

Article

Lanthanide-Based Langmuir–Blodgett Multilayers: Multi-Emissive, Temperature-Dependent Thin Films

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Abstract: Multi-emissive compounds have attracted significant attention from the research community owing to the wide array of potential application areas. However, to move towards application, such systems should be readily immobilized by solution-based methods to form soft materials such as gels and films. Herein we report the use of Langmuir–Blodgett (LB) deposition to easily immobilize luminescent lanthanide-based amphiphilic solids into multi-emissive ultrathin LB films, by multilayering different luminescent amphiphiles. Utilizing this technique, we have reliably fabricated dual- and triple-emissive films where the overall emission from the film is tuned. Furthermore, we have demonstrated that these multi-emissive films are temperature-dependent, with emission profiles significantly altering from 294 to 340 K, resulting in colour changes and potential application as ultrathin, contactless ratiometric thermometer coatings.

Keywords: lanthanides; supramolecular materials; Langmuir–Blodgett films; multi-emissive materials; colour-tunable materials; temperature sensors; ratiometric thermometer



Citation: O’Neil, A.T.; Kitchen, J.A.

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Langmuir–Blodgett Multilayers:

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Chemistry **2022**, *4*, 1457–1465.

[https://doi.org/10.3390/](https://doi.org/10.3390/chemistry4040096)

[chemistry4040096](https://doi.org/10.3390/chemistry4040096)

Academic Editor: Craig Rice

Received: 15 September 2022

Accepted: 3 November 2022

Published: 7 November 2022

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1. Introduction

Multi-emissive supramolecular materials are highly sought after systems within modern chemistry and materials research sectors [1–3]. Whilst many luminophores exist for inclusion into multi-emissive materials [2,4], luminescent lanthanide-based materials are particularly attractive owing to their unique optical properties, including long-lived excited states, line-like emission bands, easily tuned quantum yields, and solid-state emission [1,5–9]. Whilst single emissive lanthanide compounds have found use as molecular sensors [10], imaging agents [10], and optical displays [6,11], their use as multi-emissive materials lends them to more advanced and complex applications including, but not limited to, ratiometric sensors [12–14], molecular barcodes [15], logic gates [16], multicolour emissive materials [17], and white light generation [1]. In order to move from bulk solids/solution towards applications, the ability to immobilise multiple-emissive lanthanides onto surfaces is required. However, to the best of our knowledge, only a few examples of surface immobilised Ln^{3+} -based multi-emissive systems exist in the literature [9,14,16,18–21].

The Langmuir–Blodgett technique is an ideal method for the fabrication of ultra-thin emissive films [22]. It allows for direct monitoring of film formation and can readily form layered materials from amphiphilic molecules, allowing for the rapid development of functional coatings [22–24]. Furthermore, this technique can be utilised to effortlessly form multi-emissive materials by layering different amphiphilic luminophores [25–27]. Recently, we reported an amphiphilic ligand **1** (Figure 1) and four visibly emissive lanthanide complexes $\text{Ln}(\textbf{1})_3$ (where Ln^{3+} = red emissive Eu^{3+} , green emissive Tb^{3+} , yellow and blue emissive Dy^{3+} , and orange emissive Sm^{3+}) and we demonstrated the ability to form multi-emissive monolayer LB films by mixing the lanthanides in solution [9]. Herein, we demonstrate this can also be easily accomplished by multilayering the different complexes, effectively forming dual and triple emissive films, without impacting the emission intensity of different lanthanide complexes (Figure 1).

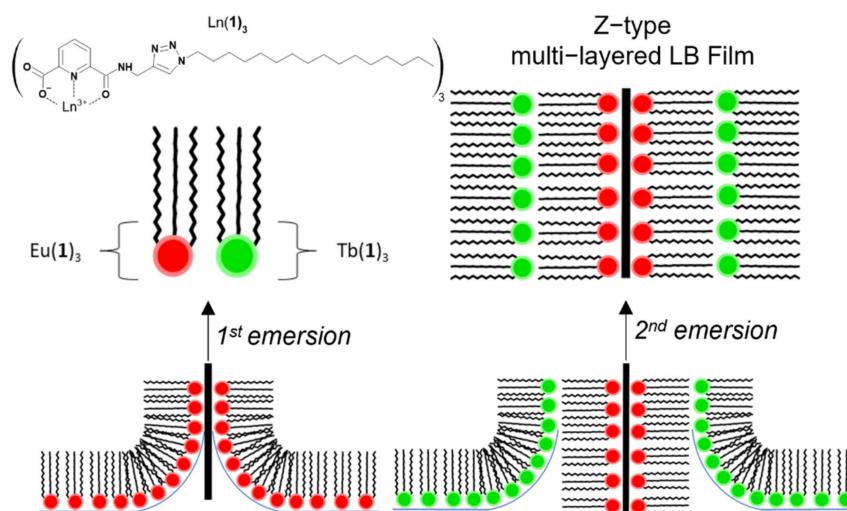


Figure 1. Diagram showing ligand 1 and corresponding $\text{Ln}(\mathbf{1})_3$ complexes (where $\text{Ln} = \text{Eu}^{3+}$, Tb^{3+} , and Dy^{3+}), which has been utilised to fabricate multilayered Z-type mixed LB films. The figure represents an example of an $\text{Eu}(\mathbf{1})_3$: $\text{Tb}(\mathbf{1})_3$ dual-layered film, with an initial emersion of $\text{Eu}(\mathbf{1})_3$, resulting in a monolayer $\text{Eu}(\mathbf{1})_3$ film, followed by a 2nd emersion of $\text{Tb}(\mathbf{1})_3$.

The multi-emissive ultrathin films that we have prepared herein also display temperature-dependent emissions—giving them potential application as ultrathin, contactless ratiometric thermometer coatings [12,14,28–30]. Lanthanide-based contactless luminescent thermometers have attracted significant attention owing to their range of potential applications in nanotechnology and biomedicine [31–33]. Furthermore, by combining different Ln^{3+} ions such as Eu^{3+} and Tb^{3+} , ratiometric thermometers can be developed with the Eu^{3+} emission intensity shown to be less affected in comparison to Tb^{3+} [12,14,28–30,33–36]. By utilising our multilayered LB films, we have demonstrated the straightforward fabrication of mixed Ln^{3+} ultra-thin transparent coatings, which are excited by soft UV light (250–290 nm), a combination ideal for contactless ratiometric thermometer coatings [14].

2. Materials and Methods

2.1. General Experimental Details

All reagents, solvents, and starting materials were purchased from Sigma–Aldrich. Ligand **1** and corresponding lanthanide complexes ($\text{Eu}(\mathbf{1})_3$, $\text{Tb}(\mathbf{1})_3$, and $\text{Dy}(\mathbf{1})_3$) have been described in our previous paper [8,9]. Langmuir–Blodgett measurements and film formation were carried out on a Kibron G2 Microtrough with a platinum DyneProbe. Photo-physical measurements of LB films were carried out on a Shimadzu UV-1800 for UV/Vis measurements, Shimadzu RF-6000 Spectrofluorophotometer for steady-state fluorescence measurements, and an Agilent Technologies Cary Eclipse spectrophotometer for phosphorescence time-resolved measurements. Unless otherwise stated an excitation wavelength of 279 nm was used, with excitation slit widths of 3 nm and 5 nm for fluorescence and phosphorescence, respectively, and emission slit widths of 3 nm and 10 nm for fluorescence and phosphorescence, respectively. Lifetime measurements were obtained by monitoring 616 nm for Eu^{3+} and 545 nm for Tb^{3+} with an excitation wavelength of 279 nm and emission/excitation slit widths of 5 nm. Lifetime measurements were run in triplicate and averaged results have been reported. CIE plots were generated in OSRAM LED ColorCalculator software [37].

2.2. Multilayer Langmuir–Blodgett Deposition

Before each deposition, the Langmuir trough and barriers were cleaned with EtOH and milli-Q water before filling the trough with milli-Q water subphase. The DyneProbe was cleaned by flaming and then washed with EtOH and milli-Q water before being

calibrated in air and on the water interface. Initial barrier compression isotherms were run, and if the surface pressure remained stable throughout, the trough was deemed clean. A square quartz slide (30 mm $\times$ 30 mm, 1 mm thick) which had been cleaned by nitric acid, piranha solution, and milli-Q water was then placed 20 mm into the subphase. A 1 mg/mL solution in $\text{CHCl}_3\text{:MeOH}$ (20:1) of complex was prepared and 20 μL aliquots of the solution was loaded onto the trough. Barrier compression was carried out until a surface pressure of 30 mN m^{-1} was reached. The resulting Langmuir film was then deposited onto the quartz slide by emersion of the slide, and film deposition was confirmed by visible lanthanide emission under a UV lamp. The Langmuir trough and DyneProbe were then cleaned and reset, and the now monolayer-coated quartz slide was re-immersed into the subphase monitoring surface pressure for any sign of film loss. Subsequently, a 1 mg/mL solution [$\text{CHCl}_3\text{:MeOH}$ (20:1)] of a different complex was prepared and 20 μL aliquots of the solution was loaded onto the trough. Barrier compression was again carried out until a surface pressure of 30 mN m^{-1} was reached. The resulting Langmuir film was then deposited onto the quartz slide by emersion of the slide resulting in a Z-type multilayer film. This was repeated one more time for the triple-layered film. Successful transfer of the molecular units was monitored during film depositions by measuring the change in trough area (between barriers) as the quartz substrate was removed from the water subphase. Transfer ratios (TR) were calculated by taking the change in the area of the trough and dividing it by the area of the immersed slide (1270 mm^2).

3. Results

Three multi-emissive Z-type LB films were fabricated from $[\text{Ln}(\mathbf{1})_3]$ (where $\text{Ln} = \text{Eu}^{3+}$, Tb^{3+} , and Dy^{3+}) utilizing the LB deposition method described above. Deposition occurred on emersion (up-stroke) of the slides from the water sub-phase layer with the order of Ln^{3+} layers determined by the overall quantum yields ($\Phi_{\text{Ln}}^{\text{L}}$) with the strongest emitting lanthanide complexes deposited first [9]. Initially a dual emissive and layered $\text{Eu}(\mathbf{1})_3\text{:Tb}(\mathbf{1})_3$ was fabricated as part of a study into multi-emissive mixed-amphiphiles [9]. In this system, the more emissive $\text{Eu}(\mathbf{1})_3$ ($\Phi_{\text{Ln}}^{\text{L}} = 22.4\%$) [9] complex was deposited first as a monolayer coating with a transfer ratio (tr) of ≈ 1 indicating near complete coverage of the slides. The resulting film deposition was confirmed by the bright red emission from the film, which could be observed under shortwave UV irradiation (Figure 2). Deposition of the second layer of the less emissive $\text{Tb}(\mathbf{1})_3$ ($\Phi_{\text{Ln}}^{\text{L}} = 14.2\%$) [9] layer was carried out successfully, with $\text{tr} \approx 1$. The second layer resulted in the film's overall emission becoming orange/yellow as a result of mixing Eu^{3+} and Tb^{3+} emissions (Figure 3). However, there are also regions of the film which have not been evenly covered resulting in dual and mono emission—nevertheless, most of the film shows dual emission.

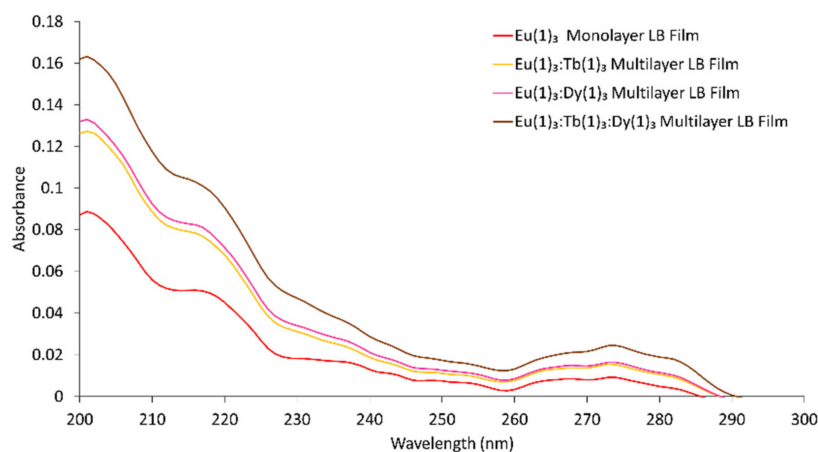


Figure 2. UV-visible absorption of $\text{Ln}(\mathbf{1})_3$ LB films (where $\text{Ln} = \text{Eu}^{3+}$, Tb^{3+} , and Dy^{3+}) showing the absorbance enhancement observed from increasing layers on the LB films.

Successful deposition of both layers of the lanthanide complex was confirmed by photophysical characterisation. UV/Vis spectra (Figure 2) clearly indicated the presence of the **1** on the substrate with an absorption spectrum matching **1** in solution. Furthermore, there was a noticeable absorbance enhancement compared to previous monolayer films, indicative of the increased thickness from the second layer (Figure 2). Fluorescent and phosphorescent spectra (Figure 3a and Figure S4) confirmed the presence of both complexes with clear transitions from $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0-4$) and $\text{Tb}^{3+} {}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 6-3$). While the excitation spectrum (Figure S4) monitoring wavelengths at 616 nm and 545 nm for Eu^{3+} and Tb^{3+} , respectively, further supported the presence of **1**, with the spectrum matching the absorbance region of the organic ligand.

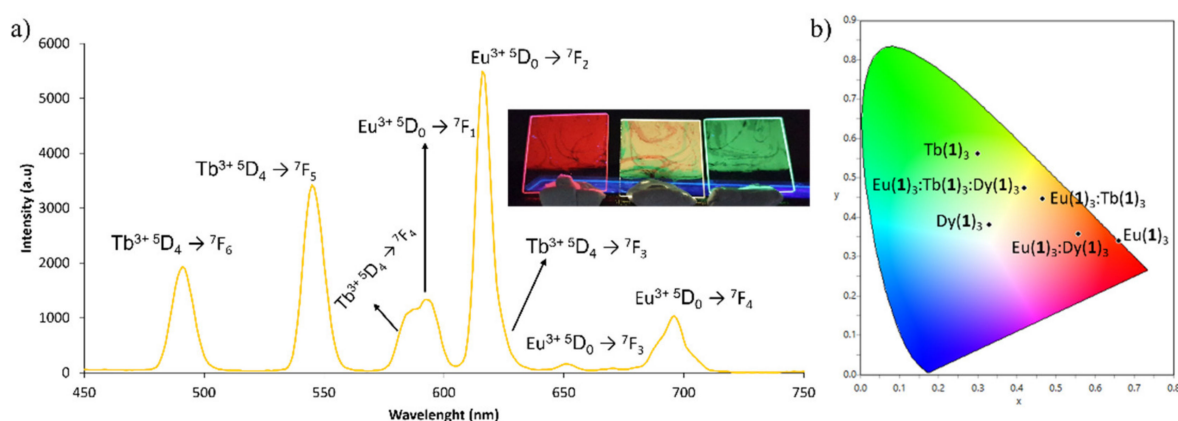


Figure 3. (a) $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3$ LB film fluorescence spectrum showing both Ln^{3+} distinct emission transitions. Insert: $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3$ mixed multi-layered film in the centre with a monolayer $\text{Eu}(\mathbf{1})_3$ film on the left and $\text{Tb}(\mathbf{1})_3$ on the right under shortwave UV irradiation ($\lambda_{\text{ex}} = 254$ nm). (b) CIE 1931 chromaticity diagram with calculated CIE coordinates for emissions of $\text{Ln}(\mathbf{1})_3$ complexes (where $\text{Ln} = \text{Eu}^{3+}$, Tb^{3+} , and Dy^{3+}) of monolayer LB films [9] and mixed multilayer LB films. $\text{Eu}(\mathbf{1})_3$ $x,y = 0.66, 0.34$; $\text{Tb}(\mathbf{1})_3$ $x,y = 0.30, 0.56$; $\text{Dy}(\mathbf{1})_3$ $x,y = 0.33, 0.38$; $\text{Eu}(\mathbf{5})_3:\text{Tb}(\mathbf{1})_3$ $x,y = 0.47, 0.45$; $\text{Eu}(\mathbf{5})_3:\text{Dy}(\mathbf{1})_3$ $x,y = 0.56, 0.36$ and $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3:\text{Dy}(\mathbf{1})_3$ $x,y = 0.42, 0.47$.

Similarly a dual emissive multilayered $\text{Eu}(\mathbf{1})_3:\text{Dy}(\mathbf{1})_3$ LB film was successfully fabricated, following a similar procedure to that described for the $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3$ film above. The initial deposition of the more emissive $\text{Eu}(\mathbf{1})_3$ ($\text{tr} = 1$) layer was now followed by a second layer of the less emissive $\text{Dy}(\mathbf{1})_3$ ($\Phi_{\text{Ln}}^{\text{L}} = 2.9\%$, $\text{tr} = 1$) [9]. Although emission from the $\text{Dy}(\mathbf{1})_3$ complex is clearly weaker, the second layer results in the overall emission being tuned to a lighter red (Figures 3b and 4), however, film uniformity in terms of emission is again observed to be poor in comparison to the previously reported mixed-amphiphile monolayer films [9]. Photophysical characterisation confirmed the deposition of both layers, with the UV/Vis spectrum having a near identical profile and absorbance intensity as the previous dual layer LB film (Figure 2). The fluorescence spectrum (Figure 4) confirmed the presence of both lanthanide ions with clear transitions from $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0-4$) and $\text{Dy}^{3+} {}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_J$ ($J = 15/2-9/2$), however, the phosphorescence spectrum (Figure S6) only showed emission from $\text{Eu}(\mathbf{1})_3$ —a result of Dy^{3+} shorter lifetimes.

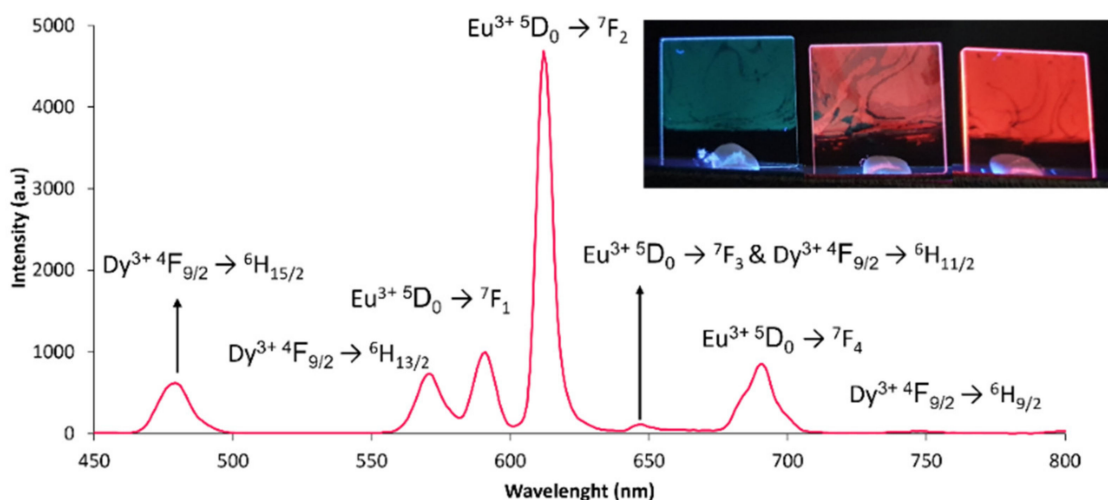


Figure 4. Mixed multilayered $\text{Eu}(\mathbf{1})_3:\text{Dy}(\mathbf{1})_3$ LB film fluorescence spectrum showing both distinct Ln^{3+} emission transitions. Insert: $\text{Eu}(\mathbf{5})_3:\text{Dy}(\mathbf{5})_3$ mixed multilayered film in the centre with a monolayer $\text{Dy}(\mathbf{1})_3$ film on the left and $\text{Eu}(\mathbf{1})_3$ on the right under shortwave UV irradiation ($\lambda_{\text{ex}} = 254 \text{ nm}$).

Finally a triple emissive, and triple-layered $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3:\text{Dy}(\mathbf{1})_3$ multilayered LB film was successfully fabricated (Figure 5). Production of the multilayered film occurred with relative ease as indicated by the high transfer ratios for depositions. Initially, $\text{Eu}(\mathbf{1})_3$ ($\text{tr} = 1.05$) was deposited, followed by a second layer of $\text{Tb}(\mathbf{1})_3$ ($\text{tr} = 1.09$), and a final layer of $\text{Dy}(\mathbf{1})_3$ ($\text{tr} = 1.13$). The resulting triple-layered film had a similar tuned emission profile to the dual-layered $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3$ LB film, under shortwave irradiation.

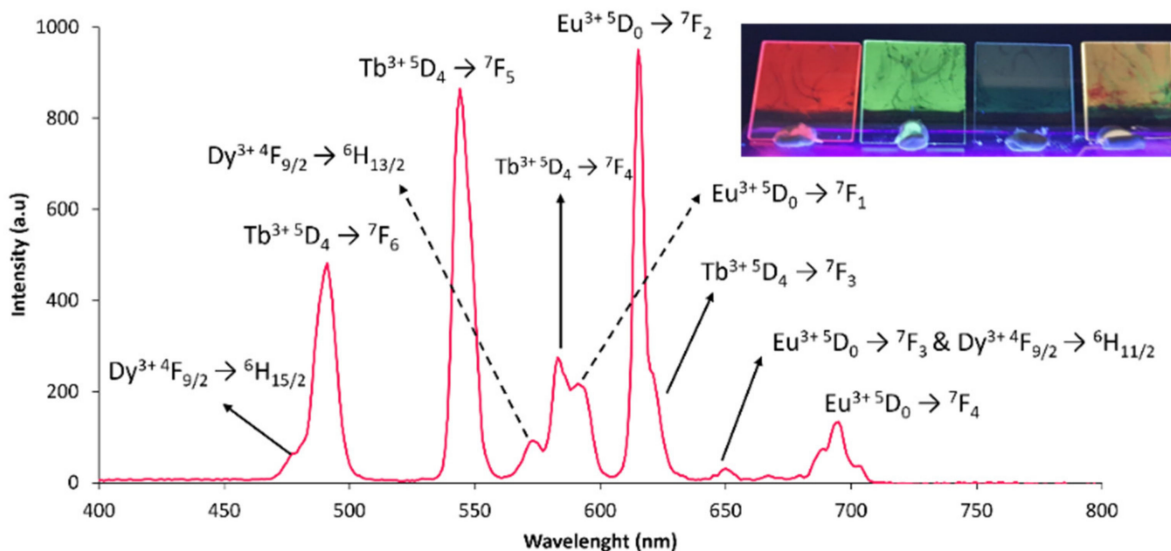


Figure 5. Mixed multilayered $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3:\text{Dy}(\mathbf{1})_3$ LB film fluorescence spectrum showing most of the distinct Ln^{3+} transitions. Insert: monolayer and multilayered LB films of $\text{Eu}(\mathbf{5})_3$, $\text{Tb}(\mathbf{5})_3$, $\text{Dy}(\mathbf{5})_3$ and $\text{Eu}(\mathbf{1})_3:\text{Tb}(\mathbf{1})_3:\text{Dy}(\mathbf{1})_3$ is shown on the right under shortwave UV irradiation ($\lambda_{\text{ex}} = 254 \text{ nm}$).

Photophysical characterisation confirmed the deposition of all three layers. The UV/Vis spectrum again indicated the presence of **1**, but importantly showed an absorbance enhancement indicative of the thicker coating (Figure 2), as previously seen in the literature [38]. The fluorescence spectrum (Figure 5) confirmed clear transitions from all three lanthanide ions, $\text{Eu}^{3+} 5\text{D}_0 \rightarrow 7\text{F}_j$ ($j = 0-4$), $\text{Tb}^{3+} 5\text{D}_4 \rightarrow 7\text{F}_j$ ($j = 6-3$), and $\text{Dy}^{3+} 4\text{F}_{9/2} \rightarrow 6\text{H}_j$ ($j = 15/2-11/2$), although the transition associated with Dy^{3+} is merged within both Tb^{3+}

and Eu^{3+} emission peaks. The phosphorescence spectrum (Figure S8) again only showed emission from the longer lifetime $\text{Eu}(\text{1})_3$ and $\text{Tb}(\text{1})_3$ with Dy^{3+} signals absent.

The ability of the multi-layered thin films to act as ratiometric thermometer coatings was also investigated. For the dual-layered $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ LB film, fluorescence emission was monitored from 294 to 340 K. Upon heating the $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ film from room temperature to ≈ 340 K, the Tb^{3+} centered emission ($^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6-4$)) was observed to significantly decrease while the Eu^{3+} centered emission remained relatively unchanged (Figure 6). Upon slow cooling of the LB film to r.t, the Tb^{3+} emission recovered linearly vs temperature (Figure 6), while the Eu^{3+} centred emission remained constant. As a result of the emission profile changing with temperature, the overall emission colour moves towards red as the Tb^{3+} emission is quenched (Figure 6). Furthermore, with the Eu^{3+} emission remaining relatively unchanged it can be utilised as a self-calibrating signal. Comparing the ratio of integrated emission intensity for $\text{Eu}^{3+} \text{ } ^5\text{D}_0 \rightarrow ^7\text{F}_2$ (604–634 nm) to $\text{Tb}^{3+} \text{ } ^5\text{D}_4 \rightarrow ^7\text{F}_5$ (530–568 nm) ($I_{\text{Tb}}/I_{\text{Eu}}$) [33] vs temperature (K), a linear relationship was observed, thus demonstrating ratiometric thermal behaviour (Figure 6). Similar properties are observed upon heating the $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3\text{:Dy}(\text{1})_3$ from ≈ 294 K to ≈ 340 . Again, the Tb^{3+} centred emission ($^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6-4$)) was observed to significantly decrease whilst the Eu^{3+} and now Dy^{3+} centred emission remained relatively unchanged, both now acting as calibrating signals (Figure 7). Once again upon the cooling of the LB film to r.t, the Tb^{3+} centred emission was observed to fully recover (see Supplementary Materials).

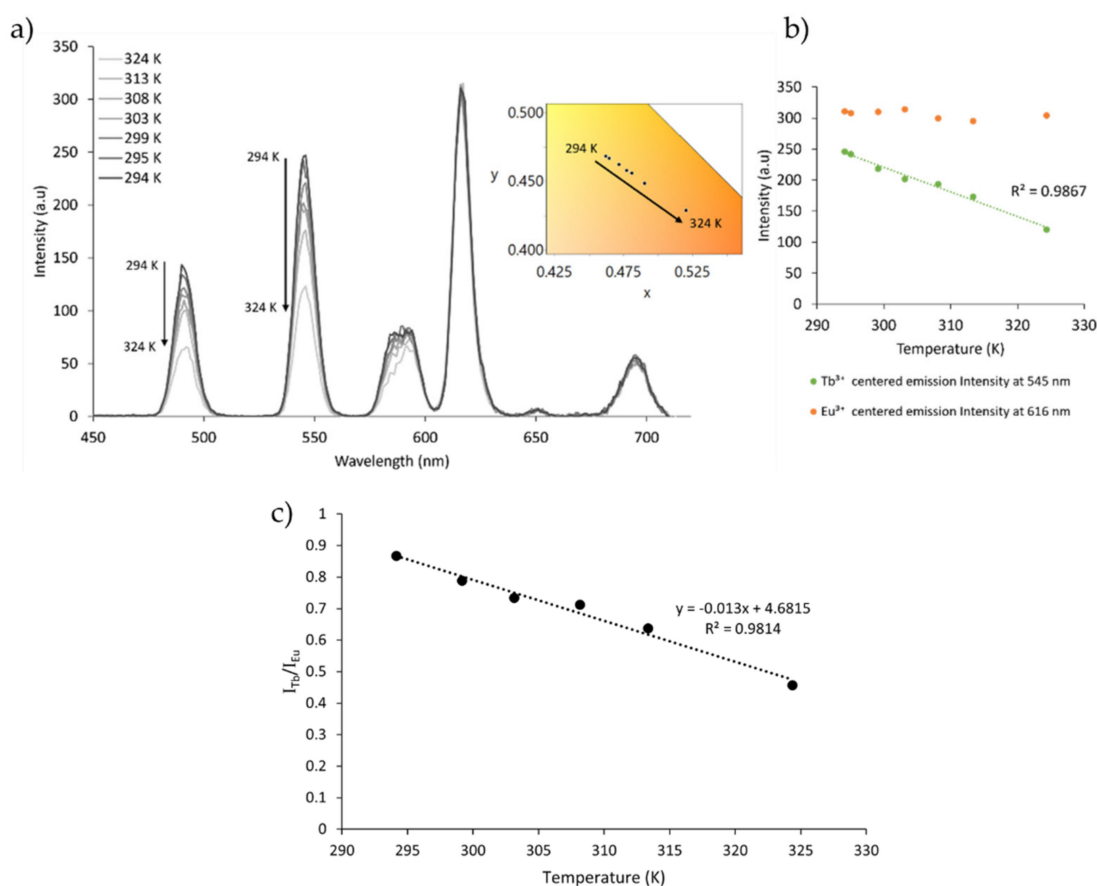


Figure 6. (a) Fluorescence spectra of $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ at varying temperatures ≈ 294 to 330 K (excitation and emission slit widths 3 and 5 nm, respectively). Insert: CIE 1931 chromaticity diagram of resulting colour change dependent on temperature, CIE coordinates: 294 K— $x, y = 0.46, 0.47$; 295 K— $x, y = 0.46, 0.47$; 299 K— $x, y = 0.47, 0.46$; 303 K— $x, y = 0.48, 0.47$; 308 K— $x, y = 0.48, 0.46$; 313 K— $x, y = 0.49, 0.45$; 324 K— $x, y = 0.52, 0.43$. (b) Emission intensity vs temperature monitoring emission at 616 nm for Eu^{3+} and 545 nm for Tb^{3+} . (c) Ratio of integrated Eu^{3+} and Tb^{3+} emission intensities vs temperature.

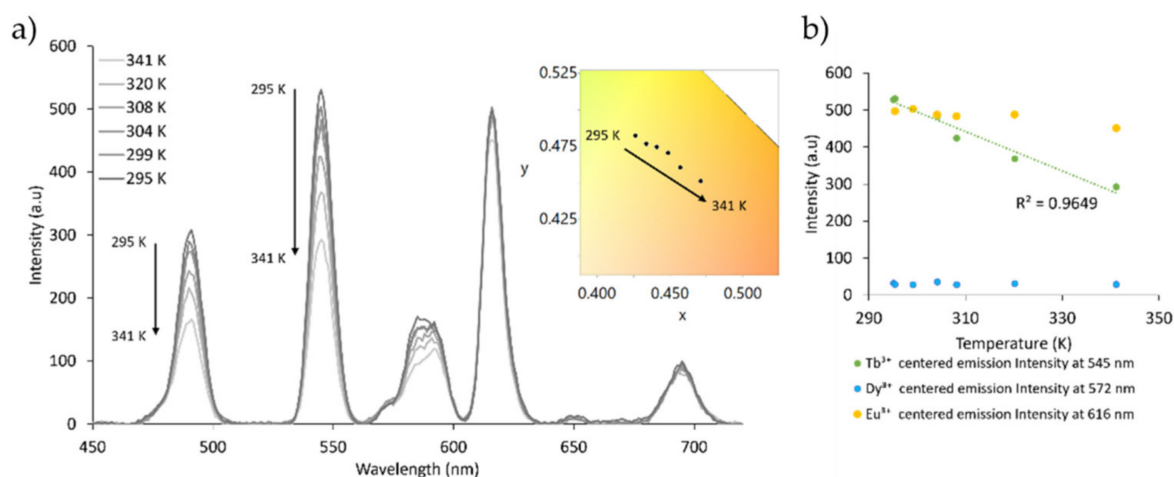


Figure 7. (a) Fluorescent spectra of $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3\text{:Dy}(\text{1})_3$ at varying temperatures ≈ 294 to 340 K (excitation and emission slit widths 5 nm). Insert: CIE 1931 chromaticity diagram of resulting colour change dependent on temperature, CIE coordinates: 295 K— $x, y = 0.42, 0.48$; 299 K— $x, y = 0.43, 0.48$; 304 K— $x, y = 0.44, 0.47$; 308 K— $x, y = 0.45, 0.47$; 320 K— $x, y = 0.46, 0.46$ and 341 K— $x, y = 0.47, 0.45$. (b) Emission intensity vs temperature monitoring emission at 616 nm for Eu^{3+} , 545 nm for Tb^{3+} , and 572 nm Dy^{3+} .

4. Conclusions

In conclusion, we have demonstrated that the visibly emissive amphiphilic complexes $\text{Ln}(\text{1})_3$ can form multilayered ultra-thin films using LB deposition. In doing so we have readily and reliably developed a range of multi-emissive materials where the overall emission profile is tuned by layer composition. Furthermore, $\text{Tb}(\text{1})_3$ was observed to display a temperature-sensitive emission with emission quenching upon increasing temperature from 294 to 340 K. The mixed-multilayering LB approach allowed for the easy fabrication of ratiometric thermometer coatings as demonstrated by the temperature-dependence of the dual-layered and triple-layered $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ and $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3\text{:Dy}(\text{1})_3$ LB films. Here the Tb^{3+} emission was quenched upon heating, while Eu^{3+} (and Dy^{3+}) emission remained relatively unchanged therefore acting as a self-calibrating signal. Unlike previous examples of $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ temperature sensors, we have utilised discrete lanthanide complexes, allowing for self-assembly into transparent LB films that retain temperature sensitivity and do not require doping into polymers to form transparent coatings [14]. Work is now focusing on multilayering mixed amphiphile films [9] for transparent ultrathin, contactless ratiometric thermometer coatings.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry4040096/s1>, Figures S1–S3: LB deposition plots; Figure S4: $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ LB film phosphorescence emission and excitation spectra; Figure S5: $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$ LB film lifetime plots; Figure S6: $\text{Eu}(\text{1})_3\text{:Dy}(\text{1})_3$ LB film phosphorescence emission and excitation spectra; Figure S7: $\text{Eu}(\text{1})_3\text{:Dy}(\text{1})_3$ LB film lifetime plots; Figure S8: $\text{Eu}(\text{1})_3\text{:Dy}(\text{1})_3$ LB film phosphorescence emission and excitation spectra; Figure S9: $\text{Eu}(\text{1})_3\text{:Dy}(\text{1})_3$ LB film lifetime plots; Table S1: lifetimes of $\text{Eu}(\text{1})_3$ and $\text{Tb}(\text{1})_3$ complexes on multi-layered LB films of $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3$; Table S2: lifetimes of $\text{Eu}(\text{1})_3$ and $\text{Tb}(\text{1})_3$ complexes on multilayered LB films of $\text{Eu}(\text{1})_3\text{:Tb}(\text{1})_3\text{:Dy}(\text{1})_3$

Author Contributions: A.T.O.: Conceptualisation, Investigation, Methodology, Analysis, Writing—Original Draft, Writing—Review & Editing. J.A.K.: Conceptualisation, Writing—Review and Editing, Supervision, Project Administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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