

**Tetraphenylethylene-based Eu³⁺-metallopolymer with
aggregation-enhanced white emission for self-calibrating
temperature sensing and white light-emitting diodes (WLEDs)**

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Materials and Methods

High performance liquid chromatography (HPLC)-grade tetrahydrofuran (THF) or acetonitrile (MeCN) was purchased from Fisher Scientific and purified over solvent columns. Other solvents were used as received from Sigma Aldrich and stored over 3 Å activated molecule sieves. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization twice from absolute MeOH prior to use. Other chemicals were commercial products of reagent grade and were used without further purification. All manipulations of air and water sensitive compounds were carried out under dry N₂ using the standard Schlenk line techniques. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5700 XPS system equipped with a dual Mg X-ray source and monochromatic Al X-ray source complete with depth profile and angle-resolved capabilities. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000-600 cm⁻¹ using KBr pellets. ¹H NMR spectra were recorded on a Bruker Plus 400 spectrometer with SiMe₄ as the internal standard in CDCl₃ and/or DMSO- δ_6 at room temperature. Electronic absorption spectra in the UV/Visible region were recorded with a Shimadzu UV-3159 UV-Vis-NIR spectrophotometer. Emission and excitation spectra in solid state were collected through Hitachi F-7000 spectrometer. The absolute fluorescence quantum yield and lifetime in solution were measured on a combined fluorescence lifetime and steady-state spectrometer (FLS-1000, Edinburgh). The PL spectra as well as fluorescence lifetime at different temperatures were measured on JY HORIBA FluoroLog-3 spectrometer. Gel permeation chromatography (GPC) analyses of the polymers were performed using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with HPLC THF as the eluant on American Polymer Standard 10 μ m particle size. Transmission electron microscopy (TEM) images were obtained via a FEI Tecnai G2

F20 microscopy. The Commission International de l'Eclairage (CIE) coordinates of each sample were calculated on the basis of the international CIE standards.

Fabrication of the WLED device

The WLEDs was fabricated by combining a NUV chip (Sanan Optoelectronics, 1 W, $\lambda_{em} = 370$ nm) with as-synthesized white light emitting **Poly-Eu(TTA)₃ (2)**. Initially, 10 mg of **Poly-Eu(TTA)₃ (2)** and 50 mg of organic silica gel (ZWL8820) were thoroughly mixed. Then the slurry was kept in vacuum to remove air bubbles, coated on the lead frame of the NUV chip, and cured under 100 °C for 4 h. The obtained N-UV-WLEDs was tested by the Hongpu HP-9000 LED tester.

Synthesis of (2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (VTPE)

To a stirred solution of (2-bromoethene-1,1,2-triyl)tribenzene (2.00 g, 6 mmol), 4-vinylphenylboronic acid (0.89 g, 6 mmol), and Pd(PPh₃)₄ (0.23 g of 0.2 mmol) in 20 ml toluene in three-necked round-bottom flask equipped with a condenser, an addition funnel, and a magnetic stirrer. Degassed aqueous solution of Na₂CO₃ (2 M, 6 mL) was added. The resulting mixture was further refluxed at 90 °C for 24 h. After cooling down to room temperature, the mixture was extracted by using CH₂Cl₂ (3 × 30 mL) and dried over MgSO₄. Then, the organic layer was poured into n-hexane (50 mL). The precipitate was further purified through silica column chromatography by using dichloromethane and n-hexane (v/v, 1/4) as the eluent to give a pale-yellow powder product. Yield: 1.85 g (86%). ¹HNMR (400MHz, CDCl₃): δ (ppm) 7.19 (s, 1H, -Py), 7.17 (s, 1H, -Py), 7.12 (m, 9H, -Py), 7.06 (m, 6H, -Py), 7.02 (s, 1H, -Py), 7.00 (s, 1H, -Ph), 6.64 (q, 1H, -CH=), 5.71 (d, 1H, =CH₂), 5.22 (d, 1H, =CH₂).

Synthesis of 4-([2,2':6',2''-terpyridin]-4'-yl)phenol (TPY-OH)

2-acetylpyridine (4.84g, 40 mmol), p-hydroxybenzaldehyde (2.44 g, 20 mmol), KOH

pallants (3.08 g, 6.27 mmol) and ammonia (60 mL) were added to the round-bottom flask under room temperature and stirred for 24 h. After stirring, ethanol was added to precipitate the product. Then water was used to wash the solid product for three times. Yield: 5.44 g (61%). ^1H NMR (400MHz, $\text{DSMO}-d_6$) δ (ppm): 9.94 (s, 1H, -OH) 8.76 (d, 2H, -Py) 8.66 (d, 4H, -Py) 8.05 (t, 2H, -Py) 7.79 (d, 2H, -Py) 7.53 (d, 2H, -Py) 6.96 (d, 2H, -Py).

Synthesis of 4'-((4-vinylbenzyl)oxy)phenyl)-2,2':6',2''-terpyridine (VTPY)

TPY-OH (13 g, 20 mmol), p-chloromethyl styrene (4.89 g, 40 mmol), KOH (2.25 g, 40 mmol) and DMF (100mL) were added to the round-bottom flask under room temperature and stirred for 12 h. Then the product was precipitated by water. After precipitation, the solid product was washed and dried. Yield: 5.72 g (64%). ^1H NMR (400MHz, CDCl_3) δ (ppm): 8.68-8.75 (m, 6H, -Py), 7.88-7.92 (t, 4H, -Py), 7.44-7.49 (d, 4H, -Py), 7.35-7.38 (t, 2H, -Py), 7.11-7.13 (d, 2H, -Py), 6.72-6.80 (q, 1H, -CH=), 5.77-5.82 (d, 1H, =CH₂), 5.28-5.30 (d, 1H, =CH₂), 5.15 (s, 2H, -CH₂).

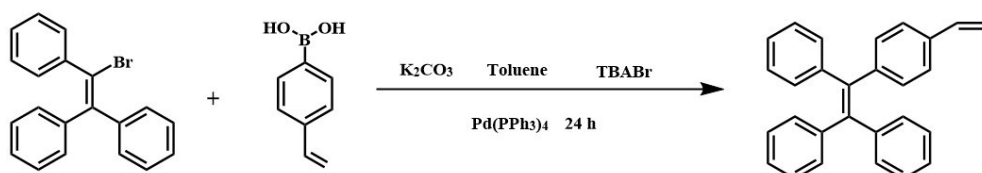
Synthesis of the reference Gd³⁺-metallopolymer Poly-Gd(TTA)₃ and Poly-GdCl₃

To a stirred solution of the polymer backbone Poly(VTPY-co-TPE-co-MMA) (1:2:50) 100 mg in THF, Gd(TTA)₃•2H₂O (0.01 mmol, 8.56 mg) or GdCl₃•6H₂O (0.01 mmol, 3.71 mg) were added, respectively. Then, the solution was refluxed under the protection of N₂ for 24 h. After cooling to room temperature, the resulting solution was precipitated with hexane for three times, washed with diethyl ether and warm ethanol several times, collected by filtration, and dried at 45 °C to constant weight.

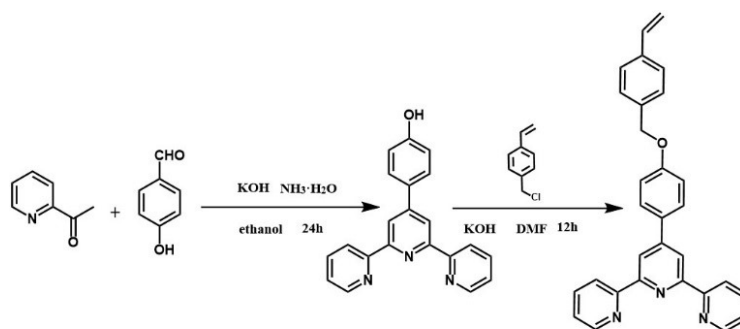
For Poly-Gd(TTA)₃: Yield: 55%. FT-IR (KBr, cm⁻¹): 2988 (w), 2955 (w), 2354 (w), 2347 (w), 1736 (vs), 1543 (w), 1482 (w), 1475 (w), 1452 (m), 1436 (w), 1383 (w), 1272 (m), 1244 (m),

1141 (vs), 987 (w), 845 (w), 746 (w).

For Poly-GdCl₃: Yield: 64%. FT-IR (KBr, cm⁻¹): 2357 (w), 2340 (w), 2359 (w), 2341 (w), 1722 (vs), 1688 (w), 1558 (w), 1541 (w), 1508 (m), 1492 (w), 1478 (w), 1439 (m), 1389 (m), 1269 (m), 1242 (m), 1145 (vs), 987 (w), 840 (w), 750 (w).



Scheme S1. Synthesis procedure for VTPE.



Scheme S2. Synthesis procedure for VTPY.

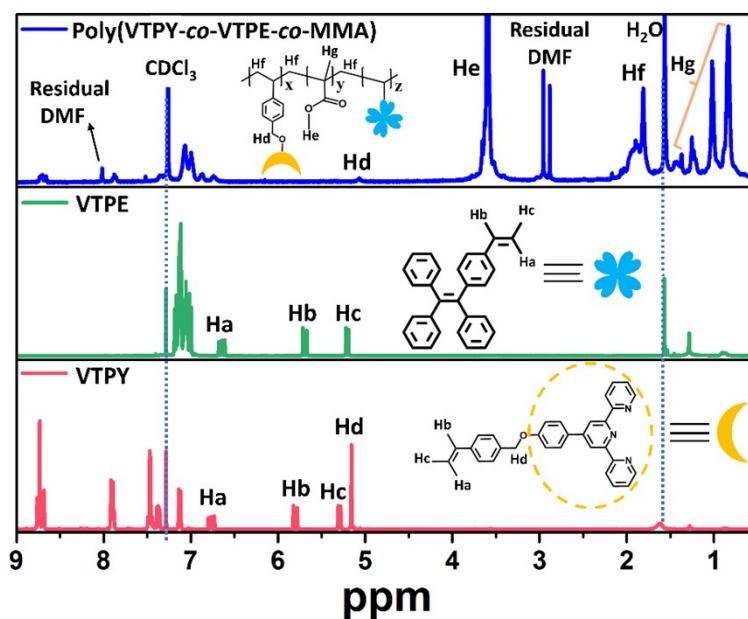


Fig. S1 ¹H NMR spectra of Poly(VTPY-co-VTPE-co-MMA), VTPE and VTPY (CDCl₃, room

temperature).

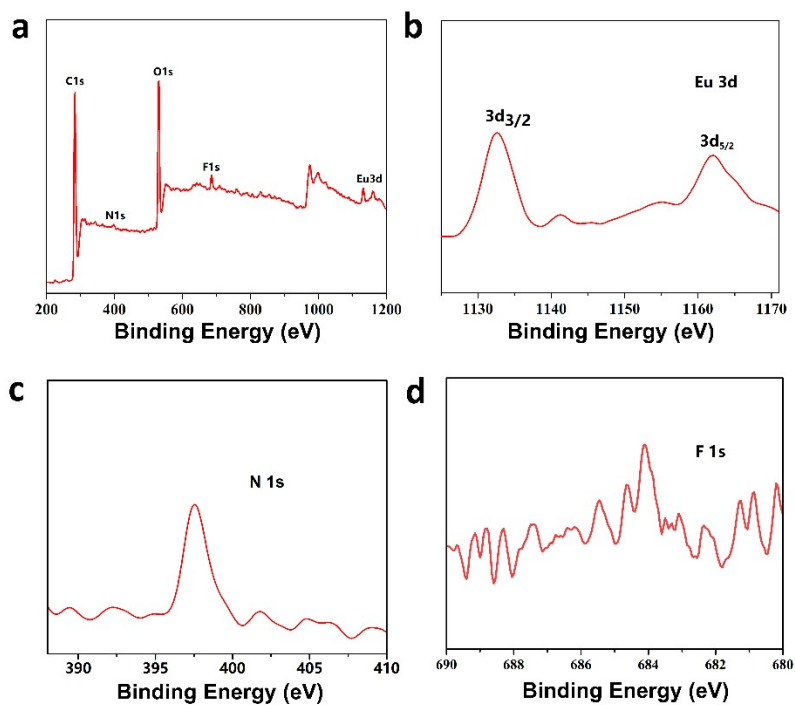


Fig. S2 XPS patterns of Poly-Eu(TTA)₃ (2).

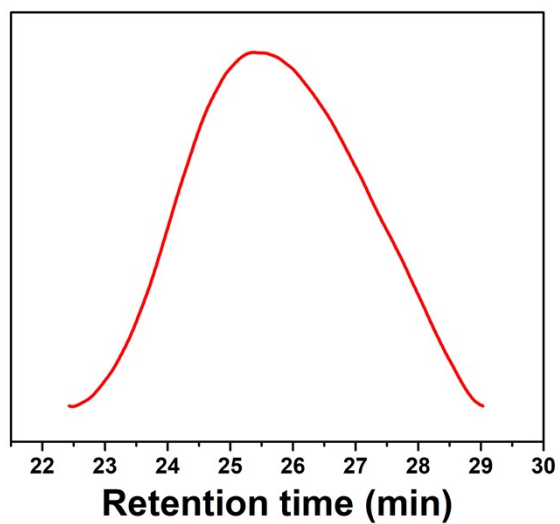


Fig. S3 GPC curve of Poly-Eu(TTA)₃ (2).

Table S1. GPC data for Poly-Eu(TTA)₃ (2).

Polymer	<i>M_n</i>	<i>M_w</i>	<i>M_z</i>	<i>M_z+1</i>	PDI
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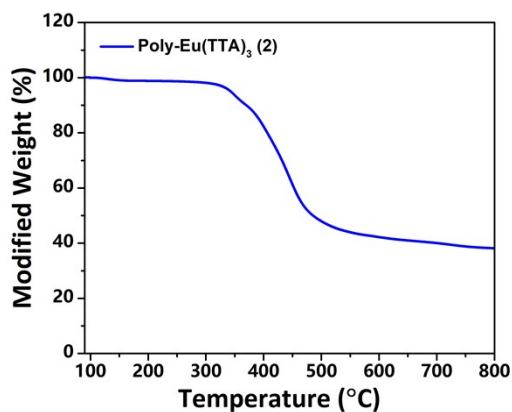


Fig. S4 TGA curve of Poly-Eu(TTA)₃ (2).

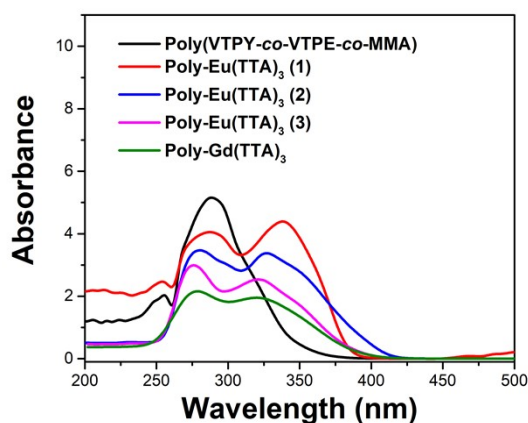


Fig. S5 UV-visible absorption spectra of Poly(VTPY-co-VTPE-co-MMA), Poly-Eu(TTA)₃ (1-3) and Poly-Gd(TTA)₃ in MeCN solution at room temperature (0.1 mg/ml).

Table S2. Photoluminescent properties of the PMMA-supported Poly-Eu(TTA)₃ (1-3), Poly-GdCl₃ and Poly-Gd(TTA)₃ in solid state at RT or 77 K.

Polymer	Excitation	Emission
	λ_{ex}/nm	λ_{em}/nm (Φ)
Poly-Eu(TTA) ₃ (1)	378	483, 598, 618, 656 and 704
Poly-Eu(TTA) ₃ (2)	380	484 ($\Phi_{484 nm}$: 18.51%), 597, 618, 655 and 704 (Φ_{all} : 51.99%)
Poly-Eu(TTA) ₃ (3)	381	484, 596, 618, 654 and 703
Poly-Gd(TTA) ₃	383	487 (Φ : 19.67%)
Poly-GdCl ₃	389	476
	391	484 (77 K)

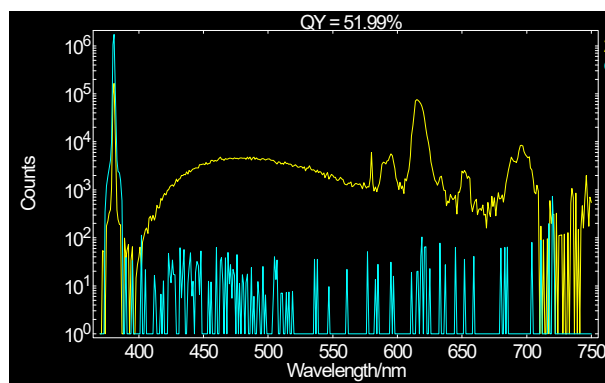


Fig. S6 The absolute fluorescence quantum yield for the Poly-Eu(TTA)₃ (2) excited at 380 nm.

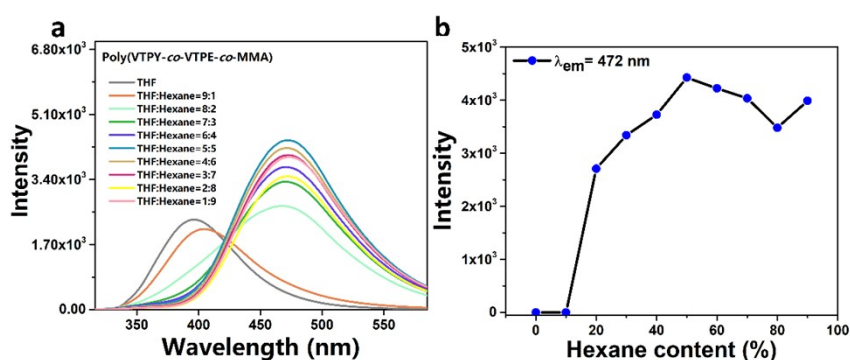


Fig. S7 (a) PL spectra of Poly(TPY-co-TPE-co-MMA) in THF-Hexane mixtures with different hexane content and (b) the intensity of the emission monitored at 472 nm.

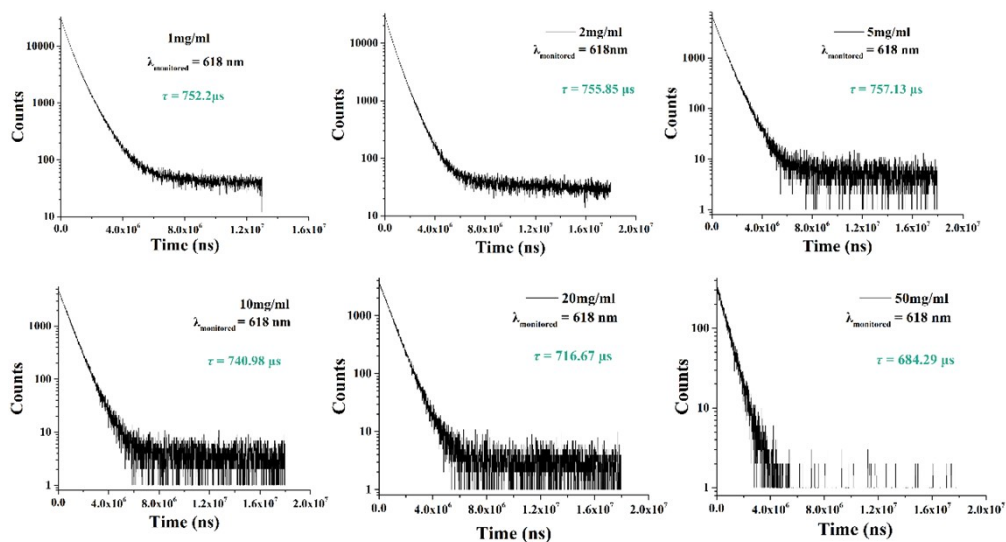


Fig. S8 Luminescence lifetime of Poly-Eu(TTA)₃ (2) THF solution monitored at 618 nm in different concentrations.

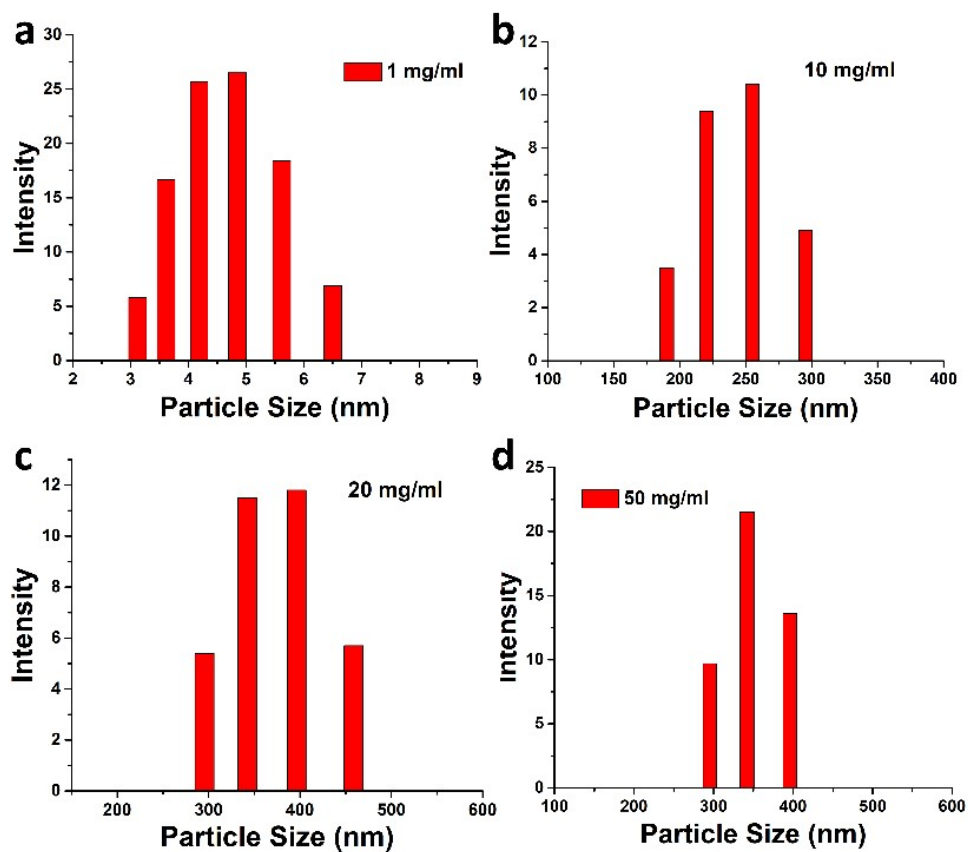


Fig. S9 Particle size of high proportion aggregate of Poly-Eu(TTA)₃ (2) THF solution at the concentration of (a) 1 mg/ml; (b) 10 mg/ml; (c) 20 mg/ml and (d) 50 mg/ml.

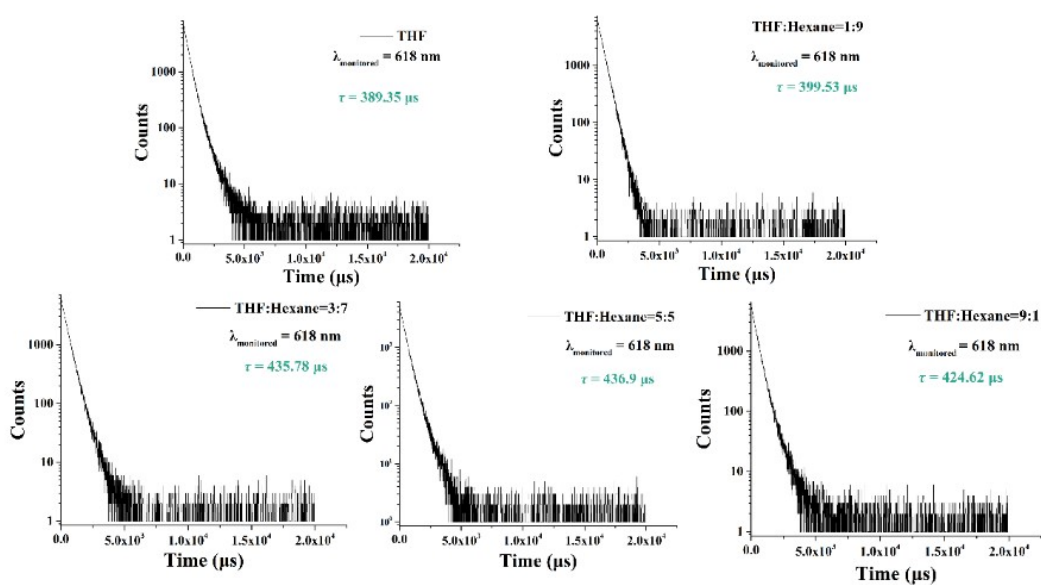


Fig. S10 Luminescence lifetime of 0.1 mg/ml Poly-Eu(TTA)₃ (2) monitored at 618 nm in THF-Hexane mixtures with different hexane content.

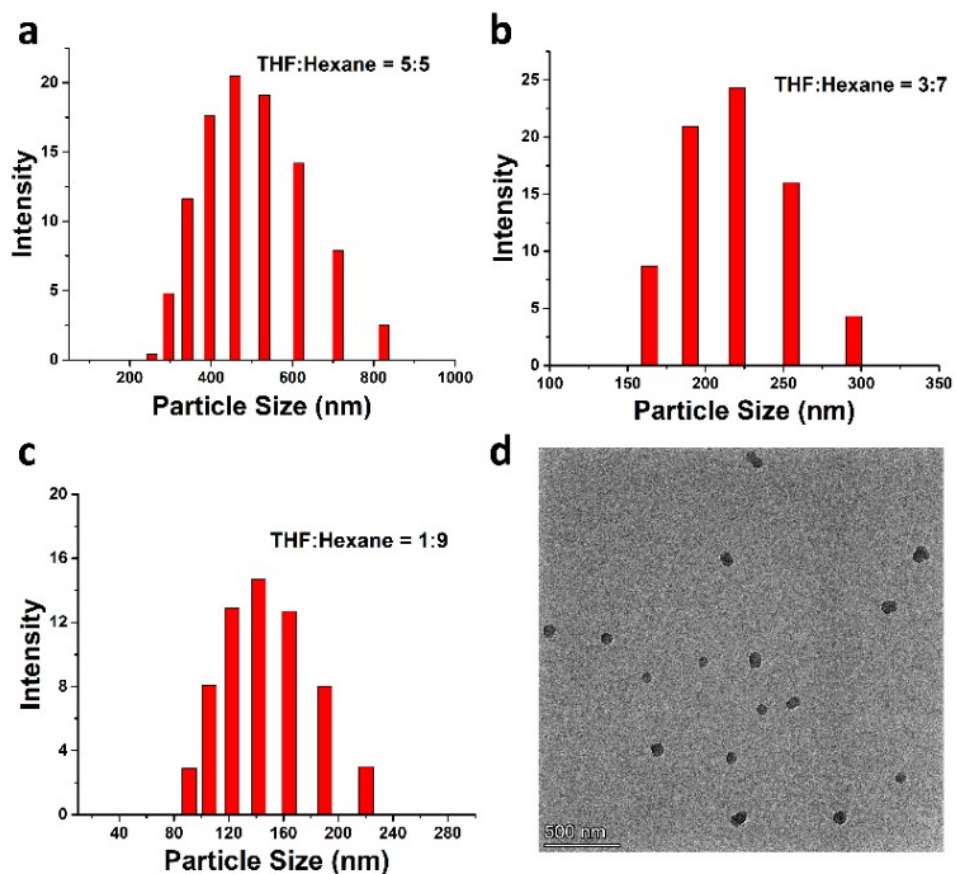


Fig. S11 (a-c) Particle size of high proportion aggregate of Poly-Eu(TTA)₃ (2) in THF-Hexane mixtures with different hexane content; (d) TEM micrograph of Poly-Eu(TTA)₃ (2) self-assembly morphology in THF-Hexane at the molar ratio of 1:9.

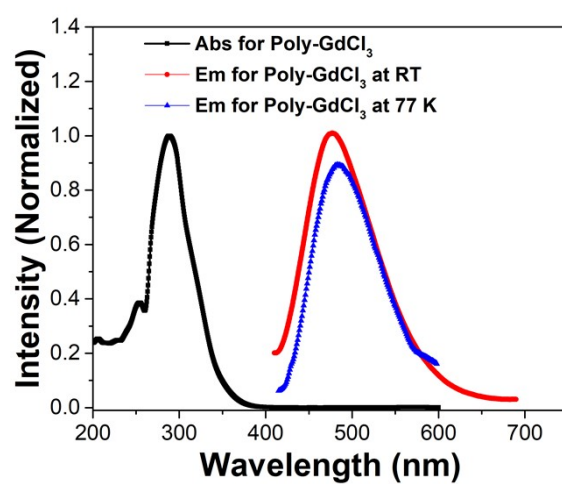


Fig. S12 UV-vis spectrum of Poly-GdCl₃ in MeCN solution, and its emission spectra in solid state at room temperature or 77K.

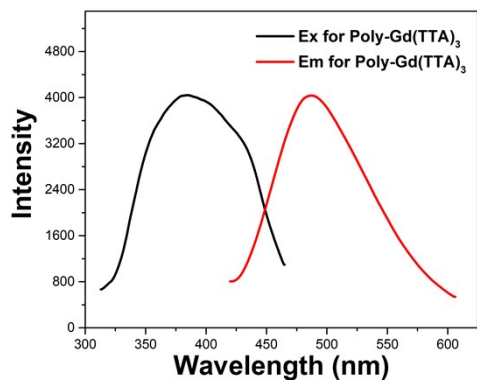


Fig. S13 PL spectra of Poly-Gd(TTA)₃ in solid state at RT.

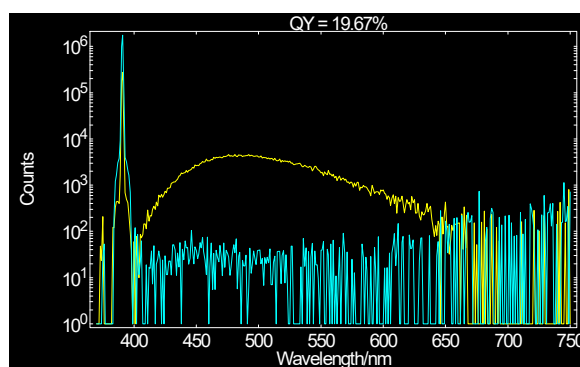


Fig. S14 The absolute fluorescence quantum yield for the Poly-Gd(TTA)₃ excited at 383 nm.

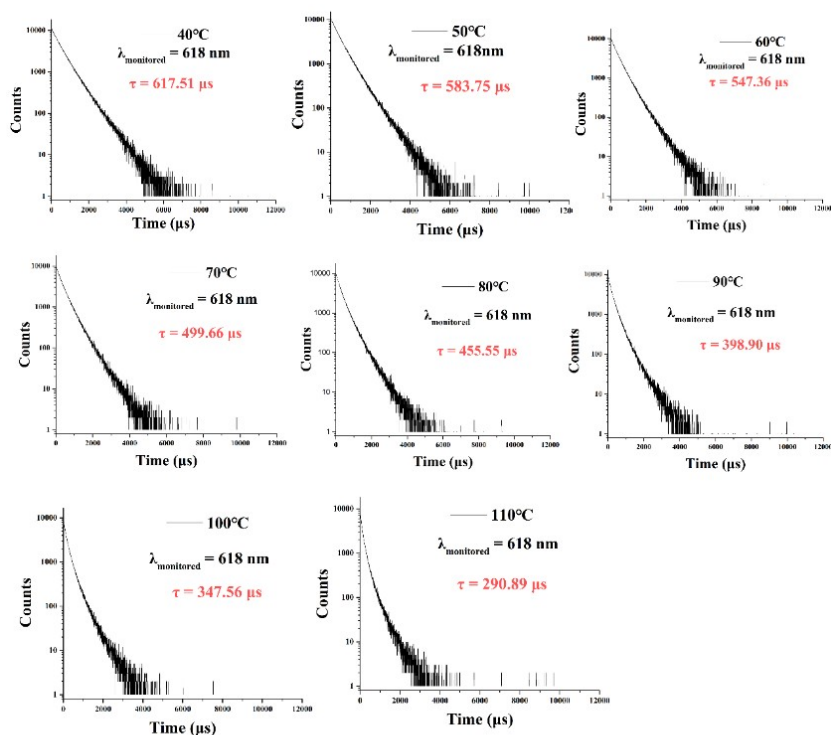


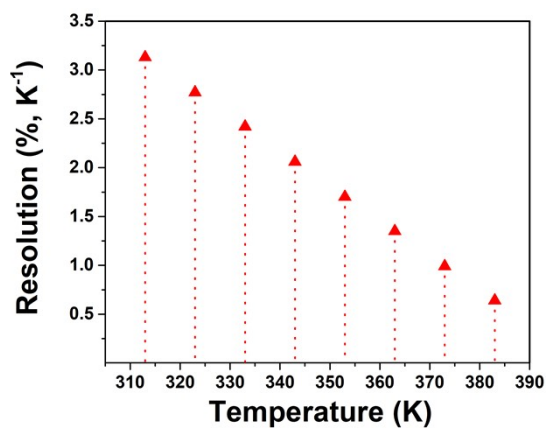
Fig. S15 Luminescence lifetime of Poly-Eu(TTA)₃ (2) monitored at 618 nm at different temperature.

Table S3. Color-integration results and lifetime of Poly-Eu(TTA)₃ (2) at different temperatures.

Metallopolymer	Temperature (°C)	$\tau_{\text{Eu}^{3+}}$ (μs)	CIE coordinates
Poly-Eu(TTA) ₃ (2)	40	617.57	(0.331, 0.310)
	50	583.75	(0.321, 0.310)
	60	547.36	(0.311, 0.311)
	70	499.66	(0.297, 0.312)
	80	455.55	(0.282, 0.313)
	90	398.90	(0.267, 0.314)
	100	347.56	(0.252, 0.316)
	110	290.89	(0.240, 0.319)

Table S4. Comparison of the Maximum Relative Sensitivities (Sr) between the present Poly-Eu(TTA)₃ (2) and other Eu³⁺-contained thermometers reported recently.

Material	Temp range	Max S _r (T)	ref
CsPbBr ₃ @Eu-BTC	20-100 °C	3.9% °C ⁻¹ (20 °C)	(1)
LaPPS75Eu	260-380 K	3.29% K ⁻¹ (380 K)	(2)
[Tb _{0.94} Eu _{0.06} (bpy) ₂ (NO ₃) ₃]	0-400 K	2.0% K ⁻¹ (262 K)	(3)
Tb _{0.95} Eu _{0.05} (btb)	10-320 K	2.85% K ⁻¹ (14 K)	(4)
Tb _{0.98} Eu _{0.02} -BDC-DSTP	77-400 K	2.4% K ⁻¹ (275 K)	(5)
Tb _{0.9} Eu _{0.1} PIA	14-300 K	3.53% K ⁻¹ (300 K)	(6)
Eu _{0.0062} Tb _{0.0087} Gd _{0.9851} L	77-450 K	6.11% K ⁻¹ (430 K)	(7)
Poly-Eu(TTA) ₃ (2)	313-383 K	5.16% K ⁻¹ (383 K)	This work

**Fig. S16** Calculation of temperature resolution for Poly-Eu(TTA)₃ (2).

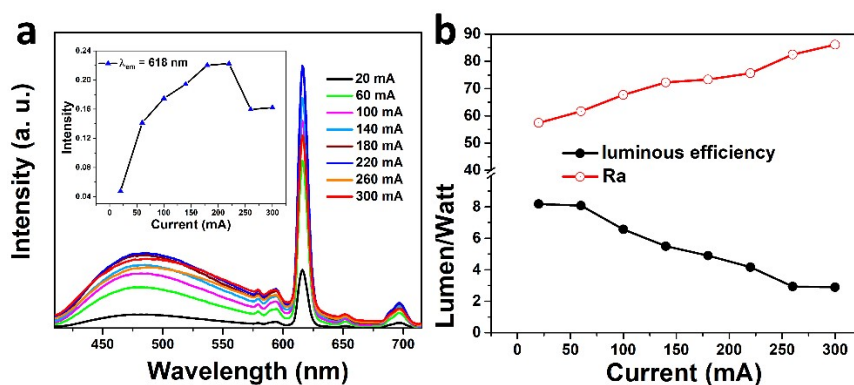


Fig. S17. (a) Electroluminescence spectra of the WLED under different operating currents (the inserted figure is the intensity of the emission at 618 nm versus the current) (b). The LER and Ra of the device under different operating currents.

Table S5. Performance parameters of the LED device under different operating voltages.

Voltage [V]	Current [mA]	CIE coordinates	Ra	R9	CCT[K]	Luminous efficiency [Lm/W]
3.3	20	(0.336,0.316)	57.4	15.1	5261	8.18
3.39	60	(0.335,0.319)	61.7	23.8	5330	8.09
3.45	100	(0.331,0.324)	67.7	39.5	5547	6.57
3.49	140	(0.330,0.330)	72.3	49.4	5610	5.51
3.53	180	(0.328,0.330)	73.3	51.4	5702	4.91
3.56	220	(0.328,0.333)	75.6	59.4	5687	4.17
3.59	260	(0.324,0.341)	82.5	81.6	5848	2.94
3.62	300	(0.317,0.339)	86.1	89.8	6201	2.89

References

- (1) J. Liu, Y. Zhao, X. Li, J. Wu, Y. Han, X. Zhang, Y. Xu. Dual-emissive CsPbBr₃@Eu-BTC composite for self-calibrating temperature sensing application. *Cryst. Growth Des.* **2019**, *20*, 454-459.
- (2) D. A. Turchetti, A. J. Santana, L. G. Duarte, T. D. Atvars, R. A. Domingues, L. Akcelrud. Ratiometric thermochromism in europium-containing conjugated polymer. *Polymer* **2019**, *177*, 65-72.
- (3) A. N. Carneiro Neto, E. Mamontova, A. M. Botas, C. D. Brites, R. A. Ferreira, J. Rouquette, Y. Guari, J. Larionova, J. Long, L. D. Carlos. Rationalizing the Thermal Response of

Dual-Center Molecular Thermometers: The Example of an Eu/Tb Coordination Complex.
Adv. Opt. Mater. **2021**, 2101870.

- (4) D. Ananias, C. D. Brites, L. D. Carlos, J. Rocha. Cryogenic nanothermometer based on the MIL-103 (Tb, Eu) metal-organic framework. *Eur. J. Inorg. Chem.* **2016**, 1967-1971.
- (5) Y. Wei, R. Sa, Q. Li, K. Wu. Highly stable and sensitive LnMOF ratiometric thermometers constructed with mixed ligands. *Dalton Trans.* **2015**, 44, 3067-3074.
- (6) X. Rao, T. Song, J. Gao, Y. Cui, Y. Yang, C. Wu, B. Chen, G. Qian. A highly sensitive mixed lanthanide metal–organic framework self-calibrated luminescent thermometer. *J. Am. Chem. Soc.* **2013**, 135, 15559-15564.
- (7) Y. Yang, L. Chen, F. Jiang, M. Yu, X. Wan, B. Zhang, M. Hong. A family of doped lanthanide metal–organic frameworks for wide-range temperature sensing and tunable white light emission. *J. Mater. Chem. C* **2017**, 5, 1981-1989.