A NOVEL METAL-ORGANIC FRAMEWORK FOR THERMOMETRY

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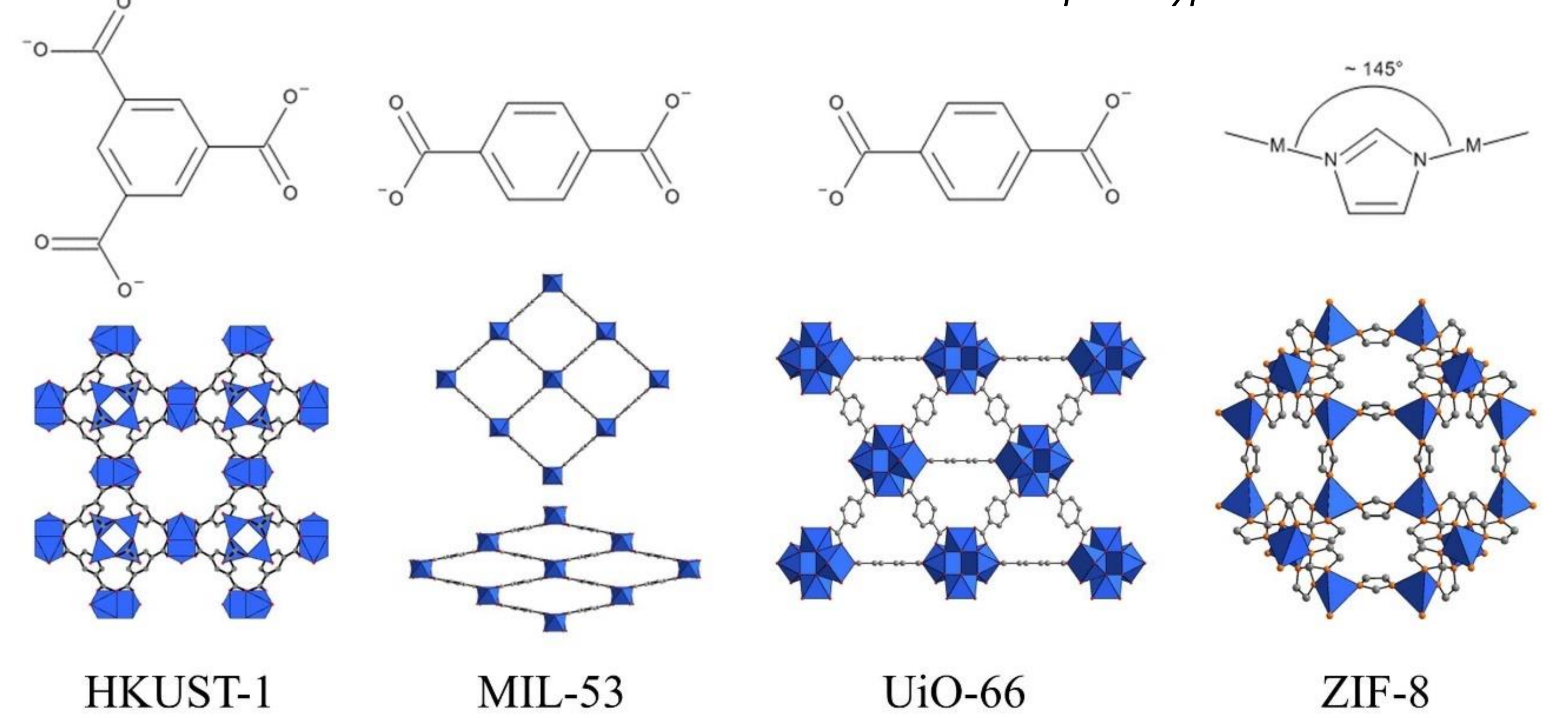
Introduction

At Warwick, we developed a novel yttrium-based metal-organic framework (MOF) $(Y_{0.89}Tb_{0.10}Eu_{0.01})_6(BDC)_7(OH)_4(H_2O)_4$ (Y_6-MOF) (BDC = benzene1,4-dicarboxylate, organic linker) derived from a material developed by Weng *et al.*[1] Originally containing yttrium as the sole metal ion, this MOF was substituted with a precise ratio of terbium and europium ions which are known to have strong luminescent properties and importantly, show inverse responses to temperature. Tb and Eu are poor absorbers of light due to forbidden 4f-4f transitions. MOFs, however, have a unique advantage as the organic linker present in the material is a very strong absorber of light, enabling energy transfer to the lanthanide ion. This results in much greater luminescence from MOFs than other lanthanide-based materials and is known as the antennae effect. This meant that we were able to measure the luminescent response of the two ions in real time to determine the temperature of the MOF powder, thus acting as an in-situ remote thermometer.[2]

Metal-organic Frameworks and Thermometry

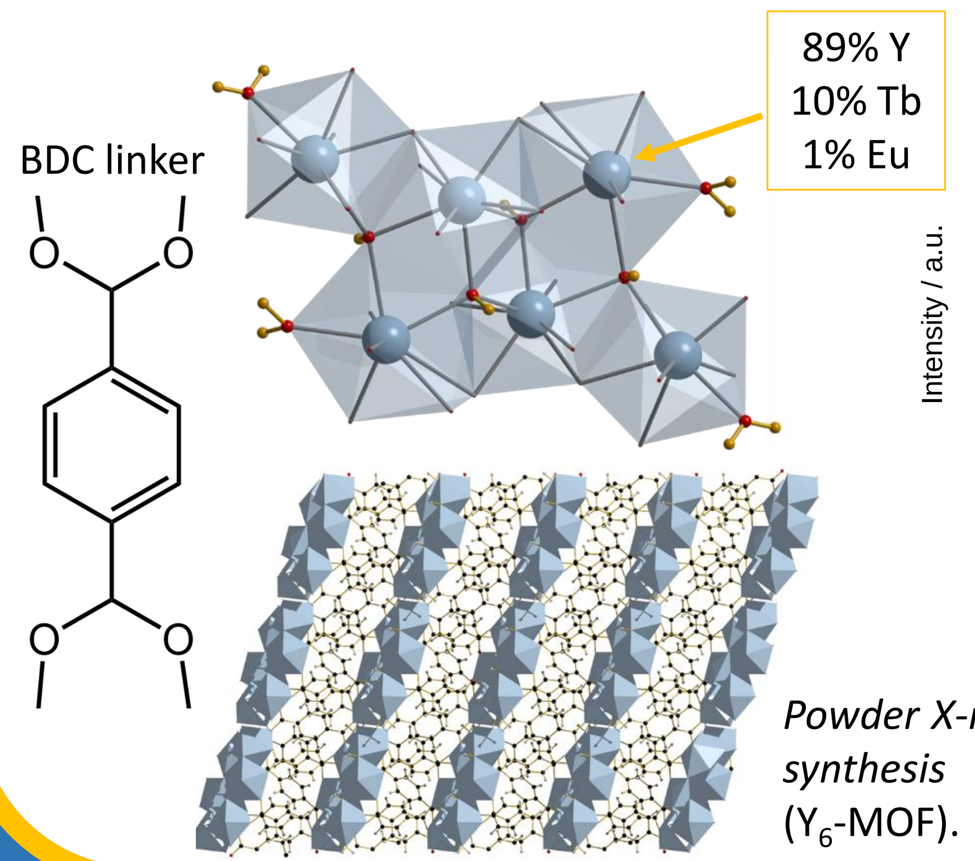
Metal-organic frameworks are an emerging class of porous materials consisting of metal ion clusters connected by organic linkers to form large cage-like structures which extend infinitely in two or three-dimensions. MOFs are well known for their large internal surface areas where in some cases, 1 gram of MOF powder can have a surface area exceeding that of a football pitch.

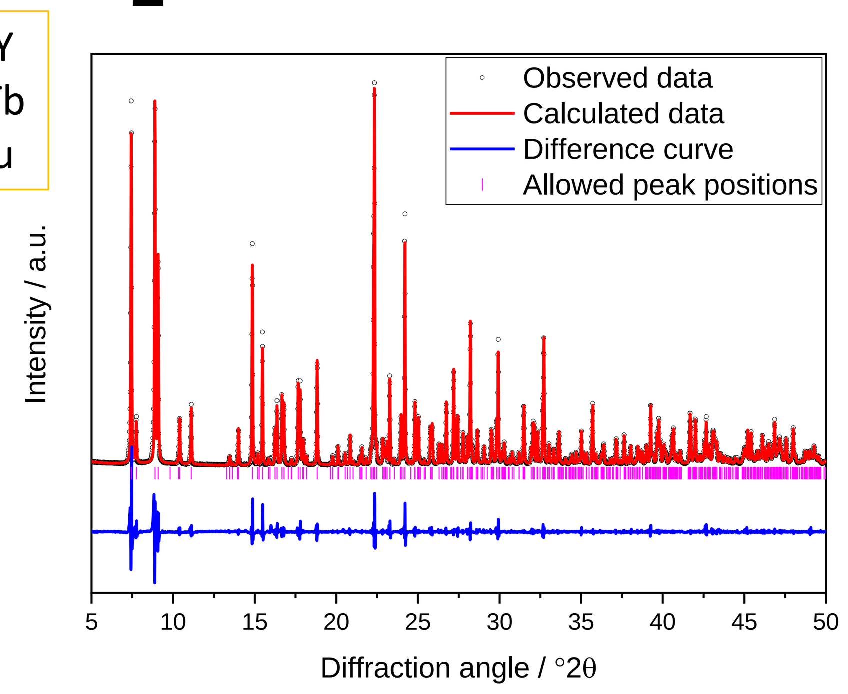
Four prototypical MOFs



- Optical thermometers are extremely useful for measuring the temperature of small or inaccessible objects such as microfluids, animal or plant cells or the bulk of a chemical reactor.
- Other MOF thermometers exist, but they lack thermal stability and generally decompose above around 200 °C.
- Other optical thermometers exist, but they are not as versatile as MOFs and lack the enhanced emission intensities of MOFs.

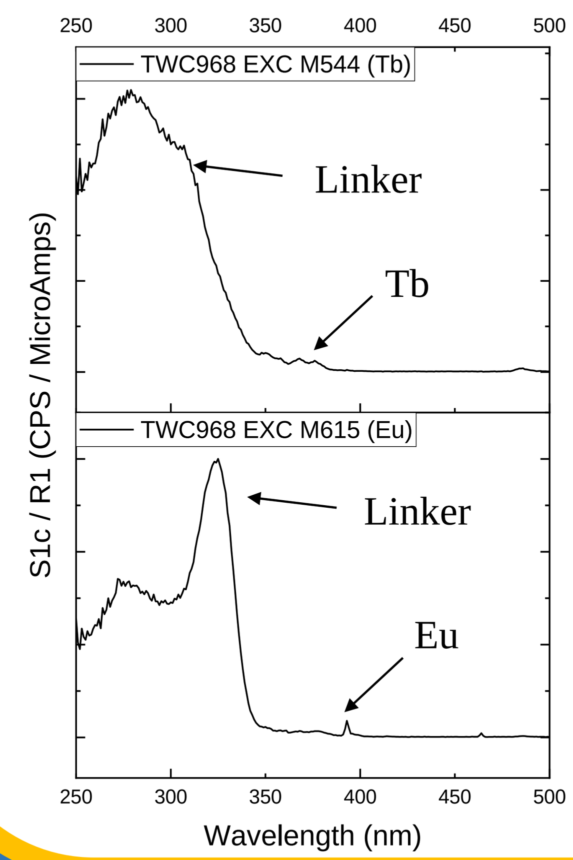
Tb and Eu Substituted Y_6-MOF

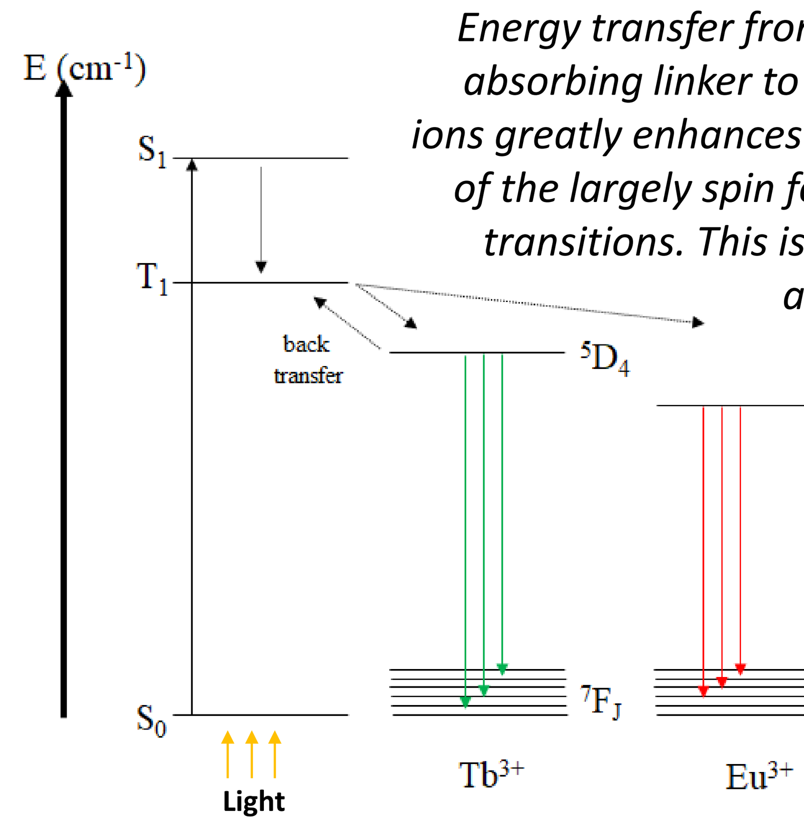




Powder X-ray diffraction confirmed the successful synthesis of $(Y_{0.89}Tb_{0.10}Eu_{0.01})_6(BDC)_7(OH)_4(H_2O)_4$ *(Y_6-MOF).*

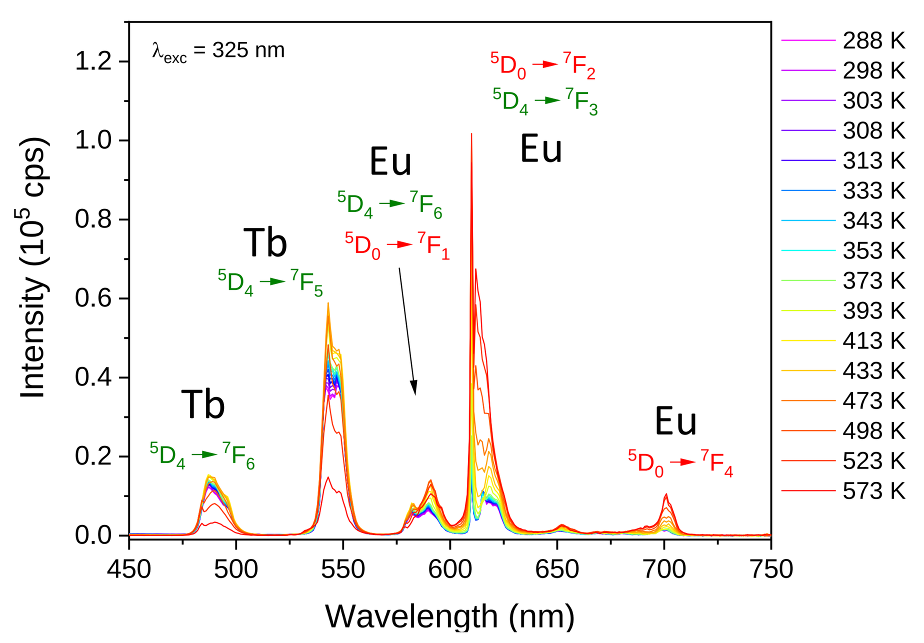
Mechanism of Photoluminescence

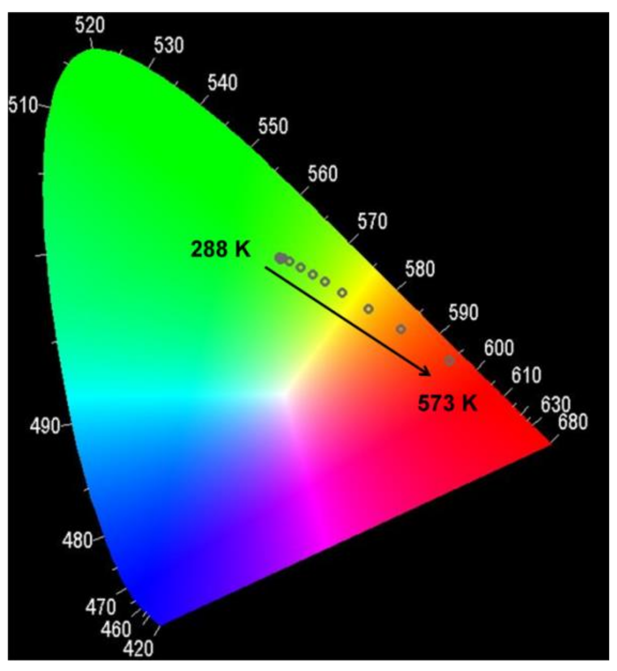




Energy transfer from the strongly absorbing linker to the Eu and Tb ions greatly enhances the emissions of the largely spin forbidden 4f-4f transitions. This is known as the antenna effect.

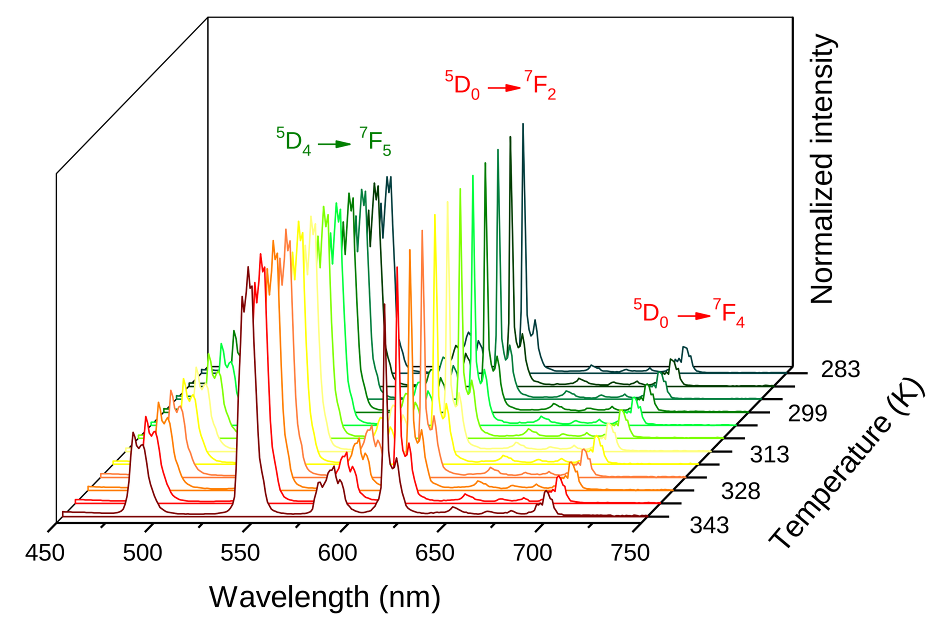
Solid Thermometric Performance to 570K

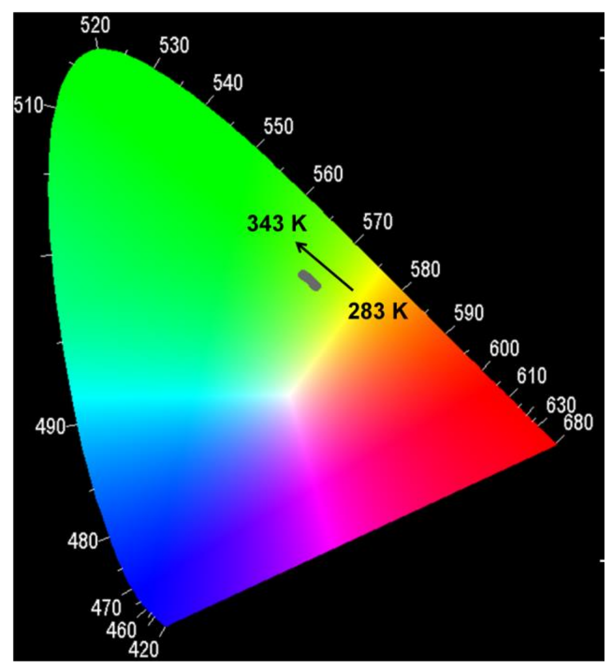




Temperature dependence of the emission intensities of Eu(III) and Tb(III) ions within the Y_6-MOF in air between 288 K and 573 K.

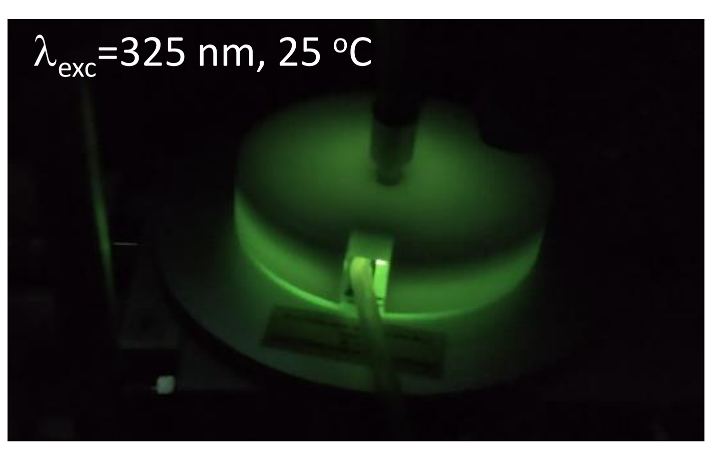
Solution Thermometric Performance to 343K





Temperature dependence of the emission intensities of Eu(III) and Tb(III) ions within the Y_6-MOF in water between 283 K and 343 K.

Optical Emissions of MOF Powder



Photographs of the MOF powder under irradiation of UV light at different temperatures in air. The image on the left was taken at 25 °C where the MOF emits a green colour and at 300 °C where the MOF emits an orange/red colour.

Conclusions

- The yttrium-based Y_6-MOF was synthesised by a hydrothermal synthesis method and successfully doped with 10% Tb and 1% Eu.
- Eu and Tb emissions are very strong due to the antennae effect from the highly absorbing organic linker.
- The MOF exhibits a reversible, temperature dependent photoluminescence across an extreme temperature range, especially in air.
- The MOF can act as a remote optical temperature sensor in air or in water from room temperature up to at least 573K / 300 °C.

References

[1] D. F. Weng, X. J. Zheng and L. P. Jin, Eur. J. Inorg. Chem., 2006, 4184-4190
[2] T.W. Chamberlain, R. V. Perrella, T. M. Oliveira, P. C de Sousa Filho and R.I. Walton, *Chem. - Eur. J.*, 2022, **28**, e202200410

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