



Improvement in fingerprint detection using Tb(III)-dipicolinic acid complex doped nanobeads and time resolved imaging



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ABSTRACT

This paper deals with the synthesis and application of lanthanide complex doped nanobeads used as a luminescent fingerprint powder. Due to their special optical properties, namely a long emission lifetime, sharp emission profiles and large Stokes shifts, luminescent lanthanide complexes are useful for discriminating against signals from background emissions. This is a big advantage because latent fingerprints placed on multicoloured fluorescent surfaces are difficult to develop with conventional powders. The complex of 2,6-dipicolinic acid (DPA) and terbium ($[\text{Tb}(\text{DPA})_3]^{3-}$) is used for this purpose. Using the Stöber process, this complex is incorporated into a silica matrix forming nanosized beads (230–630 nm). It is shown that the $[\text{Tb}(\text{DPA})_3]^{3-}$ is successfully incorporated into the beads and that these beads exhibit the wanted optical properties of the complex. A phenyl functionalisation is applied to increase the lipophilicity of the beads and finally the beads are used to develop latent fingerprints. A device for time resolved imaging was built to improve the contrast between developed fingerprint and different background signals, whilst still detecting the long lasting luminescence of the complex. The developed fingerprint powder is therefore promising to develop fingerprints on multicoloured fluorescent surfaces.

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1. Introduction

The identification of individuals based on their fingerprints is very common worldwide [1]. Fingerprint powders are widely used to develop latent fingerprints encountered during an investigation on different surfaces. The purpose of fingerprint powders is to increase the contrast between fingerprint and background, however conventional powders do not show high contrast on multicoloured surfaces [2]. To develop fingerprints on such surfaces, fluorescent powders are used which utilise the visible emission of fluorescent dyes after excitation to increase the contrast between fingerprint and background [3]. If the background is also fluorescent then these powders have a limited usability and therefore luminescent fingerprint powders which are able to develop fingerprints on fluorescent surfaces are needed [4].

Lanthanides are metals which show special optical properties including sharp emission profiles, a large Stokes shift [5] and long luminescence lifetime in solution [4]. These properties are based on the principle of their luminescence. Lanthanides absorb light

with a low efficiency on their own; therefore, they have to be sensitised using an antenna (generally an organic chromophore as a ligand [6]) which is illustrated in Fig. 1 [7]. The energy difference between the ligand and lanthanide is one reason for the large difference between excitation and emission wavelengths and therefore the Stokes shift.

The mentioned properties make lanthanide complexes suitable for use in fingerprint powders to develop latent fingerprints on fluorescent surfaces. The sharp emission profile allows the filtering of interfering wavelengths leaving only the lanthanide emission, the large Stokes shift allows for separation of excitation and emission wavelengths and the long lifetime can be used to separate the lanthanide emission from any background fluorescence [4]. The process of discriminating signals by their emission lifetime is called time resolved imaging and describes the detection of the lanthanide luminescence after the background fluorescence is extinct [8]. E.R. Menzel was the first to introduce this concept of fingerprint detection [9] and since then several publications used this approach [10–13]. Quantum yield and lifetime depend on the combination of lanthanide and ligand and their particular energy levels. Research on this field has been performed by Latva et al. [14] and others [15,16] who showed that the complex of terbium and 2,6-dipicolinic acid (DPA) has a long lifetime (around 2.2 ms) and

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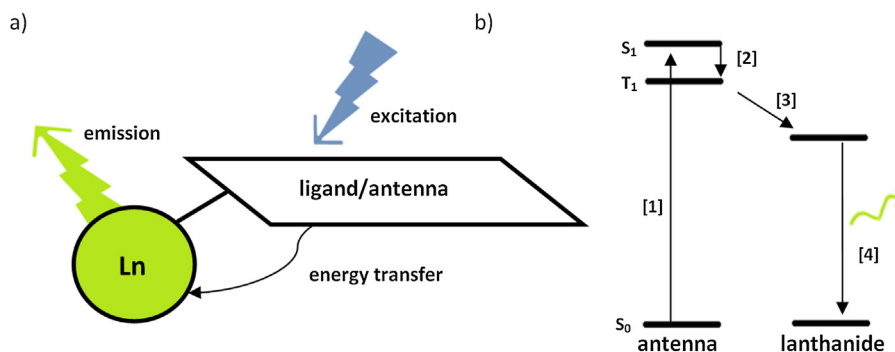


Fig. 1. (a) The ligand acts as an antenna and is excited by UV light. The absorbed energy is transferred to the lanthanide (Ln) which then emits light. (b) An energy diagram showing the luminescence of lanthanide complexes [1]. The antenna is excited by UV-light from the S_0 to the S_1 level [2]. Via intersystem crossing the S_1 level changes to the T_1 level [3]. The T_1 level of the ligand transfers energy to the emitting state of the lanthanide [4]. The lanthanide emits light.

high quantum yield (21%) [8]. The chemical structure of this complex is shown in Fig. 2. Using time resolved imaging, the complex luminescence can be separated from the background fluorescence and thereby produce a clear fingerprint image [4].

The dry complex, which forms a salt with the sum formula $\text{Na}_3[\text{Tb}(\text{DPA})_3] \cdot 9\text{H}_2\text{O}$ [15], on its own could be used as fingerprint powder but it lacks the possibility for further optimisation. By incorporating the complex into a silica matrix, homogeneous beads with different sizes can be synthesised which also can be functionalised on the surface [6]. A simple and effective route to synthesise nanobeads (bead size up to 1000 nm [3]) is by the Stöber process [17]. This method uses the hydrolysis and condensation of a silica precursor in an alkaline alcohol solution to produce silica beads. By varying the initial parameters the particle size of the produced beads can be adjusted [18]. A small particle size is preferable for a fingerprint powder because size and also shape have an influence on the effectiveness of the powder [19] but there are also health concerns about too small beads. Due to the small size nanobeads can penetrate skin or cell membranes and cause cell death. A study by Li et al. [20] compared silica beads with different sizes from 19 to 498 nm for their effect on tumor cells. It was shown that the 498 nm beads were least toxic and that the results were comparable to the control sample. A bead size of approximately 500 nm would therefore appear to be safe and suitable for fingerprint powders since smaller particles could cause health issues and larger particles would reduce the adhesion of the powder to the fingerprint residues.

By introducing the complex $[\text{Tb}(\text{DPA})_3]^{3-}$ into the precursor solution of the Stöber process, it is incorporated into the silica matrix [15,21]. The surface of silica beads is hydrophilic due to SiOH groups, but the residues of fingerprints are mainly lipophilic [4]. Therefore a functionalisation of the surface can be used to increase the lipophilicity of the powder [22], which would then increase the affinity of the silica beads to the lipophilic residue of fingerprints. One method to do this has been reported by Chen et al.

[23] by using phenyltriethoxysilane to introduce phenyl groups onto the surface of bentonite.

This paper reports on the synthesis of a luminescent fingerprint powder by the synthesis and subsequent incorporation of $[\text{Tb}(\text{DPA})_3]^{3-}$ into spherical silica nanobeads by the Stöber process and investigates the effect of a lipophilic functionalisation on the properties of the beads. The use of time resolved imaging and filters is also investigated to image the developed fingerprints, remove unwanted fluorescent background emission and determine if this kind of powder should be further researched and thus improve the detection and evaluation of fingerprints in forensic practice.

2. Materials and methods

2.1. Chemicals

All chemicals were of reagent grade and used as supplied. Ammonium hydroxide (28%) and tetraethoxy-orthosilicate (TEOS), were purchased from Sigma Aldrich. 2,6-Dipicolinic acid (DPA) was purchased from Acros Organics. Phenyltriethoxysilane (PTEOS) and terbium(III) nitrate hydrate (99.9%) were purchased from Alfa Aesar. Nitric acid (70%) of trace analysis grade, terbium mono-element standard for ICP (1000 mg/L) and ethanol (100%) were purchased from Fisher. Hydranal® Composite 5 and Hydranal® methanol dry were purchased from Fluka Analytical. Granulac® 230 lactose monohydrate was purchased from Meggle. Only ultrapure water with a resistivity above 18.2 MΩ cm was used.

2.2. Preparation of the terbium complex and the silica-based nanobeads

$\text{Na}_3[\text{Tb}(\text{DPA})_3] \cdot 9\text{H}_2\text{O}$ complex was prepared by dissolving DPA (0.02 mol, 3.342 g) in deionised water (90 mL) containing NaOH (0.0425 mol, 1.7 g). This solution was stirred until all DPA was dissolved. Then $\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (1.815 g) was first dissolved in approximately 5 mL deionised water then added to the DPA solution and a white precipitate formed immediately. Using HCl (1 M) the pH of the solution was set to 6 and the precipitate dissolved. This solution was refluxed for two hours and the solution was evaporated until crystals began to precipitate. It was cooled down, filtered and washed with small amounts of ice cold water. The precipitate was air-dried and the yield was 4.225 g of white crystals. Purification was performed by dissolving a fraction of the white crystals (2.279 g) in a mixture of water (300 mL) and ethanol (113 mL) which was then heated to the boiling point. The solution was evaporated to a final volume of 30 mL and then ethanol was added to precipitate the complex. The precipitate was filtered and dried overnight in a desiccator. The yield of this

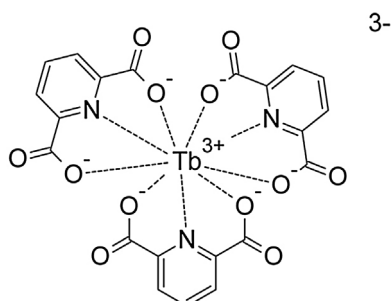


Fig. 2. Chemical structure of the complex $[\text{Tb}(\text{DPA})_3]^{3-}$.

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