Supporting Information

A ratiometric luminescence thermometer based on lanthanide encapsulated complexes

Aribam Rishikanta Sharma,^{a†} Atom Rajiv Singh,^{a†} Anju Ajayan Kongasseri,^b Swadhin Garain,^c Ann Mariella Babu,^d Rajkumari Lonibala^{*a} and Raju Laishram^{*a}

^{a.} Department of Chemistry, Manipur University, Manipur – 795003, India.

^{b.} New Chemistry Unit and School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) Jakkur, Bangalore 560064, India.

^{c.} University of Würzburg, Würzburg, Germany.

^{d.} Christ University, Bengaluru, 560029, India.

⁺Both Authors Contributed Equally

Email: rajulaishram007@gmail.com

Chemicals.

All the chemicals were brought commercially and were used as received with no further purification. 5-amino isophthalic acid (Sigma Aldrich), Calcium Acetate (Loba Chemie), Terbium Chloride Hexahydrate (SRL), Europium Chloride Hexahydrate (Sigma Aldrich), N, N-Dimethylacetamide (SDFCL), Ethanol (Analytical CS) and methanol (Merck).

Characterization and Photoluminescence Measurement.

Powder X-ray diffraction patterns were recorded using PAN analytical powder diffractometer (X'Pert PRO) with CuK α (1.5405Å) radiation (40kV and 30mA) having a step size of 0.02 and with scan step time 0.3 s in the angular range of $2\theta = 10^{\circ} \le 2\theta \le 80^{\circ}$. Fourier transform infrared spectra (FTIR) for the samples were also measured using SHIMADZU IRAffinity-1S spectrometer. Photoluminescence Emission Spectra, Excitation Spectra, Emission Lifetime and Quantum Yield were recorded using an Edinburgh FLS1000 Fluorimeter equipped with Multichannel Scaling (MCS) and Integrating Sphere. The measurements were carried out from 40 K to 380 K. Time-dependent Photoluminescence Emission Spectra of CAT was measured in Agilent Cary-Eclipse Fluorescence Spectrophotometer.

Encapsulation details

 $TbCl_3$ (60 mM), EuCl_3 (60 mM) and CA (0.6M) solution were prepared in methanol. The prepared samples were mixed as per the conditions given in Table SI1.

Sample Name	CA (ml)	Tb (ml)	Eu (ml)	Tb : Eu Ratio
CAT	1.2	2.4	0	5:0
CATE1	1.2	2.4	0.24	5:0.5
CATE2	1.2	2.4	0.48	5:1
CATE	1.2	2.4	0.96	5:2

 Table SI1 Encapsulation conditions

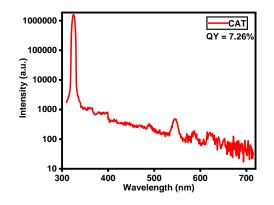


Fig. SI1 Quantum yield data of CAT

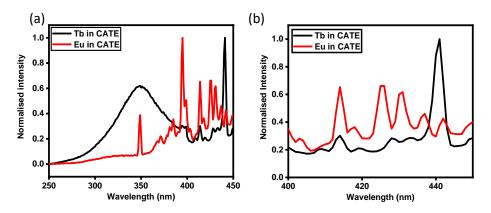


Fig. SI2 (a) Excitation spectra of Tb and Eu in CATE (b) Expansion of (a) from 400 nm to 450 nm

Samples	τ1 ms (%)	τ₂ ms (%)	τ₃ ms (%)	Intensity average lifetime, τ _{avg.}	χ ²
Tb in CAT	0.05 (20.96)	0.15 (34.67)	0.72 (44.37)	0.63	1.19
Tb in CATE	0.01 (14.25)	0.08 (22.65)	0.56 (63.09)	0.53	1.20
Eu in CATE	0.01 (2.09)	0.41 (67.05)	1.34 (30.86)	0.97	1.23

Table SI2 Lifetime data for Tb in CAT and Tb and Eu in CATE

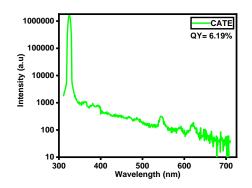


Fig. SI3 Quantum yield data of CATE

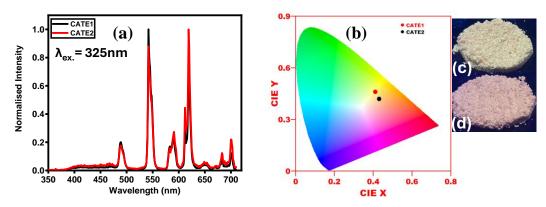


Fig. SI4 (a) Emission spectra of CATE1 and CATE2 (λ_{ex} =325 nm) (b) CIE diagram of CATE1 and CATE2 (c)-(d) Photograph of CATE1 and CATE2 under UV lamp.

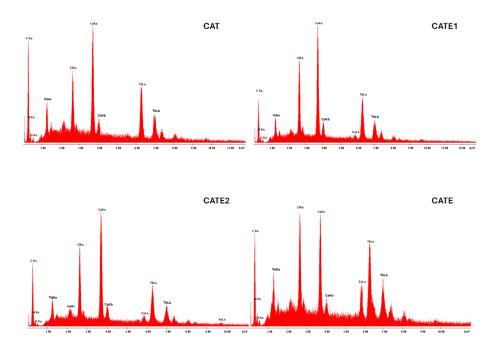


Fig. SI5 EDX graph for CAT, CATE1, CATE2 and CATE

Note: In CAT, no Eu was present. For CATE with different Tb/Eu ratios, the amount we have added matches closely with EDX data from the synthesis complexes.

Sample	Eu % w.r.t. Tb added (theoretical)	Eu % w.r.t. Tb from EDX (experimental)	Ca:Tb: Eu %
CAT (Tb:Eu. 5:0)	0	0	22:78:0
CATE1 (Tb:Eu , 5:0.5)	9.09 %	8.23 %	26:68:6
CATE2 (Tb:Eu, 5:1)	16.66 %	13.99 %	27:63:10
CATE (Tb:Eu, 5:2)	28.57 %	27.57 %	12:64:24

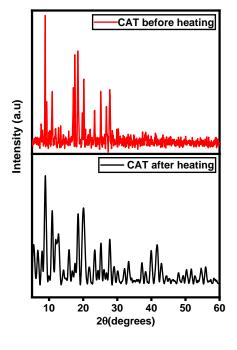


Fig. SI6 pXRD of CAT before and after heating

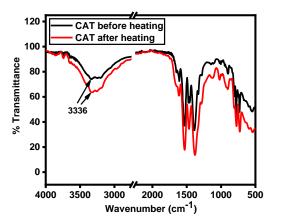


Fig. SI7 IR Spectra of CAT before and after heating

 Table SI3 Different Metal percentage

Samples	Thermometric	Maximum Sensitivity	Temperature
	parameter (∆)	(S _m)	uncertainty range (δT)
CAT (CA vs Tb)	160 K – 380 K	0.95 % K ⁻¹	0.03 K – 0.25 K
CATE (CA vs Tb)	160 K – 380 K	0.76% K ⁻¹	0.03 K – 0.46 K
CATE (Tb vs Eu)	280 K – 380 K	1.03% K ⁻¹	0.03 K – 0.31 K
CATE (CA vs Eu)	160 K – 380 K	1.11% K ⁻¹	0.02 K – 0.51 K

Table SI4 Temperature parameters for different sample

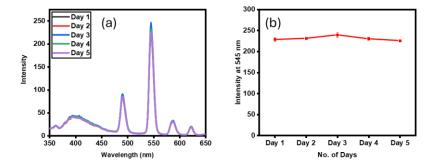


Fig. SI8 (a) Emission Spectra of CAT on storage and (b) Intensity of Tb with storage

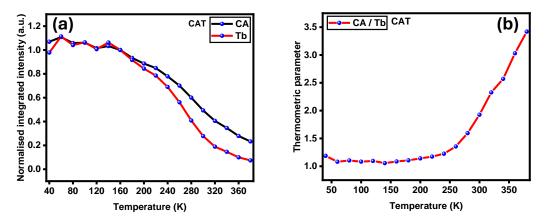


Fig. SI9 (a) Normalized integrated intensity comparison for CA and Tb in CAT. (b) Thermometric parameter for CA / Tb in CAT.

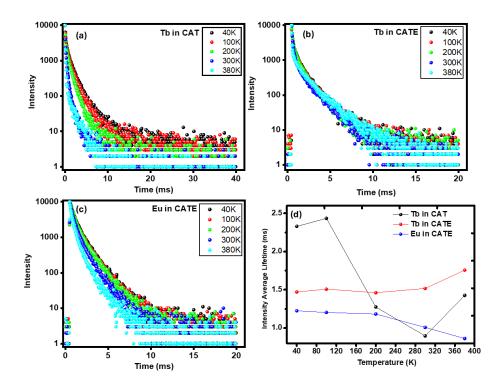


Fig. SI10 (a) Luminescence Lifetime of Tb in CAT (b) Luminescence Lifetime of Tb in CATE (c) Luminescence Lifetime of Eu in CATE (d) Intensity lifetime of Tb and Eu in CAT and CATE with temperature

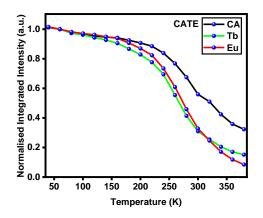


Fig. SI11 Normalized integrated intensity comparison for CA, Tb and Eu in CATE.

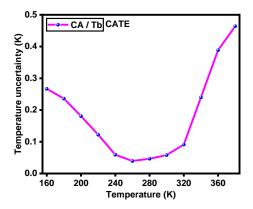


Fig. SI12 Temperature uncertainty for CA / Tb in CATE.

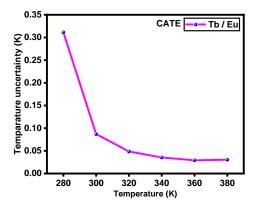


Fig. SI13 Temperature uncertainty for Tb / Eu in CATE.

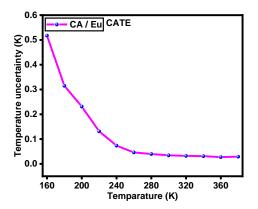


Fig. SI14 Temperature uncertainty for CA / Eu in CATE