of performance in the working solution for times of up to one week, it was found that none had occurred after this time. Prints treated with a one week old $Eu(fod)_3$ solution were found to be equally well developed as prints treated with a freshly prepared solution, indicating that the $Eu(fod)_3$ solution is at least stable for one week.

Effect of Heat Treatment—Some fingerprint reagents show accelerated and/or better development when heated, and some (such as DFO) require a heating step for development to even occur in the first place. In the case of $Eu(fod)_3$ treatment, no benefit was found in heating. Neither preheating the print before treatment, nor heating the treated print, produced any additional observed luminescence.

Enhancement of Luminescence Following $Eu(fod)_3$ Treatment—Two means by which luminescence from $Eu(fod)_3$-treated prints might potentially be enhanced were investigated; neither proved satisfactory. Both the addition of the bidentate ligand 1,10-phenanthroline, and the technique of cooling in liquid nitrogen, resulted in severe background luminescence with loss of print visibility altogether. After return of the liquid nitrogen treated print back to room temperature, only a faint luminescence was visible with no ridge detail (a possible reason was that the europium complex reacted with water present in the liquid nitrogen).

Selection of the Best Solvent for Each Surface—Visualization of latent prints on various surfaces was tested using $Eu(fod)_3$ dissolved in a number of pure solvents (no mixed solvent systems have been examined to date). Summary results are provided in Table 4. On paper, good prints were obtained using petroleum spirits (b.p. 40 to 60°C) as the solvent (Fig. 3). It was interesting to note that similar results were obtained for prints on paper with freon as the solvent; however, use of this solvent was not further investi-

TABLE 4—*Comparison of $Eu(fod)_3$ treatment using different solvents on different surfaces.*

	Surfaces							
Solvents	Paper	Vinyl Wallpaper	Banknote (NZ $5.00)	Coke® Can (inside and out)	Polyurethane-Coated Wood	Mylar Sheet	Aluminum Foil	Ceramic Tile (white)
Petroleum Spirits	***	×	×	×	×	×	×	×
Dichloromethane	*	×	×	×	×	×	…	…
Hexane	**	×	…	*	×	×	…	…
Ethyl Acetate	*	×	×	**	×	×	…	…
Dimethyl Formamide	×	×	…	×	×	×	…	…
Toluene	*	…	…	…	…	…	…	…
Chloroform	*	…	…	…	…	…	…	…
Freon	***	…	…	…	…	…	…	…

*** good print; ** reasonable print; * poor print; × no print visible; … not investigated.

gated, because its production has been discontinued as a result of environmental concerns (27).

Reasonable prints were visualized on both the outside (painted, Fig. 3) and inside surfaces of a Coke® can using ethyl acetate as the solvent. Luminescence from these prints was good, but not as good as that obtained from prints on paper using petroleum spirits as the solvent. Mekkaoui and Menzel (28) have previously reported visualization of a fingerprint on an aluminum soft drink can by treatment with europium nitrate-RP(5-methoxyninhydrin) and subsequent UV excitation. In that case, treatment required more than one step, and time-resolved imaging was employed to maximize the (print) signal-to-background ratio. In this case, treatment using $Eu(fod)_3$ dissolved in ethyl acetate consisted of a single 20 s dip, and visualization was achieved using standard illumination at 340 nm, with removal of the background by use of an orange filter.

On the basis of these results, latent prints on four other metal surfaces were also treated with $Eu(fod)_3$ dissolved in ethyl acetate, and visualized in the same way. On galvanized (zinc-coated) iron, results were as good as those achieved on the Coke® can ("reasonable"), resulting in a photographable print. On rusty iron, prints were still visible but less distinct ("fair"). On both stainless steel and brass, prints were barely visible by standard illumination techniques.

Comparison of $Eu(fod)_3$ Treatment with Superglue/Panacryl Treatment on Two Nonporous Surfaces—In the case of the nonporous metallic surfaces—the aluminum (Coke® can) and the galvanized iron—the $Eu(fod)_3$-treated prints were found to be consistently better than those treated with Superglue fuming followed by Panacryl staining. Treatment with the coordinatively-unsaturated europium complex appears to represent a significant improvement over the Superglue fuming and staining approach, because the latter requires a fuming cabinet and can take many hours, whereas $Eu(fod)_3$ treatment takes less than half a minute.

$Eu(fod)_3$ and related complexes may offer simple and inexpensive alternatives to the Superglue method on other nonporous surfaces as well. Further trials are recommended.

Compatibility with Ninhydrin and DFO on Paper—Results of these trials, summarized in Table 5, revealed that both ninhydrin and DFO can still be successfully used after treatment of latent prints on paper with $Eu(fod)_3$. Pretreatment with the europium complex does not compromise subsequent development by the amino acid-targeting reagents. On the other hand, use of $Eu(fod)_3$ after ninhydrin or DFO yielded no further improvement in print development, suggesting that ninhydrin and DFO (or presence of their solvent systems) somehow inhibit the subsequent activity of $Eu(fod)_3$.

TABLE 5—*Compatibility of $Eu(fod)_3$ with ninhydrin and DFO.*

Sequence	Development
Ninhydrin followed by $Eu(fod)_3$	No emission under UV light source but ninhydrin treatment still visible.
$Eu(fod)_3$ followed by ninhydrin	Ninhydrin treatment visible but no $Eu(fod)_3$ emission under UV light source.
DFO followed by $Eu(fod)_3$	DFO visible but $Eu(fod)_3$ not visible.
$Eu(fod)_3$ followed by DFO	DFO visible but $Eu(fod)_3$ not visible.

Targeted Components of the Latent Fingerprint—In terms of which components of the prints are being targeted, the behavior of $Eu(fod)_3$ is not straightforward. Evidence suggests that this reagent is capable of reacting with components in both the water-soluble and lipid fraction of the prints.

When prints were pretreated by soaking in water and then air-drying, luminescence after treatment dropped sharply. All twenty water-soaked (and air-dried) print halves resulted in only background fluorescence with no fingerprint visible. (Confirmation that the lipid fraction still existed in these prints was obtained by iodine fuming of a few test samples.) The other 20 halves that were treated in the normal way resulted in good development. This result implies that the luminescence visible after treatment is largely a result of $Eu(fod)_3$ reacting with water-soluble components of the print. Possible reactive functional groups in this fraction would be the carboxylic acid end of the water-soluble amino acids.

However, $Eu(fod)_3$ is also capable of reacting with lipids. All four butter prints resulted in good development. Luminescence was also obtained by treatment of butter spots placed on paper without the use of a finger (so as to eliminate the possibility of contribution from the latent print). These results suggest that $Eu(fod)_3$ is reacting with lipids in the butter, and therefore should also react with lipid components of fingerprints. Luminescence from the lipid fraction of real fingerprints (i.e., from prints that had been soaked in water and then dried) was not observed after $Eu(fod)_3$ treatment using standard illumination techniques. However, the quantity of lipid material present in a latent print would clearly be much less than that contained in a smear of butter, so the amount of reaction that occurs in this fraction of a print may be insufficient for any luminescence to be obvious.

Examination of the reactivity of $Eu(fod)_3$ with specific compounds known to occur in latent prints is the focus of the next section.

Chemistry of the $Eu(fod)_3$ Reaction with Latent Fingerprints

Nonlipid Fingerprint Components—Preliminary spot tests, where dried drops of glycine, triethylamine, and urea solutions on paper were treated with $Eu(fod)_3$, resulted in development of luminescence in the area of the spots in all cases. $Eu(fod)_3$ treatment of a glucose spot also resulted in luminescence. In the case of glucose, the luminescence formed a ring around the circumference of the spot, probably as a result of paper chromatography occurring by capillary action before treatment (causing outward migration of the glucose from the center of the spot).

Electrospray Mass Spectrometry (ES-MS) results showing the species formed by reaction of $Eu(fod)_3$ with acetic acid, propionic acid, glycine, triethylamine, and urea are presented in Table 6. It should be noted that the two main peaks found for each ion (twin peaks) reflect the natural abundance of the two major europium isotopes. Species listed in Table 6 were assigned on the basis of correspondence of theoretical and observed isotope patterns; an example of the theoretically calculated isotope pattern for the ion $Eu(fod)(MeO)_2 + H^+$ is given in Table 7.

Electrospray ionization is capable of transforming ions in solution directly to gas phase ions, and thus often provides a means of probing of the solution chemistry almost directly. The ES-MS spectra observed in this work (Table 6) suggest that there are ligand exchange processes occurring in solutions that involve reactions of $Eu(fod)_3$ and acetic acid, propionic acid, and urea, as all of these adducts were observed. However, these results are regarded as strongly suggestive rather than absolutely definitive, because

TABLE 6—*Europium species detected by Electrospray Mass Spectrometry on addition of various ligands to Eu(fod)$_3$ in methanol.*

Complexing Ligand	Assigned Formula of Europium Species	Mass-to-Charge Ratio (*m/z*)	Relative Intensity (%)
Acetic Acid (AcOH)	$Eu(fod)(MeO)_2+H^+$	509.2, 511.1	90, 100
	$Eu(fod)(AcO)(MeO)_2+2H^+$ or $Eu(fod)(AcO)(MeOH)_2^+$	569.0, 571.0	8, 9
	$Eu(fod)(AcO)_3+2H^+$	625.0, 627.0	2, 2
	$Eu(fod)_2(AcO)_2+2H^+$	861.4, 863.2	3, 3
Propionic Acid (PrOH)	$Eu(fod)(PrO)^+$	519.1, 521.1	25, 28
	$Eu(fod)(MeO)_3+2H^+$	541.0, 543.1	1.1, 1.3
	$Eu(fod)(PrO)(MeO)+H^+$	550.9, 553.0	3.1, 3.5
	$Eu(fod)(PrO)_2+H^+$	593.1, 595.1	90, 100
	$Eu(fod)(PrO)_3+2H^+$	667.2, 669.4	3, 3
	$Eu(fod)_2^+$	740.6, 742.7	3, 3
	$Eu(fod)_3+H^+$	…, 1039.6	…, 0.3
Glycine	$Eu^{II}(fod)(H_2O)^+$	464.0, 466.2	15, 19
	$Eu(fod)(MeO)_2+H^+$	509.0, 511.0	89, 100
	$Eu(fod)(AcO)(MeOH)_2^+$	568.8, 570.9	13, 14
Urea	$Eu(fod)(PrO)^+$	519.1, 521.2	15, 16
	$Eu(fod)(PrO)(MeO)+H^+$	551.2, 553.3	8, 8
	$Eu(fod)(PrO)(Urea)^+$	579.1, 581.1	9, 11
	$Eu(fod)(PrO)_2+H^+$	593.2, 595.1	12, 14
	$Eu(fod)(PrO)(Urea)_2^+$	639.2, 641.0	11, 12
	$Eu(fod)(PrO)(Urea)_3^+$	699.1, 701.2	5, 5
Triethylamine	$Eu(fod)(MeO)_2+H^+$	508.9, 510.9	85, 100
	$Eu(fod)_2(H_2O)_3(MeO)+H^+$	826.8, 829.4	12, 14

TABLE 7—*Theoretically calculated isotope pattern of Eu(fod)(MeO)$_2$+H$^+$.*

Mass to Charge Ratio (*m/z*)	Intensity
509	90.18
510	12.52
511	100
512	13.8
513	1.67
514	0.14
515	0.01

when using ES-MS, a residual possibility remains that some adducts observed at the detector were formed by recombination of ions in the gas phase.

No ions resulting from the ligand exchange of glycine or triethylamine with Eu(fod)$_3$ were directly observed, but this may have been because of the presence of the moderately high concentration of acetic acid in the carrier solution (required for the dissolution of Eu(fod)$_3$). Acetic acid may well have dominated the metal-ligand exchange chemistry, both by providing a competing ligand (acetate), and by causing significant protonation of triethylamine, thus reducing its ability to bind to europium. Acetic acid adducts were expected from these solutions, but it was hoped that glycine or triethylamine adducts might also make minor appearances in the same spectra. In this case, their absence in the spectra cannot be taken to imply that such complexes will not form; the fact that complexes are observed with acetic acid suggest that Eu(fod)$_3$ should also spontaneously accept the carboxylic acid end of amino acids such as glycine.

Lipid Fingerprint Components—Significant changes in Eu(fod)$_3$ emission intensities were observed after the addition of a small amount of octanoic acid (10 μL octanoic acid in 2 mL). For excitation at 340 nm, the intensity of Eu(fod)$_3$ luminescence at the 614 nm line decreased by 40%. For excitation at 225 nm, Eu(fod)$_3$ luminescence at the 614 nm line decreased by 63%, whereas the intensity at the 350 nm emission line increased by 17%. Results obtained after octanoic acid addition were monitored over a period from 1 min to 1 h after addition and were found to be stable.

Changes also occurred in the UV-visible absorption spectrum of a Eu(fod)$_3$ solution on addition of a small amount of octanoic acid. Before addition, the absorbance of the solution was 0.604 at 294 nm; after addition this decreased to 0.558 at a slightly shifted peak position of 288 nm.

Though not definitive, these results are suggestive of octanoic acid binding to the europium complex in some way. Reaction might involve either direct coordination of the carboxylate group of the octanoic acid with intact Eu(fod)$_3$, or coordination accompanied by displacement of a fod ligand.

The ability of Eu(fod)$_3$ to react with compounds containing carboxylic acid functional groups, and also urea, correlates with the earlier observations that this reagent is likely to be capable of interacting with both the water-soluble material of latent prints, and the lipids (many of which will terminate in hydroxyl or carboxyl groups).

Summary

Coordinatively-unsaturated europium complexes represent a straightforward means of visualizing latent prints by luminescence, because they are capable of direct reaction with the print components. In this work, luminescent prints were obtained by use of the lanthanide shift reagent Eu(fod)$_3$ on white photocopy paper, aluminum drink cans and galvanized iron.

Optimum treatment conditions for prints on paper, with petroleum spirits (b.p. 40 to 60°C) as the solvent, were a 20 s dipping time in a solution of 6.67 g/L Eu(fod)$_3$. Under these conditions, Eu(fod)$_3$ treatment consistently resulted in good print visualization; however, in terms of a comparative benchmark, prints formed on DFO treatment were always brighter. On the other hand, Eu(fod)$_3$ treatment took less than 30 s, and did not compromise subsequent treatment with either ninhydrin or DFO.

Although petroleum spirits was the best solvent (of those tested) for detecting prints on paper, ethyl acetate proved better for visualizing prints on aluminum and galvanized iron. On these surfaces, Eu(fod)$_3$ treatment was found to yield brighter prints than those obtained by Superglue fuming followed by Panacryl staining.

This early success of Eu(fod)$_3$ on both porous and nonporous surfaces is encouraging, given that it is so easy to use, and that mixed solvent systems (or alternative means of delivery) have not yet been explored or optimized.

There is good evidence that Eu(fod)$_3$ can react readily with both lipid and nonlipid components of latent fingerprints. However, most of the luminescence observed using standard illumination techniques probably represented reaction of Eu(fod)$_3$ with compounds in the water-soluble fraction, because luminescence drops sharply if this fraction is removed before treatment. Such compounds might include urea and the most abundant amino acids. Partial dissolution of lipids in the solvent (usually petroleum spirits in this study) might be part of the reason that luminescence was not observed from the lipid fraction of real prints. It is suspected that increased emission from the lipid material in latent prints (and

stronger emission overall) might be achievable through selection of the right solvent (or mixed-solvent) system.

In addition to investigation of alternative reagent delivery options, further work that may yield useful results could be an examination of other coordinatively-unsaturated complexes of europium ($Eu(fod)_3$ is only one of many such possible complexes) and investigation of analogous complexes of the other significantly luminescent lanthanide metal, which is terbium. Jenkins and Murray (6) provide an excellent introductory discussion of strategies for enhancing lanthanide luminescence.

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