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ORIGINAL ARTICLE

Coloration Technology

Investigation into the development of novel lanthanide-based luminescent colorants for application to textiles and paper materials

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Abstract

This article describes the synthesis and application of lanthanide-based luminophores for visualisation under short wavelength ultraviolet (UV) activation (typically 254 nm). Luminophores are chemical compounds which re-emit light of longer wavelength than typical fluorescence and phosphorescence, following photoexcitation, because of efficient energy transfer from the ligands to the lanthanide ion emission levels. The luminophores described in this article are all derived from europium and terbium metal complexes and cover the complete colour gamut. Selection of appropriate ligands allows for water solubility or water insolubility (if required pigment or disperse "dye" applications). Similar to dyeing or printing processes, the anionic complexes can be applied to polyamide fibres or to cellulosic fibres, whereas dispersions of the non-ionic complexes are suitable for polyester or cellulose acetate fibre application. The water-soluble derivatives are also suitable for ink-jet printing and the water-insoluble derivatives are suitable for lithographic or intaglio paper printing. The novel complexes are excited by radiation below 300 nm and thus cannot be activated by sunlight (the earth's atmosphere prevents light below about 300 nm reaching the surface). Accordingly, the photo-stability of the dyed materials and prints obtained is excellent. These materials could be used in security marking applications, for example bank-notes and passports, where they could replace the current fluorophores that are rendered visible under near UV light (typically 365 nm) illumination but exhibit relatively poor photo-stability. The development of an RGB (red, green and blue) colour palette for inkjet printing based on these innovative luminophores will significantly support the design of digitally printed security features.

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1 | INTRODUCTION

It is well known that many trivalent lanthanides are luminescent when excited under ultraviolet (UV) light conditions and when the lanthanides are complexed with certain ligands their luminescence is enhanced.[1–5] It is thought that the extent to which the luminescence is enhanced is dependent on the efficiency of the energy transfer between energy levels in the complexing ligand. For the energy transfer to be efficient, the energy of the lowest triplet state of the ligand should be nearly equal to or lie just above the resonant energy level of the rare earth ion.[6,7] Many ligands, such as sodium benzoate,[8] benzene-1,3,5-tricarboxylic acid[9] and 2,2-bipyridine derivatives,[10] have been studied in order to improve the efficiency of the energy flow and therefore to increase the luminescence of the lanthanides.

An initial screening study of rare earth metal complexes derived from cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb) revealed that the most useful lanthanide complexes could be derived from europium(III) chloride and terbium(III) chloride. Typically, europium complexes exhibit red fluorescence and terbium complexes exhibit green fluorescence following UV excitation.

The aim of this study was the development of red, green and blue (RGB) luminophores as primary colours for security printing and dyeing textile and paper substrates, where the primary colours can be suitably mixed to provide the specific colour. Europium compounds exhibit red fluorescence and terbium compounds exhibit green fluorescence, but a bright blue complex was needed to complete the primary colour mixing palette. Salicylate europium complexes were found to fulfil this requirement and the blue fluorescence of the salicylic acid complex and its derivatives have been detailed in numerous publications.[11,12] *In situ* formation of luminescent colourants has also been reported by Xiao et al who covalently bonded butane tetracarboxylic acid to silk by a pad-thermosol process and subsequently complexed the europium and terbium ions to the fibre carboxylate residues, resulting in an intense visible red and green luminescence on illuminating the treated fabrics with 365 nm radiation.[13]

In this study initial experiments indicated that simple aliphatic ligands, such as ethylenediaminetetraacetic acid (EDTA) or lactic acid, did not give the desired luminescence response on being excited at 365 nm, whereas the aromatic carboxylate complexes offered strong visible emission with 254 nm excitation. Therefore, the focus was on preparing insoluble luminophores derived from aromatic ligands such as benzoates, phthalates and salicylates and water-soluble complexes derived from 4-sulfophthalate and 5-sulfo-salicylate.

2 | EXPERIMENTAL

2.1 | Materials

All chemicals were purchased from Aldrich (Gillingham, Dorset, UK). Fabrics used for dyeing and printing were purchased from Whaleys (Bradford, UK). A woven wool botany serge fabric (200 g/m^2), a bleached Calico plain weave cotton fabric (148 g/m^2), a scoured knitted nylon 6,6 fabric (159 g/m^2), and a white plain weave polyester fabric (145 g/m^2) were used throughout this study. Whatman No.1 filter papers were used as non-fluorescently brightened paper substrates along with non-fluorescently brightened Velin paper.

The polyamide-epichlorohydrin cationic polymer (Kymene 557) used to pre-modify cotton fabric was obtained from Solenis Wilmington, USA.

2.2 | Long-Liquor application methods

Long-liquor applications of the various luminophores (“dyeings”) were performed using a Mathis Rotadyer.

Cotton fabrics were cationised by pre-treating with a polyamide-epichlorohydrin resin prior to “dyeing” with anionic fluorophore as previously reported[14,15] in order to increase electrostatic attraction and facilitate easier exhaustion of the anionic fluorophore onto the fabric. The cotton fabric was padded to 100% wet pick-up with an aqueous solution containing 200 g/dm^3 Kymene 557 (12.5% w/w aqueous polyamide epichlorohydrin polymer) plus ethylene diamine (20 g/dm^3), dried at 100°C for 5 min and then washed thoroughly with cold water.

Scoured wool, nylon 6,6 and cationised cotton fabrics (5 g) were separately “dyed” with 2% owf (on weight of fabric). of the sulfonated luminophores at pH 3, using a liquor/fabric ratio of 10:1. The dye liquor temperature was raised to 100°C from room temperature at 2°C/min and the bath held at 100°C for 1 h, followed by thorough rinsing in running cold water and air drying.

Scoured polyester fabrics were “dyed” with the water-insoluble luminophore complexes (pre-dispersed by incorporating the dispersing agent Matexil DA-AC (5 g/dm^3) into the europium or terbium metal chloride solutions prior to addition of the salicylic acid or benzoic acid ligand solutions) using either of two processing conditions: high-temperature system or carrier system.

2.2.1 | High-temperature system

The polyester fabric was dyed at elevated temperature using 2% owf disperse luminophore at pH 4, using a liquor ratio of 10:1, with the water bath temperature raised from 20 to 135°C at 2°C/min. The bath was held at 135°C for 45 min, cooled and the fabric thoroughly rinsed in running cold water followed by air drying;

2.2.2 | Carrier system

The polyester fabric was dyed using 2% owf disperse luminophore plus 5 g/dm^3 orthophenyl-phenol (carrier incorporated for dyeing under atmospheric conditions) at pH 4, using a liquor ratio of 10:1, with the water bath temperature raised from 20 to 100°C at 2°C/min. The bath was held at 100°C for 1 h, cooled and the fabric thoroughly rinsed in running cold water followed by air drying.

2.3 | Ink-jet printing with water-soluble luminophores

A Lexmark Z738 ink-jet printer containing a Lexmark No.2 tri-colour ink-jet cartridge was used throughout the study except where secondary packaging printing of outer box/cartons was performed using a commercial Wolke m600 basic ink-jet print system (Wolke Inks & Printers GmbH, Altdorf, Germany) containing an HP45 ink-jet cartridge.

The water-soluble luminophores (2% w/v green, red and blue luminophore inks) were assessed as ink-jet ink formulations by dilution to 9 ml with deionised water, followed by the addition of 1 ml of methanol to improve the stability of the ink. (In the absence of methanol, it was observed that the stability of the ink formulation was dependent on its pH.) Inks that were set at pH values of 4 or lower exhibited good storage stability and no precipitation was observed after 3 weeks. Whilst ink formulations that were set at pH values of 5 or greater exhibited poor storage stability and precipitation was observed in less than 1 week. The addition of 10–20% w/v 4-methylmorpholine *N*-oxide to the fluorescent ink formulations also resulted in an improvement in the storage stability of the ink and no precipitation was observed even after 3 weeks, even when the ink was adjusted to the higher pH values.

Non-fluorescently brightened paper (Whatman No.1 filter paper) was ink-jet printed with the red, green and blue luminophore inks where the red luminophore ink was added to the cyan chamber of the tri-colour cartridge, the blue luminophore ink to the yellow chamber and the green luminophore ink to the magenta chamber. To achieve a positive image on the printed paper substrate, the desired picture was converted to a negative image on the personal computer (PC) screen and then printed.

2.4 | K-Bar imaging and offset printing

Non-fluorescently brightened Velin paper (Aldrich, Gillingham, Dorset, UK) was printed with offset inks containing the water-insoluble luminophores using a K Control Coater (RK Instruments, Royston, UK). A Number 0 K-bar was used to deliver a wet film thickness of 4 μm. The luminophores (5% w/w) were added to a white offset base ink (Gleitsmann Security Inks) and the ink thoroughly dispersed in the ink base using an Ault & Wiborg automatic milling machine for 2 min to yield a uniform dispersion of the luminophore pigment.

2.5 | Luminescence viewing

The luminescence of the samples was viewed in darkness under the illumination of a standard UV excitation lamp commonly used in thin-layer chromatography (TLC) analysis with an excitation of 254 nm. Photographs of the various luminescent effects obtained in darkness were obtained using the Apple I-phone 6S.

Absorbance/emission spectra were obtained measuring the dye solutions (3 ml) within quartz cuvettes (1 cm path length) in a Perkin Elmer Lambda 35 UV-visible (Beaconsfield, UK) and a Horiba Fluoromax-4 spectrophotometer (Northampton, UK), respectively. Absorbance spectra were recorded by scanning from 200 to 700 nm compared to an aqueous blank (slit width 5 nm). Emission spectra were recorded following a 290 nm excitation pulse (slit width 1 nm) and scanning emission from 295 to 800 nm (slit width 1 nm). Data was collected and processed using Graphpad Prism version 9.01.

2.6 | Light-fastness assessment

Non-fluorescently brightened paper (Aldrich, Gillingham, Dorset, UK) ink-jet printed with the red luminophore ink was evaluated for light stability when subjected to light-fastness tests performed in accordance with ISO 105-B02:1999. Half of each sample was covered with card and the sample then exposed to light for increasing increments of time equivalent to the fading of each Blue Wool Standard (Society of Dyers and Colourists, Bradford, UK). The test was performed on a Q-SUN/1000 Xenon Test Chamber (Q-Panel Lab Products), using an irradiance of 0.65 W/m^2 at 420 nm and a temperature of 50°C, with exposed samples adjacent to

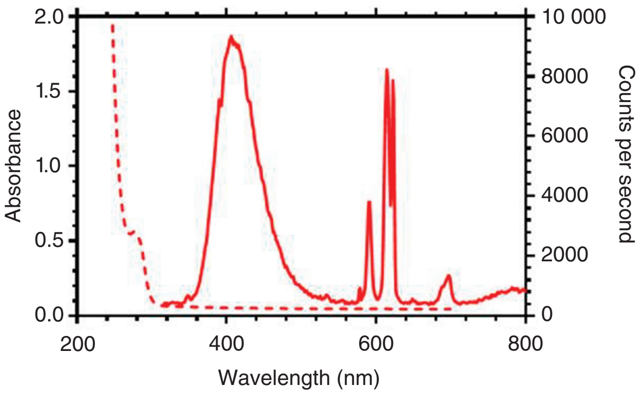

FIGURE 1 UV-visible absorbance (dashed line) and photoluminescence emission (solid line) spectra of the red, water-soluble 2:1 europium(III)/4-sulfophthalic acid complex luminophore.

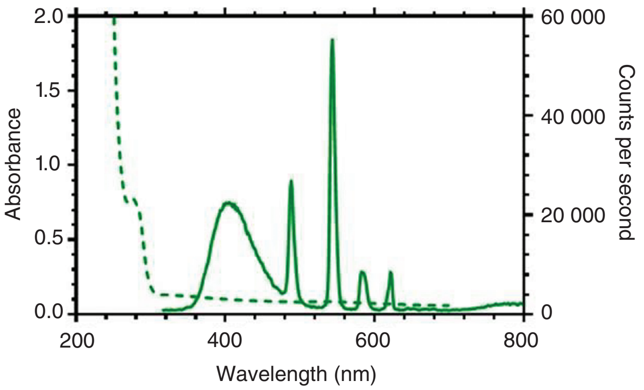

FIGURE 2 UV-visible absorbance (dashed line) and photoluminescence emission (solid line) spectra of the green water-soluble 2:1 terbium(III)/4-sulfophthalic acid complex luminophore.

Blue Wool Standard fabrics. Samples were viewed in the dark and photographed under 254 nm UV illumination in order to determine the extent of photo-fading.

2.7 | Chemical structure analysis

Fourier-transform infrared (FTIR) spectra of solid dye samples were collected using a Perkin Elmer FTIR Spectrum 100 spectrometer in the 4000–500 cm^{-1} range. X-ray diffraction data on solid crystals was collected using a Bruker D8 diffractometer (Karlsruhe, Germany) in Bragg–Brentano reflection geometry using a Cu Kα source ($\lambda = 1.5418$ Å) and a Lynxeye detector. Data was collected over the 2θ range 5°–30° with a step size of 0.02 and cost time of 0.25°/min. Reference patterns were generated in mercury using the structure obtained from the Cambridge Structural Database (Cambridge, UK). Positive ion electrospray ionisation (ESI) mass spectra of dimethyl sulfoxide (DMSO) soluble compounds were collected using a Thermo Accela ultra-performance liquid chromatography (UPLC) with Orbitrap LTQ ion trap MS^n and high-resolution mass spectrometry (HRMS) for accurate mass determination.

3 | RESULTS AND DISCUSSION

3.1 | Preparation of red water-soluble europium complex luminophores

The red water-soluble europium complex luminophores were prepared with a 2:1 reaction feed of the metal and various substituted aromatic carboxylic acids. A 50% (w/v) aqueous solution of 4-sulfophthalic acid (0.2757 g, 5.6×10^{-4} M) was mixed with deionised water (5 ml) and the solution adjusted to pH 6 by the addition of 1 M lithium hydroxide. The solution was then added dropwise into a stirred solution of europium chloride hexahydrate (0.1033 g, 2.8×10^{-4} M) in deionised water (5 ml). The pH of the mixed solution was then adjusted to 4.5 by the addition of 1 M lithium hydroxide, the mixture heated to 100°C and the temperature maintained for 5 min to produce a colourless solution of the required luminophore. This solution was diluted with deionised water to a final volume of 10 ml, which represents a 2% w/w luminophore solution. The absorbance/emission spectrum of this water-soluble red luminophore is shown in Figure 1.

3.2 | Preparation of water-soluble green terbium(III) complex luminophores

Green water-soluble terbium(III) complex luminophores were prepared with the 2:1 ratio of terbium(III) and substituted aromatic carboxylic acids. A 50% w/w aqueous solution of 4-sulfophthalic acid (0.2757 g, 5.6×10^{-4} M) was mixed with deionised water (5 ml) and the solution adjusted to pH 6 by the addition of 1 M lithium hydroxide. This solution was then slowly added to a stirred solution of terbium(III) chloride hexahydrate (0.1045 g, 2.8×10^{-4} M) in deionised water (5 ml). The pH of the solution was raised to 4.5 by the addition of 1 M lithium hydroxide and the solution then heated to 100°C for 5 min to yield a colourless solution of the required luminophore. Deionised water was finally added to the solution to give a final volume of 10 ml to produce a 2% w/v solution of the green luminophore. The absorbance/emission spectrum of this water-soluble green luminophore is shown in Figure 2.

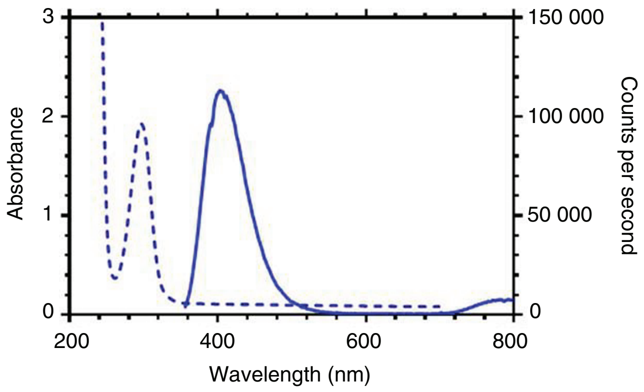

FIGURE 3 UV-visible absorbance (dashed line) and photoluminescence emission (solid line) spectra of the blue water-soluble 2:1 europium(III)/5-sulfosalicylic acid complex luminophore.

3.3 | Preparation of blue water-soluble europium(III) complex luminophores

Blue luminophores were prepared with both 2:1 and 3:1 ratios to produce europium(III) complexes of various aromatic phenols. The 5-sulfosalicylic acid dihydrate ligand proved successful at yielding stable europium(III) complexes when added to aqueous solutions of europium(III) chloride hexahydrate. The 2:1 europium(III) complex of 5-sulfosalicylic acid was prepared by dissolving 5-sulfosalicylic acid dihydrate (0.1424 g, 5.6×10^{-4} M) in deionised water (5 ml) and the solution adjusted to pH 6 by the addition of 1 M lithium hydroxide. The solution of lithium 5-sulfosalicylate was then slowly added to a stirred solution of europium(III) chloride hexahydrate (0.1033 g, 2.8×10^{-4} M) in deionised water (5 ml). The pH of the solution was raised to 4.5 by the addition of 1 M lithium hydroxide and the solution heated at 100°C for 5 min to yield a colourless solution of the luminophore. Deionised water was finally added to the luminophore solution to give a final volume of 10 ml and thus produce a 2% w/v solution of the blue fluorophore. The absorbance/emission spectrum of this water-soluble blue luminophore is shown in Figure 3.

3.4 | Synthesis of water insoluble red luminophore pigment

The europium(III) complex of benzoic acid was prepared by adding benzoic acid (0.0684 g, 5.6×10^{-4} M) to deionised water (5 ml) and the mix adjusted to pH 6 by the addition of 1 M lithium hydroxide. The solution of lithium benzoate was then slowly added to a stirred solution of europium(III) chloride hexahydrate (0.1033 g, 2.8×10^{-4} M) in deionised water (5 ml). The pH of the solution was raised to 4.5 by the addition of 1 M lithium hydroxide and the solution heated at 100°C for 5 min to yield a white precipitate of the luminophore. The precipitate was filtered, washed thoroughly with water and finally dried at 60°C.

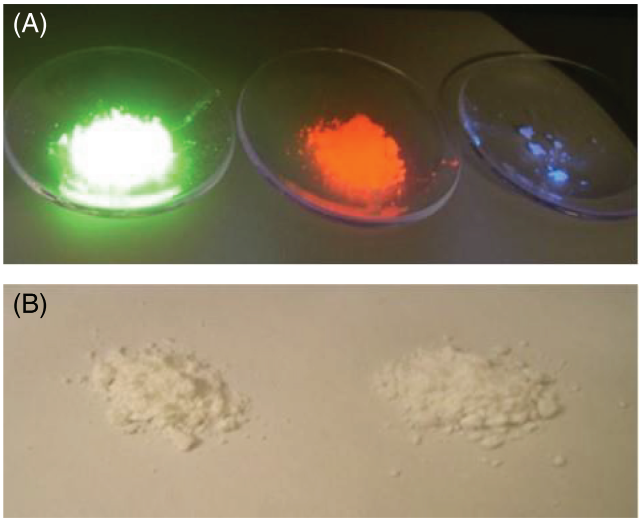

FIGURE 4 (A) Luminophore pigments illuminated with 254 nm radiation. (B) Green and red luminophore pigments viewed in daylight.

3.5 | Synthesis of water insoluble green luminophore pigment

The terbium(III) complex of benzoic acid was prepared by adding benzoic acid (0.0684 g, 5.6×10^{-4} M) to deionised water (5 ml) and the mix adjusted to pH 6 by the addition of 1 M lithium hydroxide. The solution of lithium benzoate was then slowly added to a stirred solution of terbium(III) chloride hexahydrate (0.1045 g, 2.8×10^{-4} M) in deionised water (5 ml). The pH of the solution was raised to 4.5 by the addition of 1 M lithium hydroxide and the solution heated at 100°C for 5 min to yield a white precipitate of the luminophore. The precipitate was filtered, washed thoroughly with water and finally dried at 60°C.

3.6 | Synthesis of water insoluble blue luminophore pigment

Preliminary studies indicated that only the europium salicylate complexes were capable of giving strong blue luminescence, while the terbium-salicylates were green. The europium(III) complex of salicylic acid was prepared by dissolving salicylic acid (0.0773 g, 5.6×10^{-4} M) in deionised water (5 ml) and the solution adjusted to pH 6

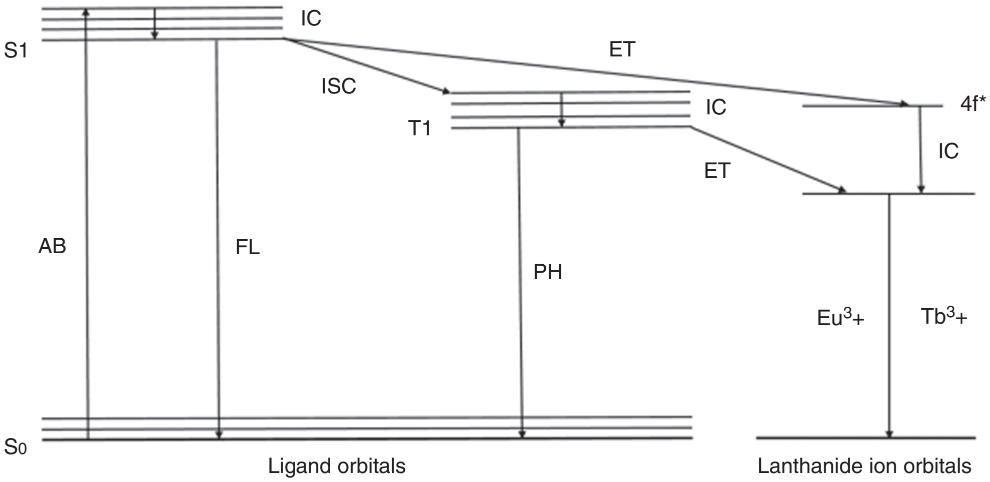

FIGURE 5 Simplified diagram showing the main energy flow paths during sensitization of lanthanide luminescence via its complexed ligands.[13,14] AB, absorption; ET, energy transfer; FL, fluorescence; IC, internal conversion; ISC, intersystem crossing; PH, phosphorescence; S, singlet state; T, triplet state.

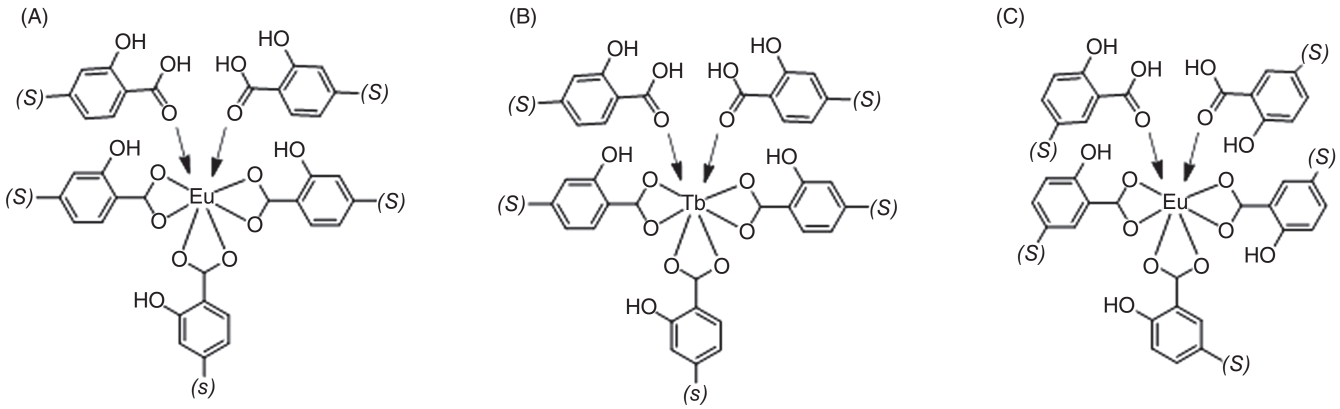

FIGURE 6 Indicated average structures of luminophore complexes. (A) Proposed structure of red phthalate/europium luminophore complex. (B) Proposed structure of green phthalate/terbium luminophore complex. (C) Proposed structure of blue salicylate/europium luminophore complex. In the structures (S) represents the optional attachment of a sulfonate residue when required for water solubility.

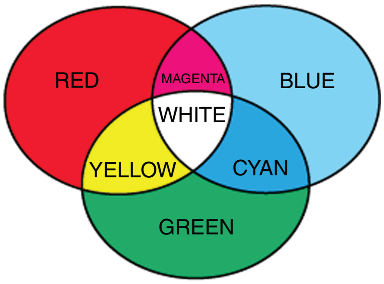

FIGURE 7 Typical colours produced by additive mixing of red, blue and green colours.

by the addition of 1 M lithium hydroxide. The lithium salicylate solution was then slowly added to a stirred solution of europium(III) chloride hexahydrate (0.1033 g, 2.8×10^{-4} M) in deionised water (5 ml). The pH of the solution was raised to 4.5 by the addition of 1 M lithium hydroxide and the solution heated at 100°C for 5 min to yield a white precipitate. The luminophore precipitate was filtered, washed thoroughly with water and finally dried at 60°C.

Figure 4A,B show the green, red and blue luminescent pigments viewed under 254 nm UV illumination and normal daylight.

3.7 | Structures of luminophores

The lanthanides selected for this study were europium and terbium chloride salts that following chelation with selected aromatic ligands produced a range of red, green and blue intensely coloured luminophores visible under far UV (254 nm) illumination. It is well known that the pure lanthanides are poor luminophores due to the low efficiency of direct absorption of the 4f-4f states.[16]

The efficiency of light absorption can be greatly improved by the use of ligands that provide an “antennae effect” via an absorption-energy transfer-emission sequence, where the ligand functions as a light collector and the metal ion emits energy.[17–19] The subsequent light emission is at much longer wavelength than the ligand fluorescence or phosphorescence and can be described as lanthanide photoluminescence (Figure 5).

In this article we assess the use of aromatic carboxylates as the reinforcing organic ligands. Such complexes based on benzoic acid have been recently reported[20] and demonstrate that europium(III) complexes can be formed from the water-based reaction of europium(III) chloride with sodium benzoate even at room temperature.

Chemical characterisation of the complexes reported in this article was performed using FTIR, MS and X-ray diffraction, indicating that a high number of ligands were coordinated to the europium and terbium metal centres, as illustrated in Figure 6. It is clear that the ligands used in our study will coordinate in a similar manner as to that reported by the aforementioned paper with the selected lanthanides, europium(III) and terbium(III) yielding similar structures but exact clarification has proven difficult and is more thoroughly detailed in the Supporting Information. Certainly when dissolved in DMSO the ligands appeared to be readily substituted by the solvent and there is a mixture of coordination numbers apparent in several samples.

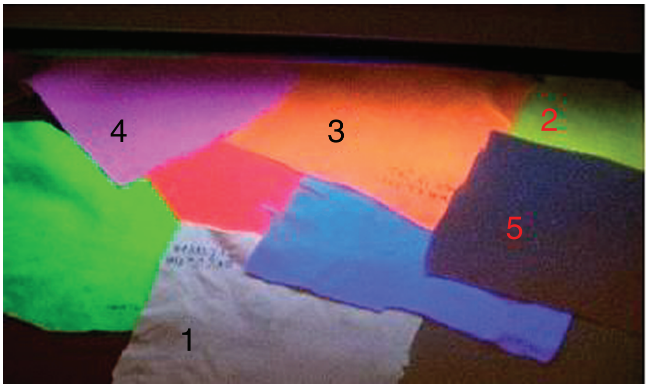

FIGURE 8 Nylon fabrics "dyed" with anionic, water soluble red, blue and green luminophore combinations (all samples viewed under 254 nm UV illumination). The fabric colours were obtained according to the co-application of two or three luminophores: 1, white is a mix of 33% of red, blue and green luminophores, respectively; 2, yellow is a mix of 25% red and 75% green luminophores; 3, orange is a mix of 75% red and 25% green luminophores; 4, violet is a mix of 25% red and 75% blue luminophores; 5, black is untreated fabric with no luminophores (viewed in darkness, hence black); green and red coloured fabrics are single luminophore applications.

3.8 | Application of luminophores to textile substrates

3.8.1 | Application to wool and nylon fabric

An important feature of the dyeing of textiles is that individual colourants can be used to obtain a desired colour and similarly in mixing colourants it is possible to broaden the individual colour gamut and deliver another specific colour. In this study, it was observed that the co-

FIGURE 9 Wool fabrics "dyed" with water soluble red, blue and green luminophores, respectively, (2% owf), illuminated under 254 nm UV radiation.

FIGURE 10 Wool fabrics "dyed" with various anionic, water soluble luminophore combinations (all samples viewed under 254 nm UV illumination). The fabric colours were obtained according to the co-application of two luminophores: 1, orange is a mix of 75% red and 25% green luminophores; 2, pinkish/white is a mix of 75% blue and 25% green luminophores; 3, pale yellow is a mix of 25% blue and 75% green luminophores; 4, bluish-red is a mix of 50% blue and 50% red luminophores; 5, yellow is a mix of 25% red and 75% green luminophores; 6, golden-yellow is a mix of 50% red and 50% green luminophores; 7, red is a is a mix of 25% blue and 75% red luminophores; 8, violet is a mix of 75% blue and 25% red luminophores; 9, creamish-white is a mix of 33% blue, 33% green and 33% red luminophores; 10, white is a mix of 50% blue and 50% green luminophores; 11, black untreated wool has no luminophores (viewed in darkness, hence black).

FIGURE 11 Pre-cationised cotton fabrics “dyed” with the water soluble red, green and blue anionic luminophores and viewed in the dark under 254 nm UV radiation.

FIGURE 12 Polyester fabrics “dyed” with the red and green disperse luminophores, using a high-temperature “dyeing” process, viewed under 254 nm UV radiation.

FIGURE 13 Polyester fabrics “dyed” with the red disperse luminophore, using a “carrier” dyeing process, viewed under 254 nm UV illumination.

application of the luminophores produced an additive colour effect analogous to mixing coloured red/green/blue lights (Figures 7, 8), which is counter-intuitive to the dyer as the normal coloration principle is based on subtractive colour mixing. Figure 8 illustrates both single luminophore applications to nylon fabric and the actual colours achieved when two luminophores were additively mixed, and viewed under the 254 nm illumination. It is apparent that the luminophores can be successfully co-applied to the nylon fabric to produce specific additive colours. In this preliminary study, the mixing of the individual luminophores was qualitative and more focused on visualising the potential effect of additive colour mixing rather than colour specification.

Similarly, the individual red, blue and green luminophores can be also applied to wool (Figure 9), and additive colouration can also be achieved by co-application of binary mixtures to the wool substrate (Figure 10). The photographic image of the additive colours in Figure 10 unfortunately does not accurately portray the “true” colour seen in the dark using 254 nm activation due to the quality of the mobile phone camera and the shadowing effect at the edge of the illumination box.

3.8.2 | Application to cationised cotton fibres

To improve the substantivity of the cotton for the acid dye type luminophores the cotton was pre-cationised and exhaust “dyed” with the red, green and blue anionic luminophores (2% owf) to again yield colourless fabrics that become intensely coloured when illuminated with 254 nm UV illumination (Figure 11).

3.8.3 | Application to polyester fabric

Polyester fabric was exhaust “dyed” with the water-insoluble luminophore dispersions using both high-temperature and “carrier” dyeing processes, respectively,

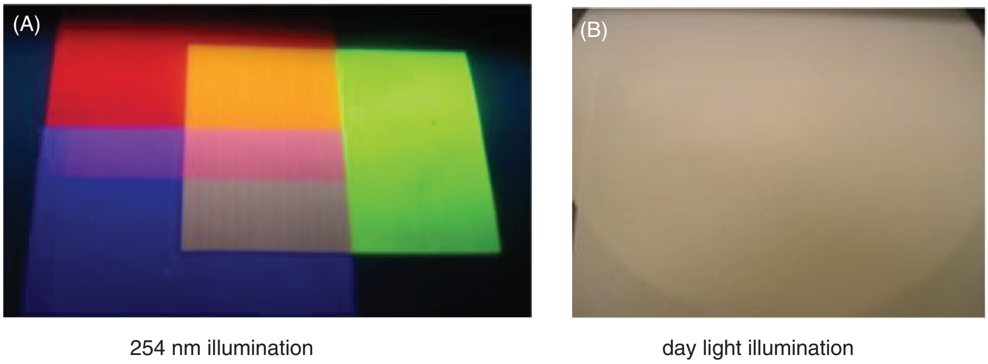

FIGURE 14 Red, green and blue luminophores ink-jet printed onto non-fluorescently brightened paper with the water-soluble fluorescent inks, viewed under (A) 254 nm UV illumination and (B) daylight illumination.

to yield colourless fabrics under daylight illumination, that similarly become intensely coloured when viewed under UV light at 254 nm (Figures 12, 13). It is noteworthy that the complexes are stable when dyeing at the boil as well as under high-temperature conditions (135°C) and hence provide processing flexibility depending on the textile substrate. For example, if the polyester is present as a component in a polyester/wool blend fabric, having the ability to exhaust at lower temperature and not damage the wool component is beneficial.

3.9 | Paper printing

The water-soluble and water-insoluble luminophores synthesised in this study were also assessed for their potential application to security printing paper. Ink-jet printing was used for the water-soluble compounds whereas the water-insoluble compounds were offset lithographic or intaglio printed.

FIGURE 15 Colour image ink-jet printed on non-fluorescently brightened paper using luminophores inks, viewed under 254 nm UV illumination.

3.9.1 | Ink-jet printing

Water-soluble luminophores were used in ink-jet ink formulations (2% w/v green, red and blue luminophore inks) and successfully produced standard blocks of colours on the printed paper (Figure 14). This application was further demonstrated by ink-jet printing a more complex image on paper, however in order to achieve a positive image on the printed paper substrate, the desired picture was converted to a negative image on the PC screen and then printed. A colourless print was obtained under daylight illumination that became intensely coloured when viewed under UV illumination at 254 nm (Figure 15).

3.9.2 | Offset printing for security marking

Green and red luminophore "pigment" inks were offset printed on the Velin paper substrates and yielded colourless prints under daylight illumination, that became intensely coloured when viewed under 254 nm UV light (Figure 16). Therefore, it appears that the inks have broad applicability, versatility and significant commercial potential.

3.9.3 | Light-fastness assessment

Non-fluorescently brightened paper ink-jet printed with the red luminophore ink was evaluated for light stability when subjected to light-fastness tests performed in accordance with ISO 105-B02:1999. Assessment after 4 h exposure and after 128 h exposure, indicated a light fastness rating of 5–6 was achieved.

The high light-fastness results achieved for these organo-metallic luminescent "dyes" and "pigments" are of particular interest since most commercially available inorganic luminophores exhibit poor light-fastness properties, generally attain a Blue Wool Standard rating of 1–2. The high light-fastness properties of these luminophores arise

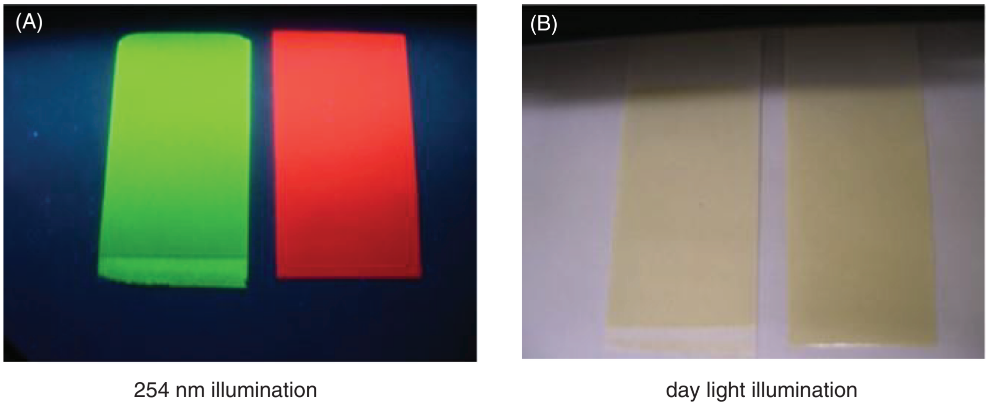

FIGURE 16 K-Bar drawdowns of luminophores "pigments" on non-fluorescently brightened paper, viewed under (A) 254 nm illumination and (B) daylight.

from their UV light absorption characteristics where the luminophores strongly absorb short wavelength UV light and very little, if any, long wavelength UV light. Due to atmospheric cut-off, natural daylight comprises wavelengths greater than 300 nm and the luminophores produced in this study absorb little UV light present in natural daylight. Therefore, they do not become decomposed or destroyed through excessive activation on prolonged daylight exposure.

4 | CONCLUSIONS

Both water-soluble luminescent dyes and water-insoluble luminescent pigments can be readily synthesised by the addition of aromatic carboxylic acids and their phenolic derivatives to aqueous solutions of europium(III) or terbium(III) salts. The materials formed are colourless under ambient lighting conditions but become intensely coloured when illuminated under UV 254 nm radiation. Red, green and blue luminophores can be mixed in binary or tertiary combinations and these primary colours used to generate a wide gamut of colours through additive colour mixing.

The sulfonated derivatives are water soluble and substantive to polyamide fibres and pre-cationised cellulosic fibres and can be applied through conventional dyeing processes. The non-sulfonated derivatives can be dispersed and applied to polyester fibres similar to that of conventional disperse dyes.

Ink formulations containing the red, green and blue water-soluble luminophores were prepared and ink-jet printed on non-fluorescently brightened paper substrates to yield colourless prints that become deeply coloured when viewed in the dark under 254 nm radiation. This concept can be expanded further and used to ink-jet print security features, such as variable data, on the packaging of high value goods and pharmaceuticals. The water-insoluble luminophores can be added as a white pigment to conventional security ink formulations and printed by offset lithographic or intaglio printing processes to yield colourless prints that become strongly coloured when viewed in the dark illuminated by 254 nm UV radiation.

These 254 nm illuminated organic luminophore "dyes" and "pigments" have been shown to exhibit excellent light-fastness characteristics, in many cases achieving Blue Wool Standard 5–6 in comparison to commercially available luminescent pigments with Blue Wool Standard 1–2 performance.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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