RESEARCH HIGHLIGHT

Circularly Polarised Luminescence from $TbPO_4 \cdot nH_2O$ Nanocrystals

RH_PL17; Iona Hill

Introduction

The design of circularly polarised luminescence (CPL) phosphors is attracting increasing interest for a wide range of applications, including security devices and inks. Lanthanide complexes are ideal candidates for obtaining efficient CPL emission as they possess large dissymmetry factor (g_{Em} or g_{lum}). In addition, CPL phosphors for use in security devices must possess good thermal stability, photostability and be relatively inexpensive to produce.

This Research Highlight discusses work published in *Inorganic Chemistry* by researchers at University of Verona, Italy.[1] The presented study describes the design of new chiroptical inorganic phosphor materials whose CPL signature can be modified by simply changing the Tb^{3+}/Eu^{3+} molar ratio within the compound (Figure 1). This is attractive for designing new and tuneable materials as security inks for anticounterfeiting applications, as the different ratios create unique optical fingerprints.

In this work they used an Edinburgh Instruments FLS1000 Photoluminescence Spectrometer for full spectroscopic characterisation of their synthesised material, including excitation, emission, luminescence decay and CPL measurements.

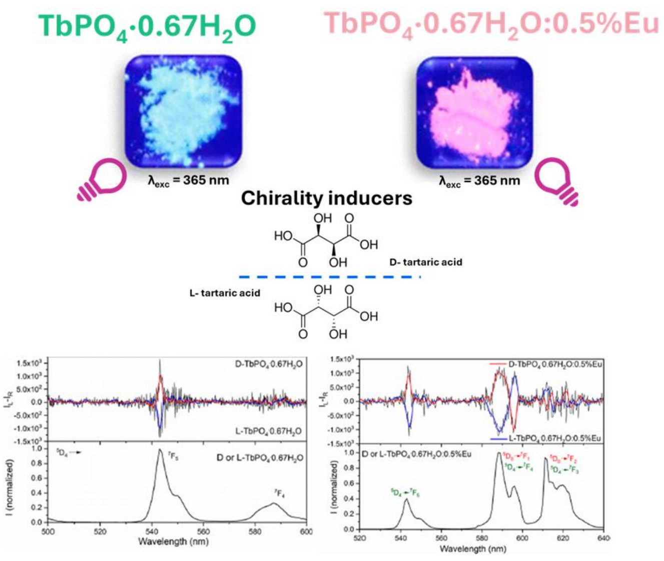

Figure 1. Lanthanide nanocrystal powders were synthesised to exhibit unique CPL properties. The image is reproduced from F. Piccinelli *et al.*[1], Copyright (2024), with permission from the American Chemical Society.

Materials and Methods

In this research, chiroptical $TbPO_4 \cdot nH_2O$ nanocrystals were investigated. Steady state and time-resolved photoluminescence of the sample were collected using an FLS1000 Photoluminescence Spectrometer with continuous and pulsed Xenon lamp excitation sources (Figure 2). The FLS1000 had a double excitation monochromator and a single emission monochromator. CPL spectra were collected using the CPL Upgrade on the FLS1000.

Figure 2. Edinburgh Instruments FLS1000 Photoluminescence Spectrometer. CPL upgrade for FLS1000 shown in inset photo.

Results

Excitation and Emission Spectra of Nanocrystals

First, the researchers investigated the effect of Eu doping on the excitation and emission spectra. The FLS1000 was used to characterise the photoluminescence properties of two representative samples: $TbPO_4 \cdot 0.67H_2O$ and $TbPO_4 \cdot 0.67H_2O$:0.5%Eu (Figure 3).

The excitation spectrum of $TbPO_4 \cdot 0.67H_2O$ showed bands from 280 to 400 nm, typical of *f-f* intra-configurational bands of the Tb^{3+} ion. The same excitation peaks were present in the Eu^{3+} doped sample ($TbPO_4 \cdot 0.67H_2O$:5%Eu), but additional peaks at 395 and 465 nm corresponding to *f-f* transitions of Eu^{3+} were also observed. These additional peaks demonstrate that a $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer process takes place in the Eu^{3+} doped sample.

The emission spectra showed $TbPO_4 \cdot 0.67H_2O$ exhibited typical *f-f* Tb^{3+} emission originating from the $^5D_4$ excited level (Figure 3c - bottom). In contrast, the emission of the Eu doped sample was due to both Tb^{3+} and Eu^{3+} emission lines (Figure 3c - top). The dominant emission feature of Eu^{3+} was the $^5D_0 \rightarrow {}^7F_4$ band at 700 nm.

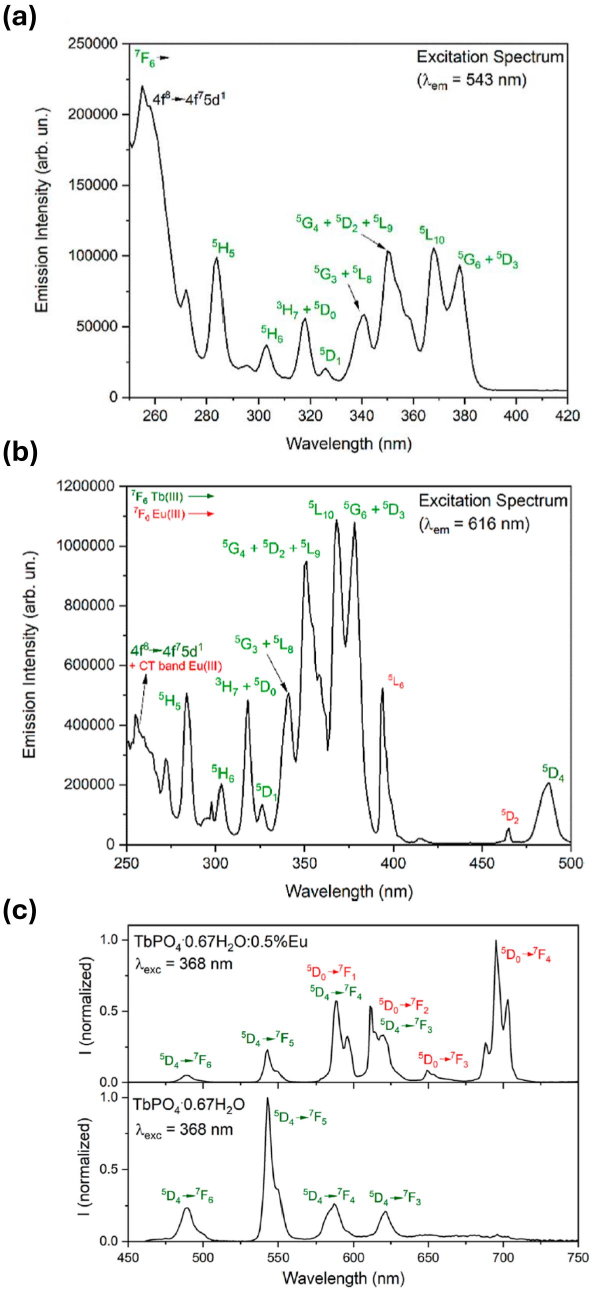

Figure 3. Excitation spectra of (a) $TbPO_4 \cdot 0.67H_2O$ and (b) $TbPO_4 \cdot 0.67H_2O$:5%Eu nanocrystals. Emission spectra of (c) $TbPO_4 \cdot 0.67H_2O$ (bottom) and $TbPO_4 \cdot 0.67H_2O$:0.5%Eu (top) nanocrystals. The image is reprinted from F. Piccinelli *et al.*[1], Copyright (2024), with permission from the American Chemical Society.

Lifetime Measurements of Nanocrystals

Lifetime measurements of the $TbPO_4 \cdot 0.67H_2O$ nanocrystal sample were acquired using the FLS1000 pulsed Xenon lamp excitation source. Luminescence decay curves of $TbPO_4 \cdot 0.67H_2O$ with increasing ratio of Tb^{3+}/Eu^{3+} are shown in Figure 4.

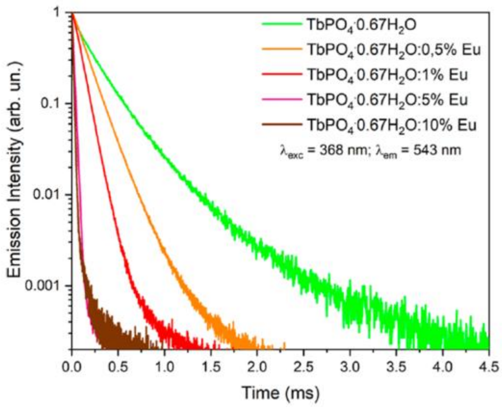

Figure 4. Luminescence decay curves of the $Tb^{3+5}D_4$ excited stated for the $TbPO_4 \cdot 0.67H_2O$:x%Eu (with x = 0, 0.5, 1, 5 and 10) nanocrystals. The image is reprinted from F. Piccinelli *et al.*[1], Copyright (2024), with permission from the American Chemical Society.

The lifetime measurements showed that as the Eu^{3+} ion concentration was increased the $^5D_4$ decay of Tb^{3+} became faster, indicating there was an increase in energy transfer efficiency between $Tb^{3+} \rightarrow Eu^{3+}$. The energy transfer approached 100% when the concentration of Eu^{3+} ion reached 10%.

CPL Spectra of Nanocrystals

Lastly, the researchers used the CPL upgrade for the FLS1000 to investigate the CPL properties of $TbPO_4 \cdot 0.67H_2O$. The spectrum of the sample showed two well-defined CPL signals at 545 nm and 590 nm (Figure 5a). Mirror CPL signatures were obtained when crystal growth was driven by two different enantiomers of tartaric acid.

For the Eu doped sample, the CPL spectrum also showed CPL emission between 580 and 600 nm due to the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}; and between 610 and 630 nm where the $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_3$ transitions of Eu^{3+} and Tb^{3+}, respectively, overlap (Figure 5b).

To confirm the tunability of the CPL signal upon changing the Tb^{3+}/Eu^{3+} molar ratio, the researchers also collected spectra of two enantiomorphic phosphates doped with 10 % mol of Eu^{3+} (D- and L-$TbPO_4 \cdot 0.67H_2O$:10%Eu) (Figure 5c). Due to the very high $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer efficiency, the main contribution to the CPL was from the Eu^{3+} ion (580-600 nm and 610-630 nm).

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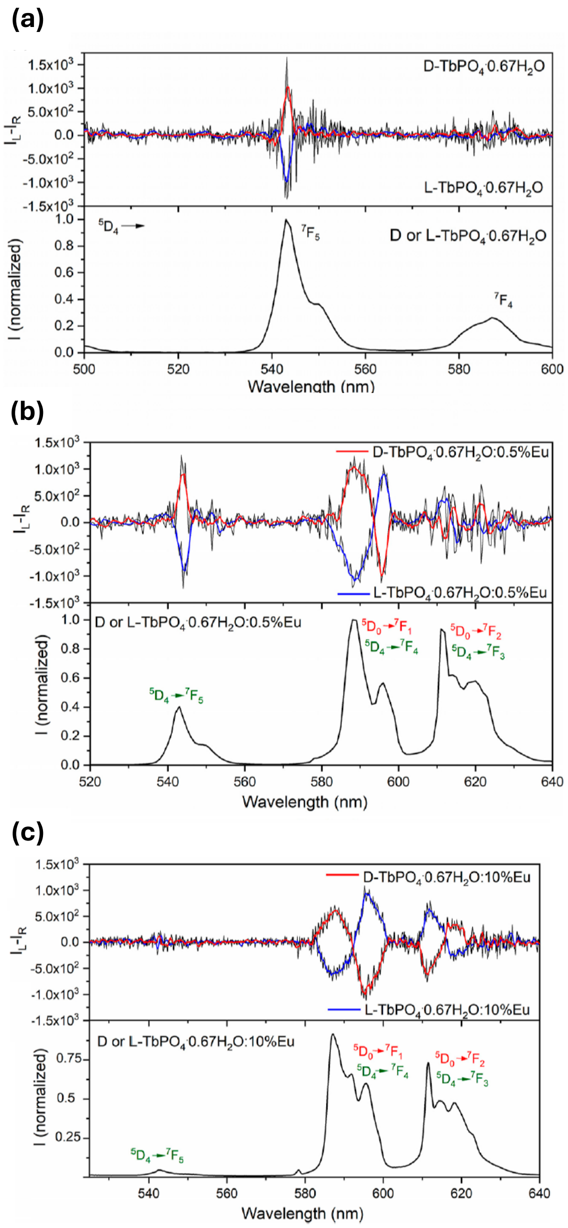

Figure 5. CPL (top) and total luminescence (bottom) spectra of (a) $TbPO_4 \cdot 0.67H_2O$, (b) $TbPO_4 \cdot 0.67H_2O$:0.5%Eu NCs, and (c) $TbPO_4 \cdot 0.67H_2O$:10%Eu nanocrystals with λ_{exc} = 368 nm. CPL spectra have been smoothed post-measurement collection. The image is reprinted from F. Piccinelli *et al.*[1], Copyright (2024), with permission from the American Chemical Society.

Conclusion

This Research Highlight demonstrates the full characterisation of CPL active lanthanide compounds using an Edinburgh Instruments FLS1000 Photoluminescence Spectrometer with CPL Upgrade. In this work, the authors investigated CPL emission from pure enantiomorphic inorganic compounds, tuned by altering the Tb^{3+}/Eu^{3+} ratio and controlling the chirality of the synthesis materials.

These materials could be used in security and anticounterfeiting, such as security ink on banknotes. The tuneable nature of the nanocrystals leads to unique optical properties vital for optical counterfeiting applications.

Full Publication

The results in this Research Highlight were published in *Inorganic Chemistry*. The full article can be found here: https://doi.org/10.1021/acs.inorgchem.4c01869

References

1. F. Piccinelli *et al.*, *Circularly Polarized Luminescence from Pure and Eu-Doped Trigonal $TbPO_4 \cdot nH_2O$ Nanocrystals*, Inorg. Chem. (2024) **63**, 29, 13636–13643

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