Supporting Information of

Luminescent Terbium and Europium Probes for Lifetime Based Sensing of Temperature between 0 and 70 °C†

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1. Synthesis and characterization of ligand 1,8-bis(4-methyl-2-hydroxy-benzamido)-3,6-dioxaoctane (L3) and it Tb (III) complex (Tb-L3)

The ligand **L3** and complex **Tb-L3** were synthesized according the literature methods (shown in Figure S1).[1, 2] The details of **L3** are given as the following: ethyl 5-methylsalicylate and triethylenetetramine mixed together and heated at 100 ˚C on an oil bath under stirring for 24 h. The mass was then crystallized from a 1:l (in volume) ethanol-water mixture, affording a white solid.

L3: ^{1}H NMR (300 MHz, Chloroform-d, δ): 2.20 (s, 6H, Ar-CH_3), 2.79 (s, 4H, 4,5-CH_2), 2.87 (t, J = 5.63 Hz, 4H, 3,6-CH_2), 3.55 (t, J = 5.49 Hz, 4H, 2,7-CH_2), 6.40

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† Electro supplementary information (ESI) available: TGA, Photostability curves, and synthesis and photophyscial properties of **Tb-L3**.

(s br, 4H, 3,6-(CH_2)-N*H* and Ar-O*H*), 6.85 (d, *J* = 8.51 Hz, 2H, Ar*H*), 7.09 (d, *J* = 8.51 Hz, 2H, Ar*H*), 7.31 (d, *J* = 1.39 Hz, 2H, Ar*H*), 7.74 (s br, 2H, 2,7-(CH_2)-N*H*). ^{13}C NMR (300 MHz, Chloroform-d, δ): 20.47 (Ar-*C*H_3), 39.06 (*C*2, 7), 48.44 (*C*3, 6), 48.54 (*C*4, 5), 115.06(*Ar*), 117.83 (*Ar*), 127.08 (*Ar*), 127.80 (*Ar*), 134.64 (*Ar*), 158.19 (Ar*C*OH), 169.40 (*C*=O). CI-MS (*m/z* (%)): 415.2 (100.0) $[M+H]^+$, 416.3 (24.36) $[M+2H]^+$, 417.3 (3.3) $[M+3H]^+$, 418.3 (5.21) $[M+4H]^+$, 419.3 (14.89) $[M+5H]^+$. Anal. Calcd for $C_{22}H_{30}N_4O_4$: C 63.75, H 7.30, N 13.52; found: C 63.47, H 7.38, N 13.63.

Tb-L3: Anal. calcd: C 22.50, H, 3.09; N, 11.93%; found for $C_{22}H_{36}N_{10}O_{26}Tb_2$: C, 22.45; H, 3.15; N, 11.84%.

2. Absorption and fluorescence spectra of Tb-L3 in solution.

The absorption spectra of ligands and complexes show some differences among the Tb (III) complexes because the different groups appear in the benzene ring of the ligands, among which ligands **L2** and **L3** and their corresponding complexes exhibit a little blue and red shift, respectively, in comparison with the ligand **L1** and its complex. Accordingly, the excitation spectra of **Tb-L2** and **Tb-L3** show a little blue and red shift, respectively, being compared with **Tb-L1**. Being different from the bright emissions of **Tb-L1** and **Tb-L2** which shows highly pure green colour due to the strongest emissive band peaks around 545 nm and its full width at half maximum (FWHM) being less than 10 nm, **Tb-L3** shows blue-green colour emission because there is a broad emission band in the blue region from its ligand (Figure S2) besides the typical emission bands of Tb^{3+} ion. This indicates that the energy transfer from the triplet state of **L3** is not such efficient as that happens in **Tb-L1** and **Tb-L2**. The other photophysical properties of **Tb-L3** are also very different from that of the other two Tb (III) complexes (listed in Table S1). Among the three Tb (III) complexes, **TbL3** shows a much lower quantum yield, shorter lifetime and weaker brightness. As we know, the methyl is electron-donating group and ethoxyl is electron-drawing group, which can lower and heighten the excited states of the ligands, respectively.

This can explain why differences appear in the absorption spectra and other photophysical properties among three Tb (III) complexes. Therefore, the fluorescence lifetime of **Tb-L3** in DMSO solution is 267 μs, which is roughly 3 times less than that of **Tb-L1** and **Tb-L2** at room. Such photophysical properties can't enable **Tb-L3** to be applied as a good indicator for the temperature-sensitive paints.

Table S1 Photophysical properties of Tb-L3.

Complex	λ_{abs} /nm[a]	λ_{ex}/nm[b]	τ/μs[c]	QY/%[d]
TbL3	319	345	267	2.4

[a] Absorption (λ_{abs}) and excitation (λ_{ex}) spectra peak in solution, 0.1 mM in acetonitrile. [b] Excitation (λ_{ex}) spectra peak, 40 μM solution in acetonitrile. [c] Decay time measured for the transmission of $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+} ion. [d] Relative quantum yield measured in DMSO.

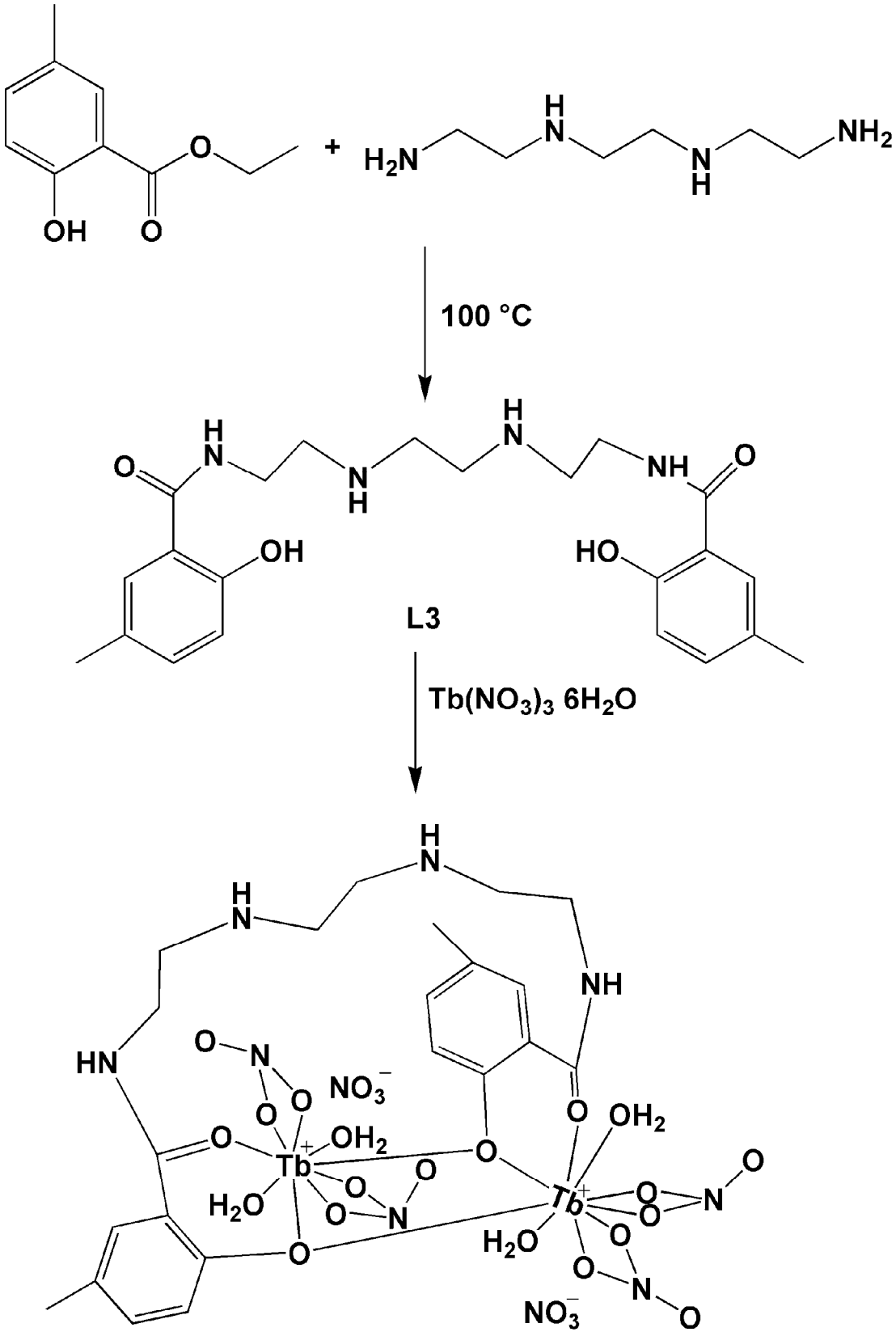

Fig. S1 Scheme of synthesis of **L3** and **Tb-L3**.

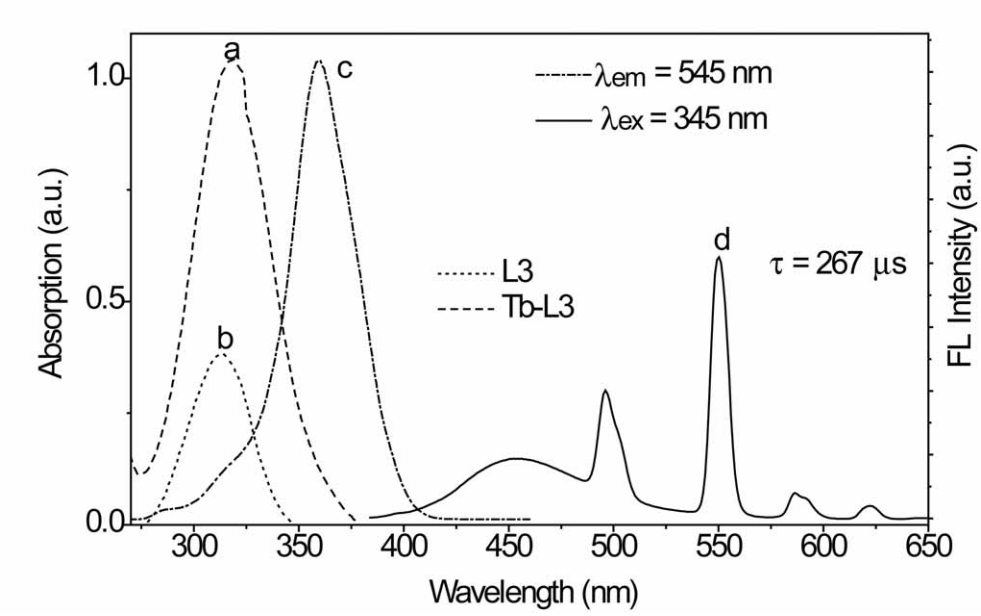

Fig. S2 Absorption and fluorescence spectra of **L3** and **Tb-L3** at RT. Plot a (----): absorption spectrum of ligand **L1** (0.1 mM in acetonitrile); plot b (·····): absorption spectrum; plot c (·-·-·-): excitation spectrum; plot d (──): emission spectrum of the **Tb-L1** complex (40 μM in acetonitrile).

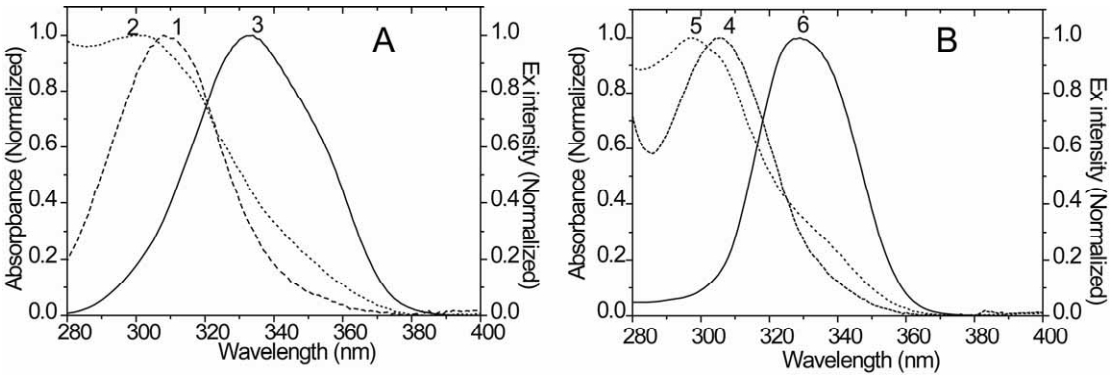

Fig. S3 Normalized absorption and fluorescence excitation spectra of **L1**, **L2**, **Tb-L1** and **Tb-L2** at RT. Graph A, plot 1 (dash): absorption spectrum of ligand **L1** in acetonitrile; plot 2 (dot): absorption spectrum of ligand **L1** in DMSO; plot 3 (solid): excitation spectrum of **Tb-L1** in DMSO. Graph B, plot 4 (dash): absorption spectrum of ligand **L2** in acetonitrile); plot 5 (dot): absorption spectrum of ligand **L2** in DMSO; plot 6 (solid): excitation spectrum of **Tb-L2** in DMSO.

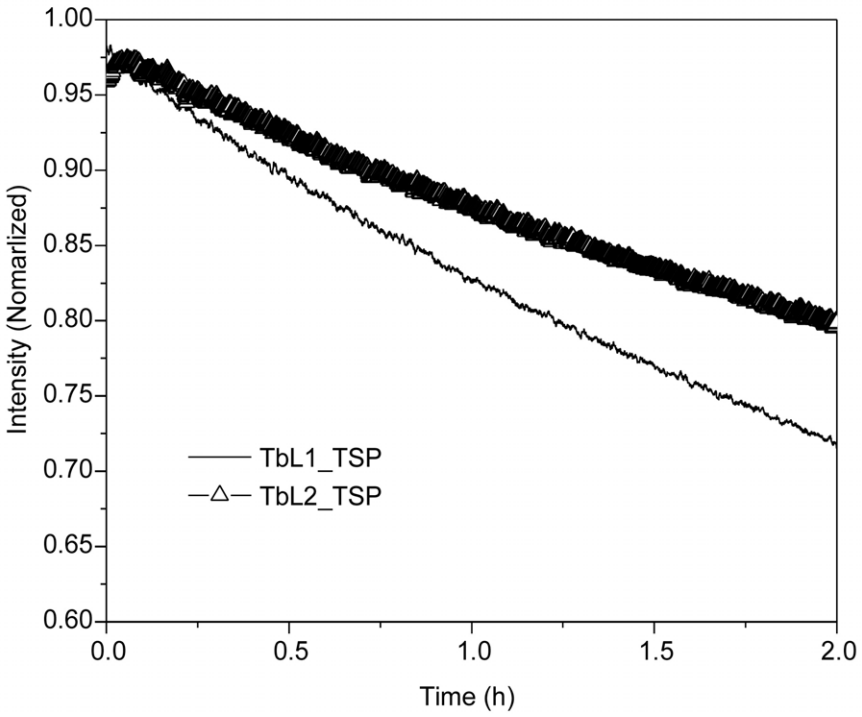

Fig. S4 Photodegradation curves of Tb (III) complexes_TSPs under continuous illumination of 330 nm UV light of Xenon lamp at a power of ~1.0 mW in air (solid, **TbL1**, 3 wt% doped into PMMA; dot, **TbL2**, 5 wt% doped into PMMA).

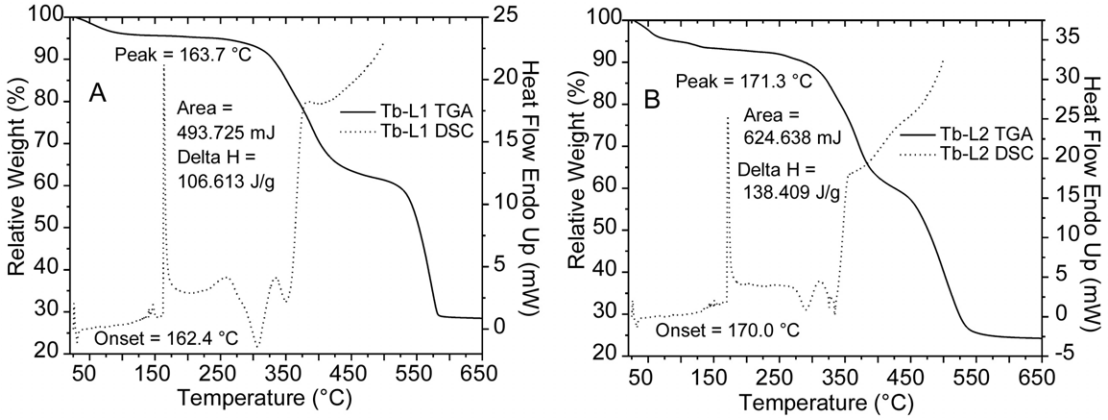

Fig. S5 TGA-DSC curves of Tb (III) complexes (solid: TGA; dot: DSC), A: **Tb-L1**, B: **Tb-L2**, measured at air condition.

References

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2 W. P. W. Lai, W. T. Wong, B. K. F. Li, K. W. Cheah, *New J. Chem.* 2002, **26**, 576.