



Luminescent ionic liquids for anticounterfeiting applications

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ABSTRACT

Counterfeiting is a global issue that causes billions worth of economic loss. Security inks play a vital role in controlling and regulating counterfeit currencies, important documents like passports, and product forgery. Addressing the issues in the security ink industry, such as non-homogeneity, solvation, formulation and thermal stability, and non-complexity, luminescent ionic liquids are introduced with a goal to be used as a security ink. Lanthanides owe their emission properties to f-f transition and are sensitised by antenna effect by an organic ligand.^{1,2} Lanthanide ionic liquids (1- Eu, 2-Tb, 3-Dy, 4-Sm) and their equimolar mixtures (5 - Eu:Dy, 6 - Eu:Tb, 7 - Dy:Sm, 8- Eu:Dy:Tb, 9 - Tb :Sm, 10 - Eu:Dy:Tb:Sm) synthesised and characterised.

AIMS AND OBJECTIVES

1. To synthesise emissive ionic liquids.
2. To investigate thermal and optical properties of ionic liquids and mixtures.
3. To test the synthesised compounds to be used as security inks.

RESEARCH PROBLEM: Challenges in the security ink industry

- Non-homogenous patterns
- Solvation
- Formulation
- Easily forged
- Low thermal stability

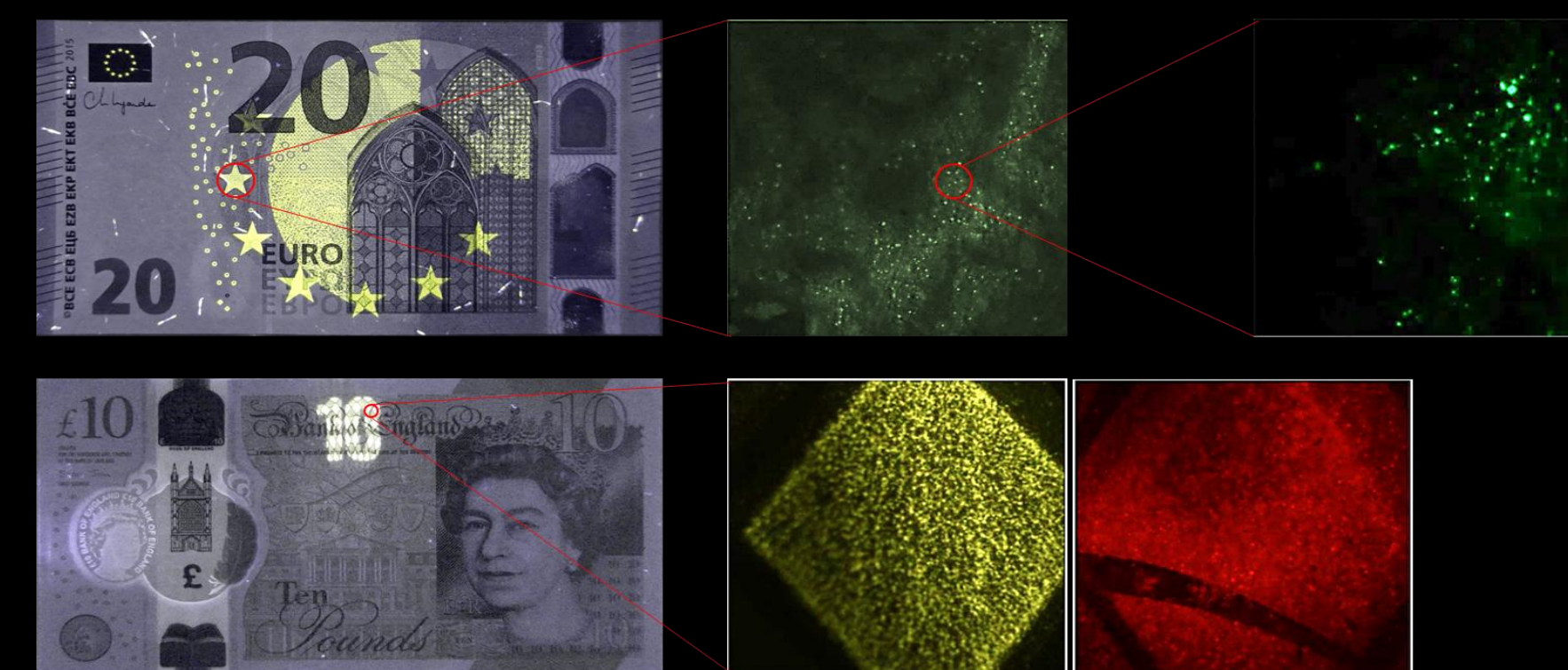


Figure 1 : Non-uniform patterns in currency notes

THERMAL PROPERTIES OF LUMINESCENT IONIC LIQUIDS

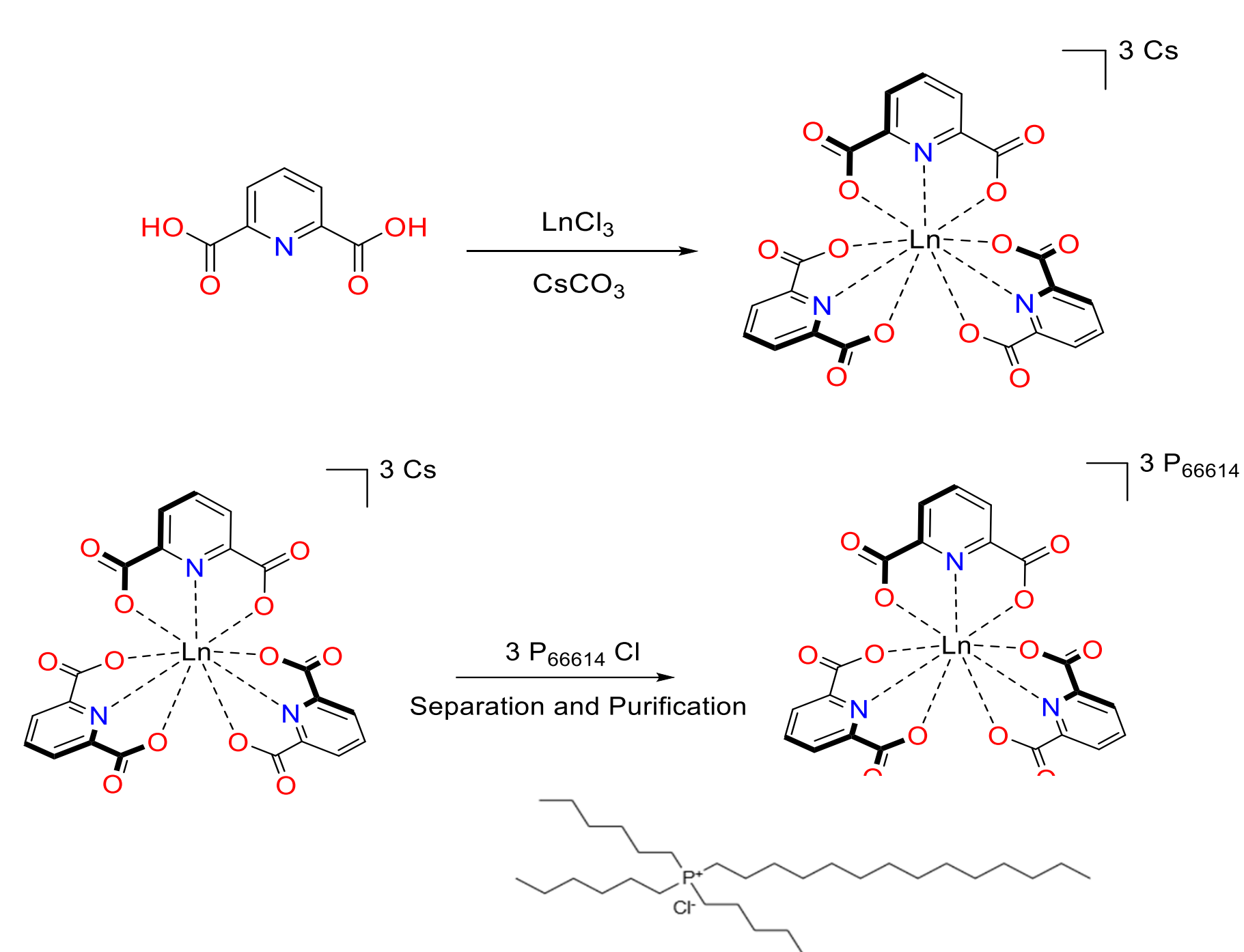


Figure 2 : Synthetic scheme (i) Synthesis of Cs salts of lanthanide coordination complexes with Eu, Tb, Dy, Sm (ii) Ionic liquids with trihexyl tetradecyl phosphonium chloride

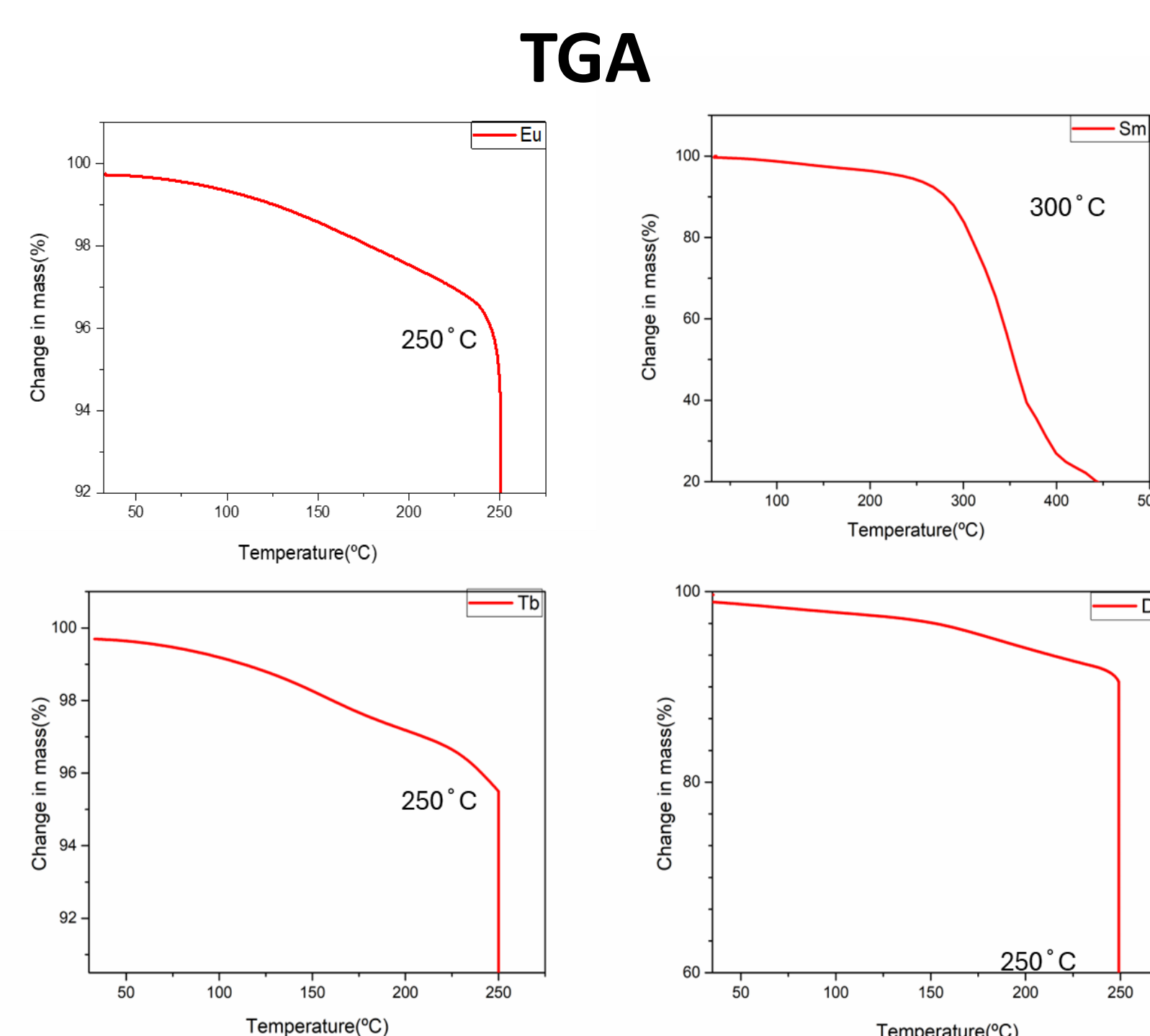


Figure 3: Thermogravimetric assay of ionic liquids. TGA shows good thermal stability for the synthesised ionic liquids up to 250 °C for Eu, Tb, and Dy, and up to 300 °C for Sm, with a gradual mass loss attributed to water loss, and dip indicating decomposition of the compound.

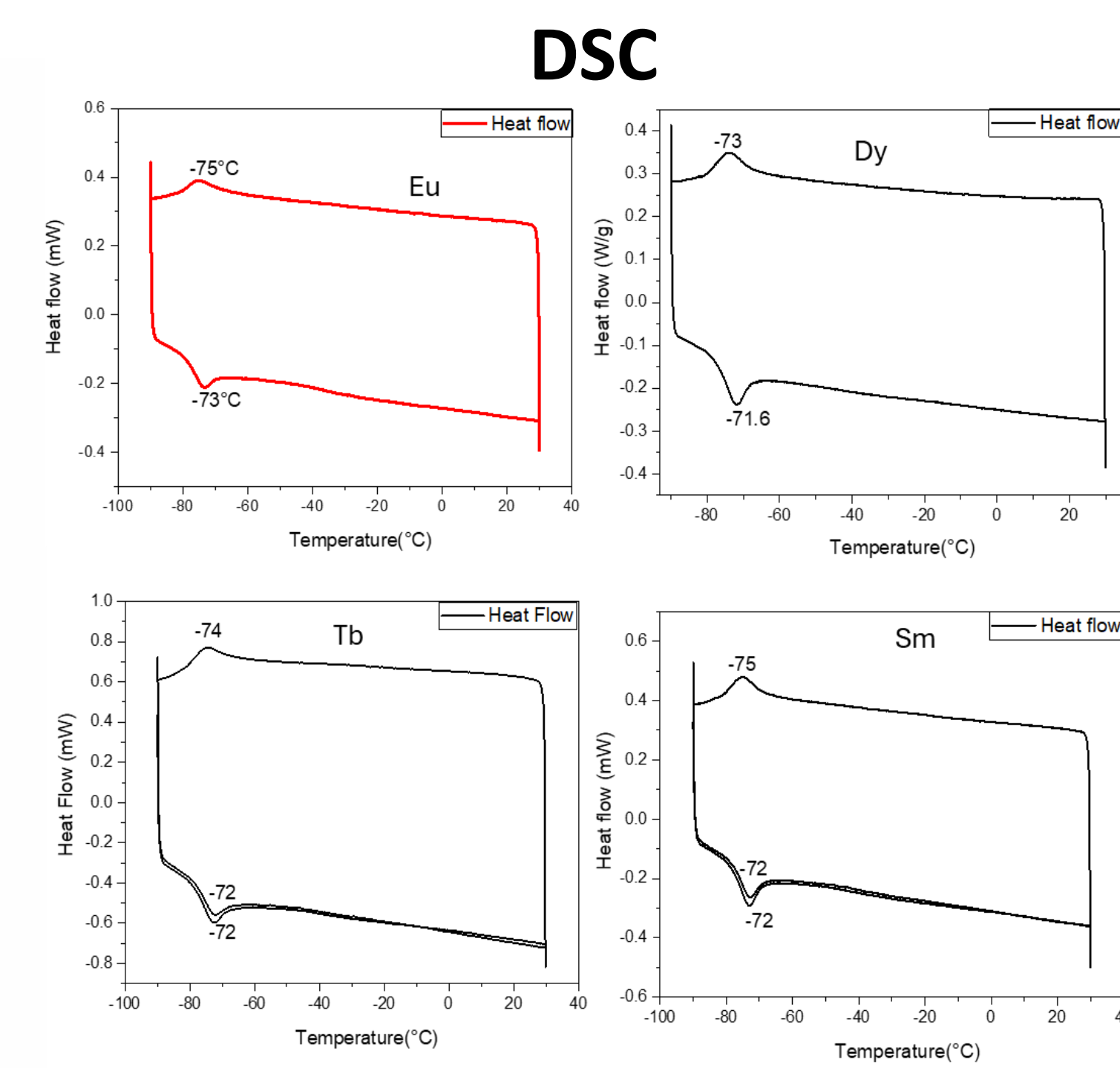


Figure 4: Differential Scanning Calorimetry; Crystallisation temperature of each ionic liquid, in cycles -90 °C to 30 °C. Crystallisation point of Eu - 73.6 °C, Dy - 72 °C, Tb - 72.6 °C, Sm - 73 °C

PHOTOPHYSICS OF IONIC LIQUIDS

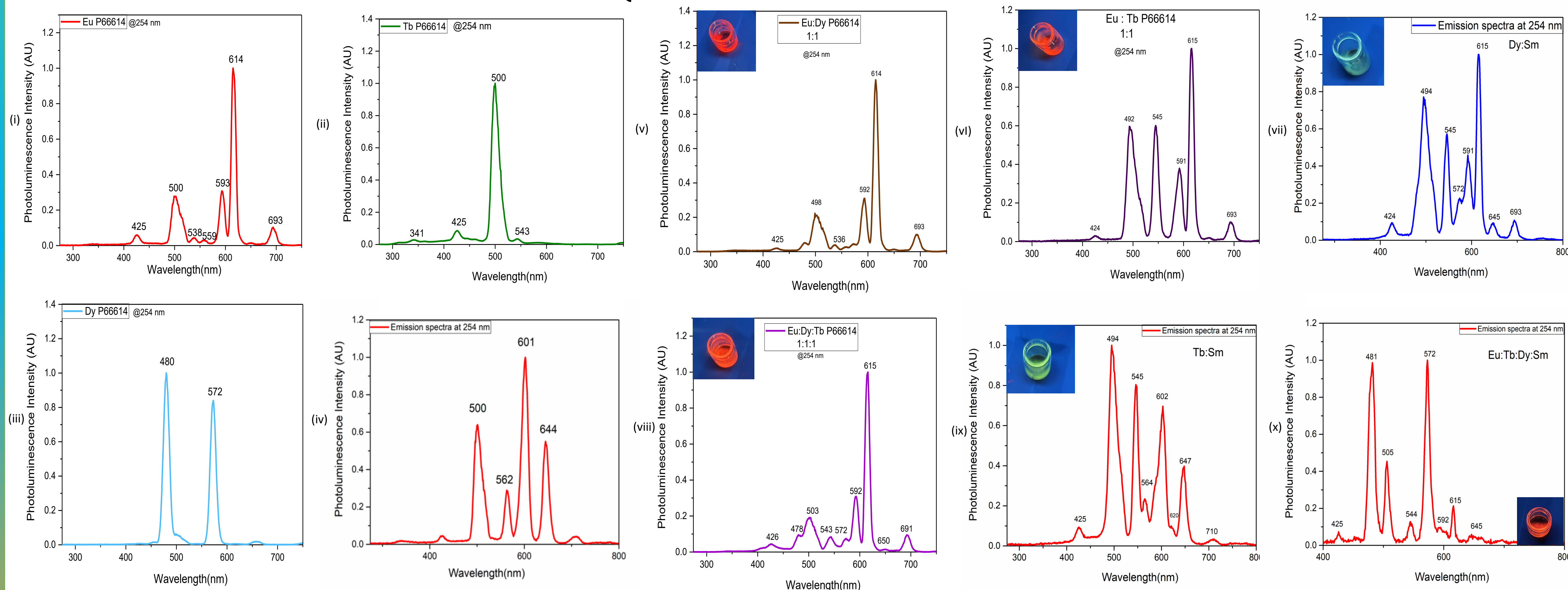


Figure 5 : Emission spectra of ionic liquids at 254 nm (i) 1 -Eu P₆₆₆₁₄, (ii) 2 -Tb P₆₆₆₁₄, (iii) 3 -Dy P₆₆₆₁₄, (iv) 4 -Sm P₆₆₆₁₄ and mixtures (v) 5 - Eu:Dy, (vi) 6 - Eu:Tb, (vii) 7 - Dy:Sm (viii) 8 - Eu:Dy:Tb (ix) 9 - Tb :Sm (x) 10 - Eu:Dy:Tb:Sm
OBSERVATION: UNIQUE NARROW PEAKS PRESENT, CORRESPONDING TO EMISSION OF ALL LANTHANIDES PRESENT IN THE MIXTURE.

CONCLUSION

- Successfully synthesised highly efficient functional ionic liquids containing Eu, Tb, Dy, and Sm coordination complexes and investigated their photophysical properties, revealing characteristic emission fingerprints in pure and equimolar mixtures. At 254 nm and 365 nm, unique colour for mixtures are observed.
- Thermal investigation reveals thermal stability up to 250 °C, and average crystallisation temperature as -72 °C.
- This research efficiently synthesised a novel luminescent ionic liquids and its mixtures that can be used for anticounterfeiting applications.

STAMP PRINTING

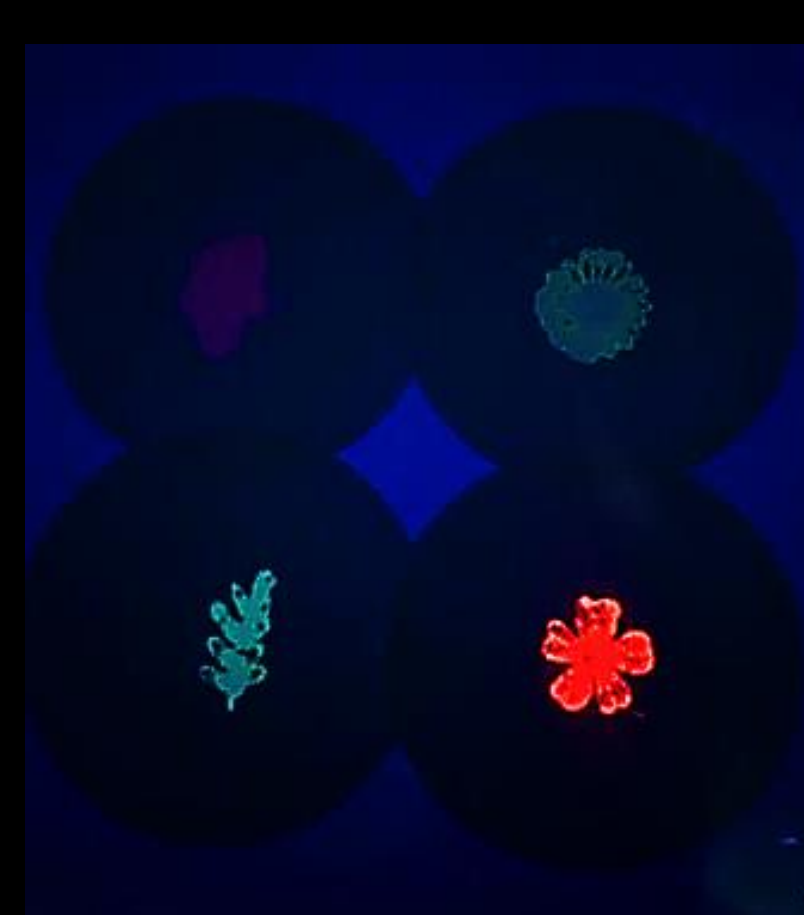


Figure 6: Stamped patterns at 254 nm

WRITING WITH IONIC LIQUIDS

Ambient 254 nm

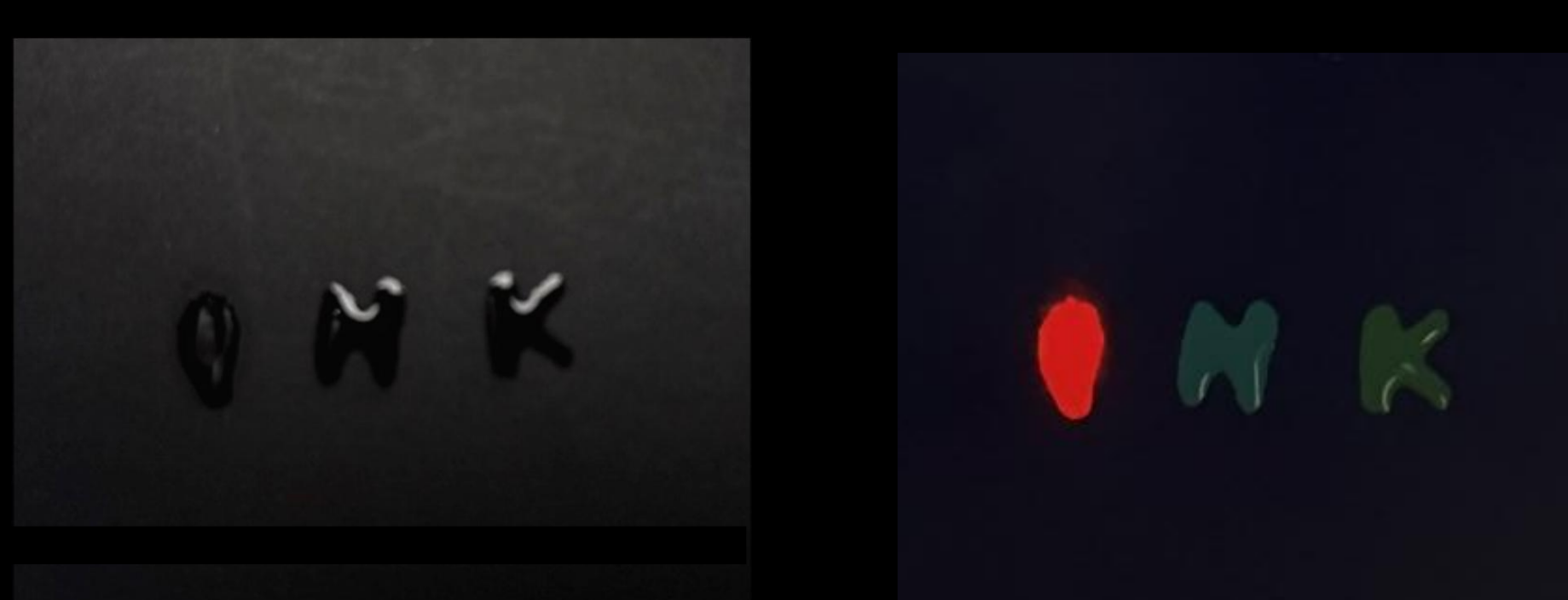


Figure 7: UV excitation at 254 nm: Colourless to luminescent red for Eu, aqua blue for Dy and green for Tb

References

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2. S. I. Weissman, *J Chem Phys*, **1942**, *10*, 214–217
3. A. G. Bispo Jr., N. A. Oliveira, I. M. S. Diogenis and F. A. Sigoli, *Coord Chem Rev*, **2025**, *523*, 216279.