Supporting Information

Lifetime thermometry with an ytterbium(III)-terbium(III) molecular upconverter

Diogo A. Gálico[†], Muralee Murugesu[†]*

[†]Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada.

*Corresponding Author: M. Murugesu (E-mail: m.murugesu@uottawa.ca)

Materials and synthesis

All chemicals were purchased and of reagent grade. All manipulations were performed under aerobic conditions. The **{$Tb_{10}Yb_{10}$}** MCA was synthesized by adding $Tb(NO_3)_3{\cdot}6H_2O$ (226.5 mg), $Yb(NO_3)_3{\cdot}5H_2O$ (224.5 mg), and 6-chloro-2-pyridinol (130 mg) in 10 mL of MeOH and 10 mL of MeCN. After solubilization, 1.00 mmol of triethylamine (139 µL) was added to the solution. The system was kept closed under stirring for 12 hours. At the end of this time, the vial was left open and undisturbed for solvent evaporation, and pale-yellow crystals were obtained in the following 5 days with yields around 30%. ICP analysis: calcd (50% Tb; 50% Yb); obtained (52.8% Tb; 47.2% Yb).

Characterizations

Powder X-ray diffraction (PXRD) data were collected in a Bruker D8 Endeavor diffractometer with CuKα (1.5418 Å) radiation source equipped with LynxEye XE-T silicon strip detector, ranging from 4° to 20° (2θ) and scan speed about 1.1° min^{-1}. Attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra were obtained in an Agilent Cary 630 spectrometer, ranging from 4000 to 600 cm^{-1}. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed with an Agilent 5110 ICP-OES instrument.

Photoluminescence studies were carried out in deuterated methanol suspension (0.1 mg mL^{-1}), using a Horiba QuantaMaster 8075-21 spectrofluorometer equipped with a Hamamatsu R13456 red extended PMT detector. The excitation of the samples was performed using a 980 nm CW laser (max power: 2 W) focused with a 62.3 mm focal length lens. The emission spectra were corrected according to the optical system of the emission monochromator and the photomultiplier response. For temperature-dependent measurements, a cuvette was placed inside a single cuvette Peltier K-155-C. At each temperature change, the system was allowed 15 minutes for stabilization before measurements. Absolute quantum yields were obtained with a K SPHERE petite integrating sphere and the **{Gd_{20}}** analogue was used as the blank reference (no absorption at 980 nm). The incident laser power was measured with a ThorLabs PM100D compact power meter.

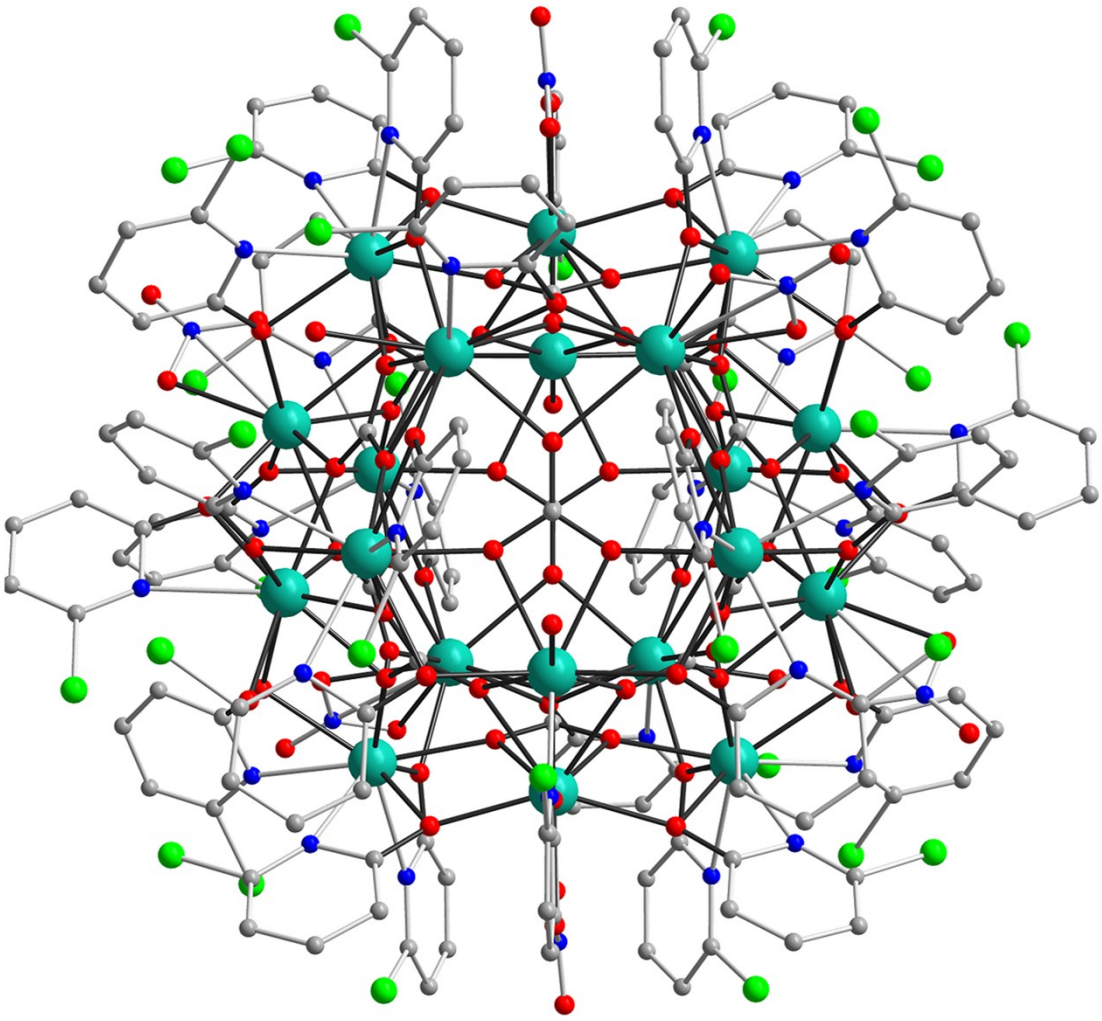

Figure S1. Crystal structure of **{Tb_{20}}** MCA (CCDC 2023789). Colour code: Cyan Ln^{III}; red O; grey C; blue N; green Cl. Hydrogen atoms were omitted for clarity.

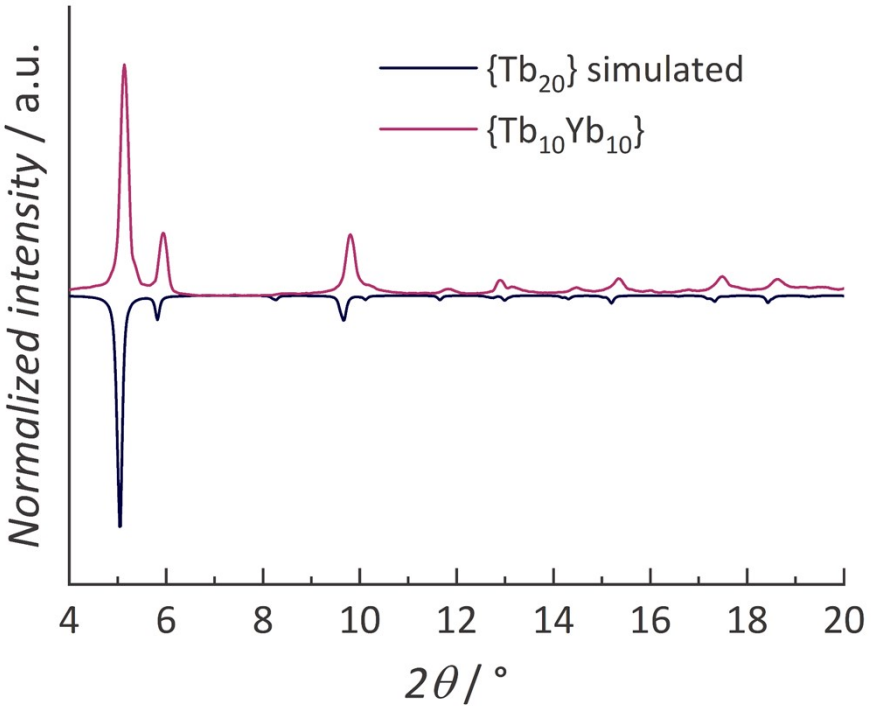

Figure S2. Simulated (black) and experimental diffractogram for **{$Tb_{10}Yb_{10}$}** MCA. Simulated pattern refers to **{Tb_{20}}** MCA (CCDC 2023789).

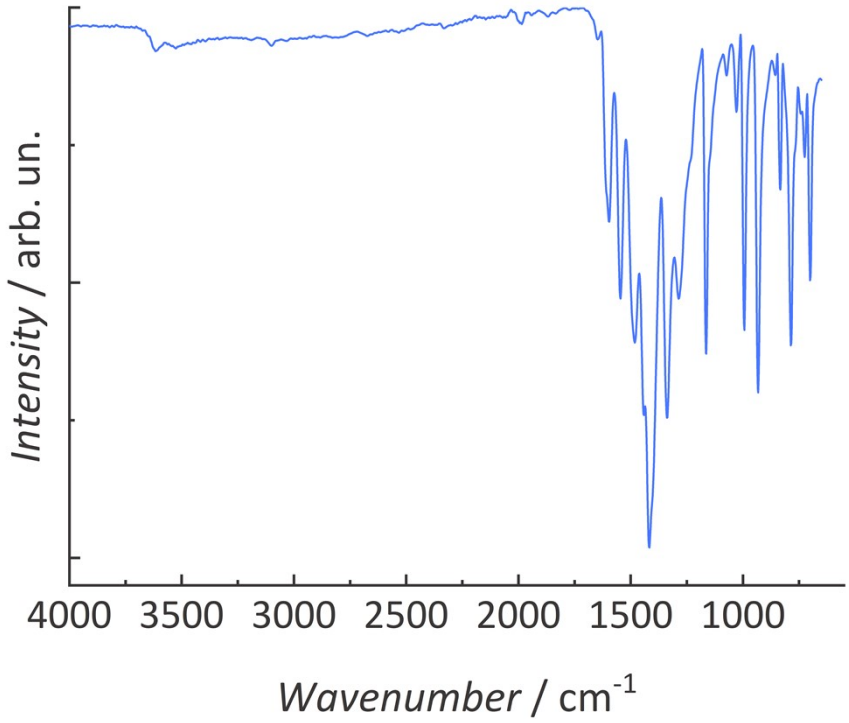

Figure S3. Fourier transform infrared spectra of **{$Tb_{10}Yb_{10}$}** MCA.

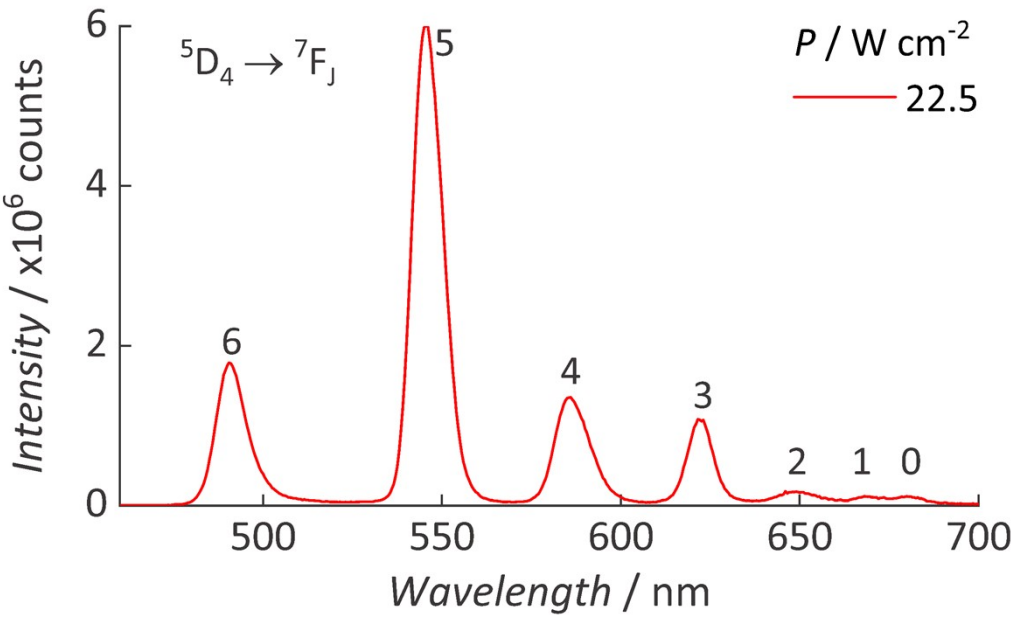

Figure S4. Upconversion spectrum of **{$Tb_{10}Yb_{10}$}** obtained at 25 °C, excited at 980 nm with an incident power density of 22.5 W cm^{-2}.

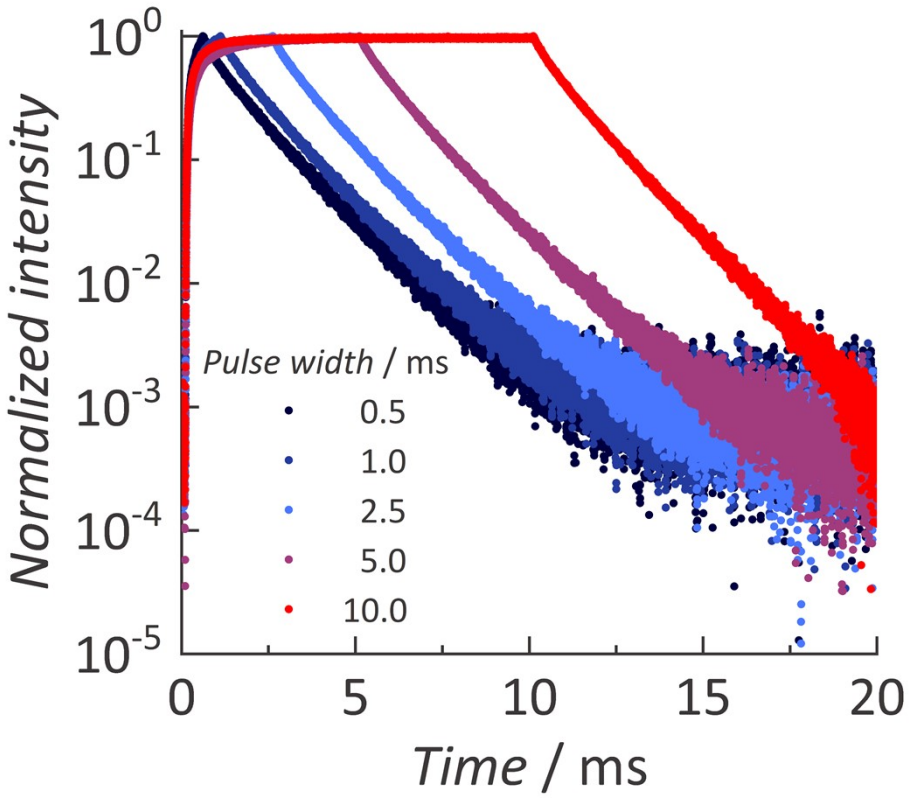

Figure S5. Emission decay curves (log scale) obtained at 25 °C monitoring Tb^{III} $^5D_4$ emitter state (545 nm), excited at 980 nm with different excitation pulse width.

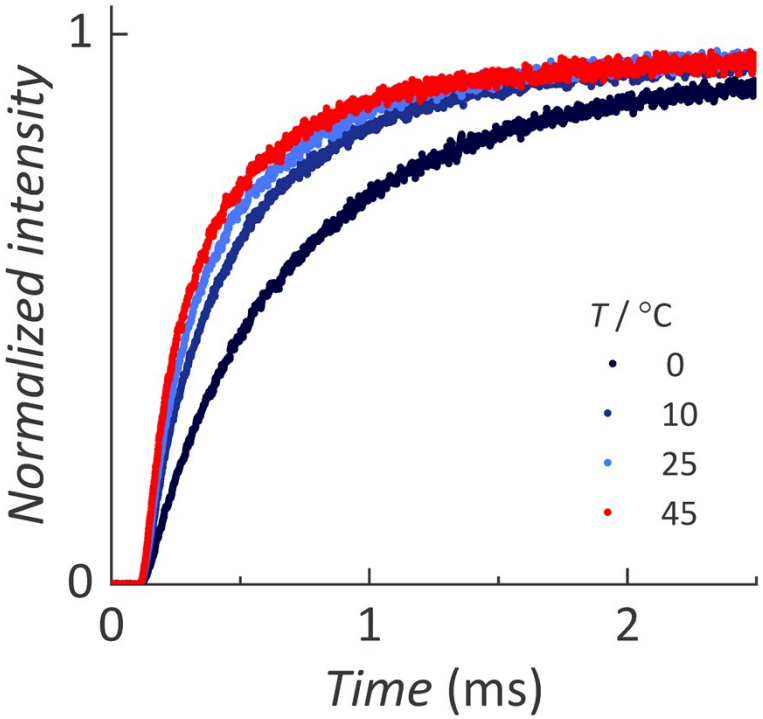

Figure S6. Magnification of the emission decay curves (Figure 3a) in the 0 – 2.5 ms time range at different temperatures.

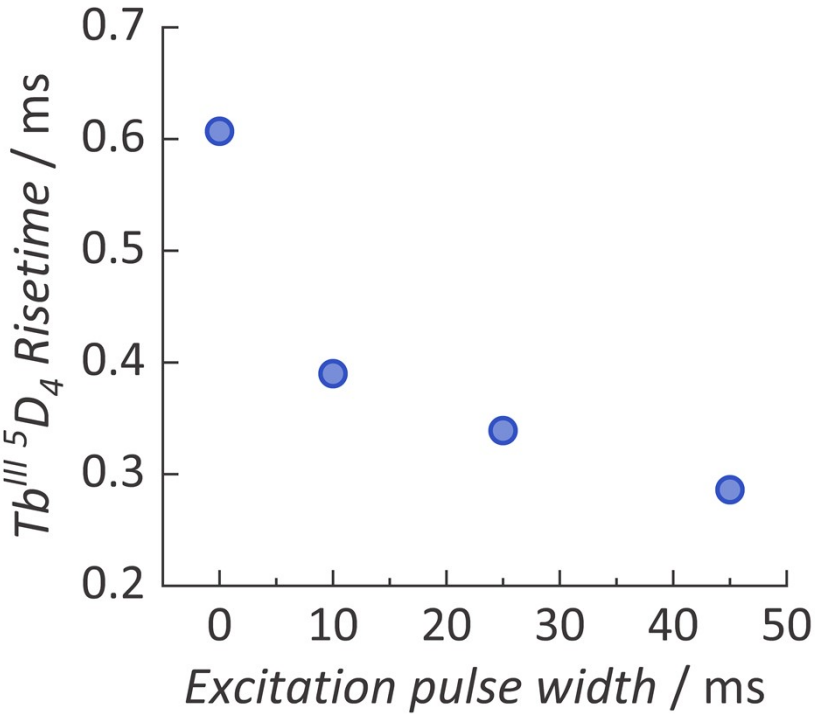

Figure S7. Tb^{III} $^5D_4$ risetime at different temperatures.

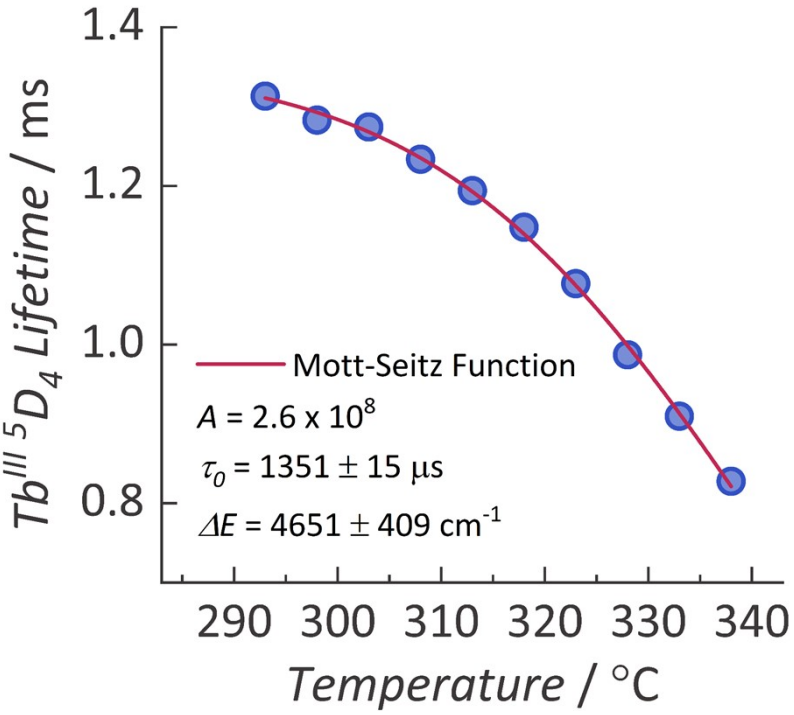

Figure S8. Mott-Seitz plot for the **{$Tb_{10}Yb_{10}$}**.