

Supporting Information

X-ray Imaging and Enantioselective Photopolymerization Enabled by Chiral Eu(III) Complex Nanoscintillators

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Materials and methods

Materials: (*S*)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (*S*-BINAP), (*R*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (*R*-BINAP), 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (NTA), Polydimethylsiloxane (PDMS), Polyethylene terephthalate (PET), 10,12-Pentacosadiynoic acid and Europium(III) chloride hexahydrate were purchased from Sigma-Aldrich. 10,12-Pentacosadiynoic acid was purified by dissolving in hexane and subsequently filtrating to remove the polymer before use.

Characterization: All UV-Vis spectra were recorded on Agilent Cary 3500 spectrophotometer. ¹H NMR spectra were recorded on Bruker Avance 400 MHz. The NMR spectra were analyzed and processed by using MestReNova-6.1.1-6384 software. The photoluminescence was recorded from a fluorescence spectrometer (FLSP920; Edinburgh Instruments, UK), equipped with a Xe lamp. Circular dichroism spectra were measured by using a JASCO CD spectrometer J-815. Circular polarized luminescence was measured using a JASCO CPL-300 spectrometer. Elemental analysis was accomplished through energy dispersive X-ray spectroscopy incidental to scanning electron microscopy (JSM-7800F PRIME; JEOL, Japan); Infrared spectrum were measured by Fourier Transform Infrared (FTIR) spectrometer (NICOLETIS20; Thermo Fisher Scientific, the US); Mass spectra were measured on Thermo Scientific Q Exactive combination quadrupole Orbitrap mass spectrometer.

Synthesis the chiral Eu(NTA)₃(BINAPO) complex: The synthesis of the chiral Eu(NTA)₃(BINAPO) complex involves several key steps. Initially, 2.5 g of *R/S*-BINAP is dissolved in 25 mL of THF within a round-bottom flask, followed by cooling the reaction flask to 0°C. Over a period of 15 minutes, 15 mL of H₂O₂ is added dropwise, after which the mixture is stirred at room temperature for 4 hours and the THF is subsequently removed under vacuum. To the resulting residue, 25 mL of CH₂Cl₂ and 10 mL of water are added, and the aqueous phase is extracted with three 10 mL portions of CH₂Cl₂. The combined organic phases are then dried using anhydrous sodium sulfate, filtered, and evaporated to yield a white solid. In a separate round-bottom flask, a mixture containing 3.0 equivalents of NTA, 2.0 equivalents of *R*- or *S*-BINAP, and 3.0 equivalents of NaOH in an ethanol solution is prepared. This mixture is stirred at 70°C for 30 minutes. Subsequently, 1.0 equivalent of EuCl₃ aqueous solution is added dropwise (approximately 2 mL) to the flask while maintaining a temperature of 60°C, and the

stirring is continued for 2-3 hours. The resulting reaction mixture is then filtered to isolate the solid product, which corresponds to the chiral lanthanide coordination compound $\text{Eu}(\text{NTA})_3(\text{BINAPO})$.

Preparation of scintillation films: The chiral $\text{Eu}(\text{NTA})_3(\text{BINAPO})$ complexes were grinded into powders using a mortar. The grinded powders (150 mg) were mixed with 150 mg PDMS (mass ratio of 10:1 to curing agent). Finally, the blade coating was utilized to coat the mixture onto PET substrate with a thickness of $\sim 150 \mu\text{m}$.

X-ray-triggered photopolymerization: In a typical experiment, a 50 μL hexane solution containing chiral $\text{Eu}(\text{NTA})_3(\text{BINAPO})$ complex (5 mg/mL) was mixed with 1 mL diacetylene monomer (10 mg/mL in chloroform). Then the mixed solution was spin-coating onto a quartz substrate (pre-treated with UV-Ozone). The hybrid films were kept in darkness, and the chloroform evaporated after a few seconds before being irradiated by X-rays. The intensity of the X-ray was set to be 4 W. Various barriers can be put directly on the top of the hybrid films. After photopolymerization, the polymer films were subjected to CD spectroscopy, measurements were carried out by rotating the samples about the normal of the film to exclude the linear dichroism and/or linear birefringence effects.

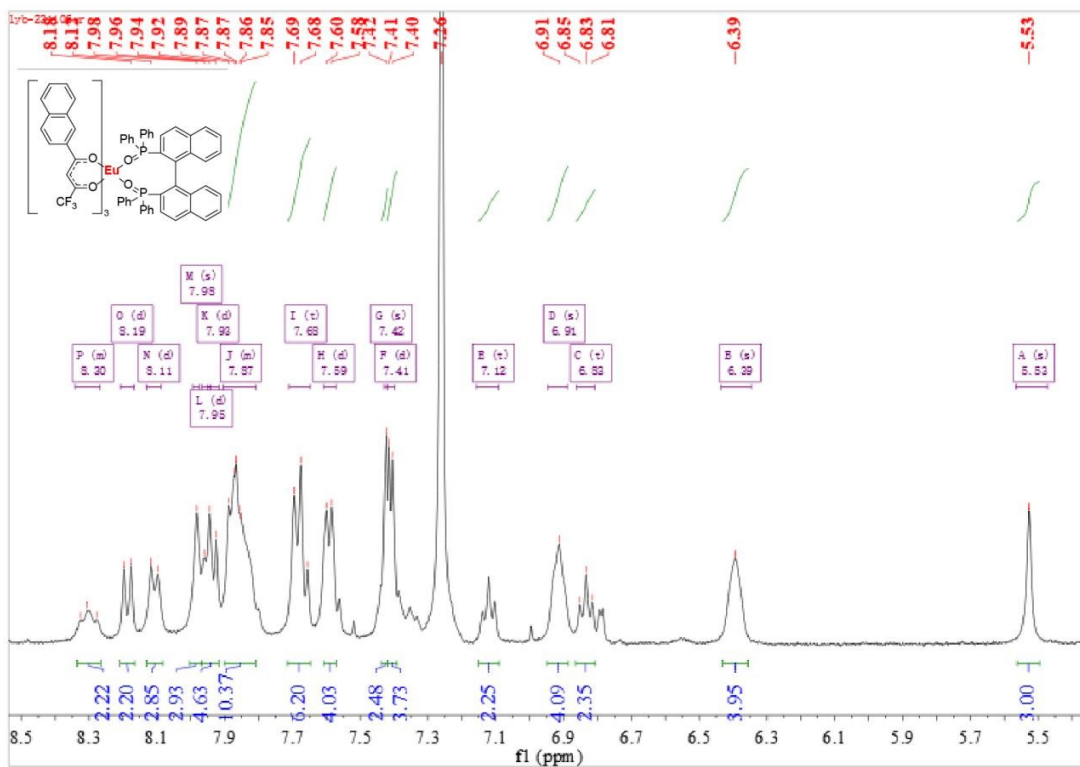


Figure S1. 400 MHz ¹H NMR spectrum of Eu(NTA)₃(BINAPO) in CDCl₃: δ 8.34-8.27 (m, 2H, H_{BINAPO}), 8.19 (d, J = 8.4 Hz, 2H, H_{BINAPO}), 8.11 (d, J = 7.6 Hz, 3H, H₈), 7.98 (s, 3H, H₆), 7.95 (d, J = 6.3 Hz, 2H_{BINAPO}), 7.93 (d, J = 7.9 Hz, 3H₁₄), 7.90-7.81 (broad, 10H, 6H_{11,13}+4H_{BINAPO-Ph}), 7.68 (t, J = 8.0 Hz, 6H, H_{9,10}), 7.59 (d, J = 6.1 Hz, 4H, H_{BINAPO}), 7.42 (s, 2H, H_{BINAPO}), 7.41 (d, J = 3.9 Hz, 4H, H_{BINAPO-Ph}), 7.12 (t, J = 7.2 Hz, 2H, H_{BINAPO-Ph}), 6.91 (s, 4H, H_{BINAPO-Ph}), 6.83 (t, J = 7.5 Hz, 2H, H_{BINAPO-Ph}), 6.39 (s, 4H, H_{BINAPO-Ph}), 5.53 (s, 3H, H₃).

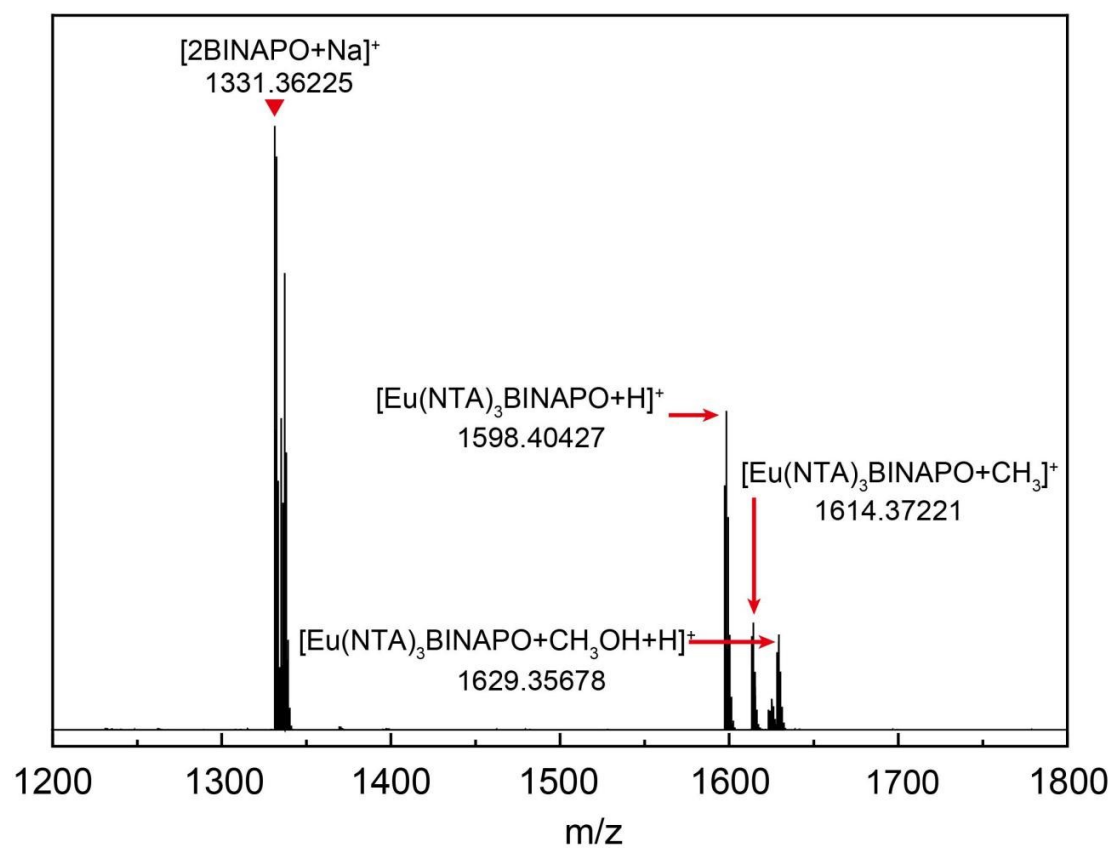


Figure S2. ESI-TOF-MS of $\text{Eu}(\text{NTA})_3(\text{BINAPO})$.^[1]

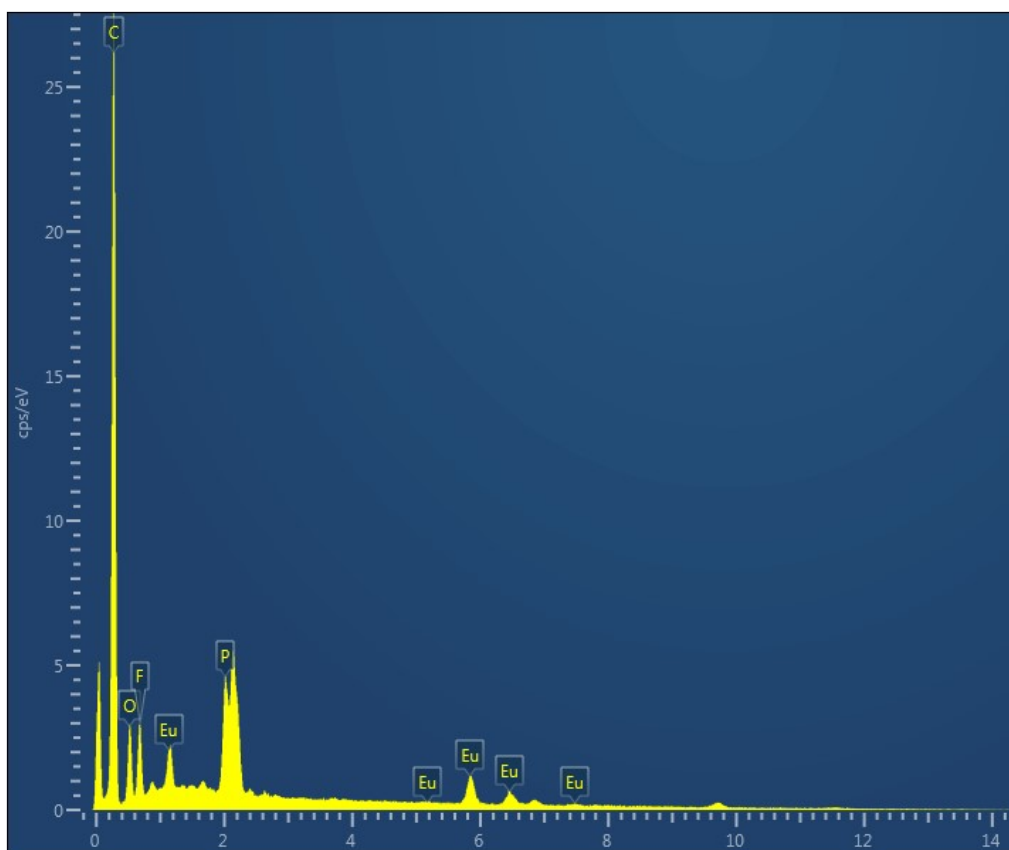


Figure S3. EDS of $\text{Eu}(\text{NTA})_3(\text{BINAPO})$.

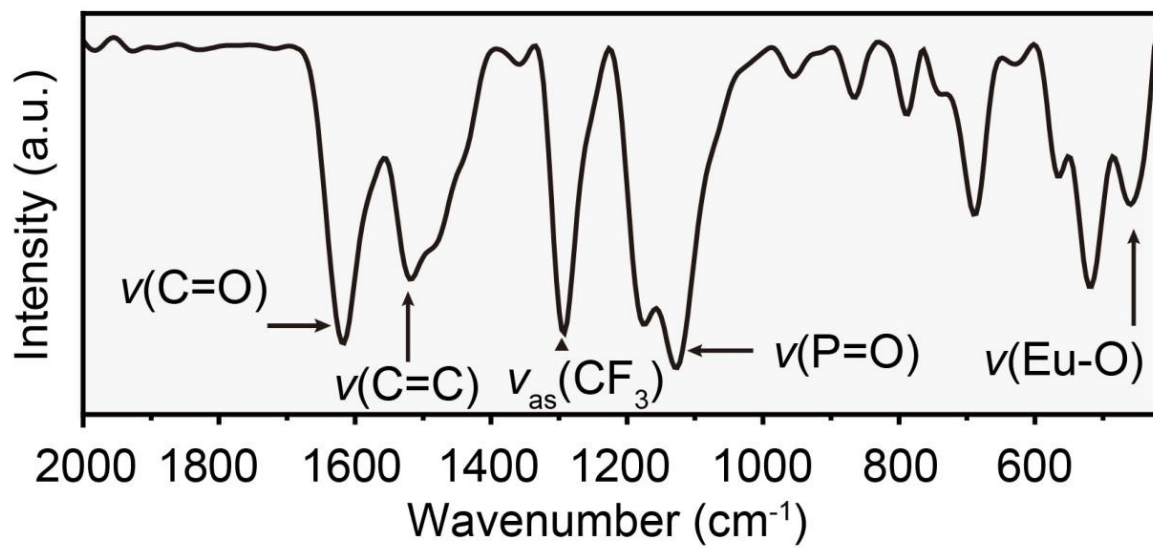


Figure S4. Infrared spectra of the Eu(NTA)₃(BINAPO) complex.

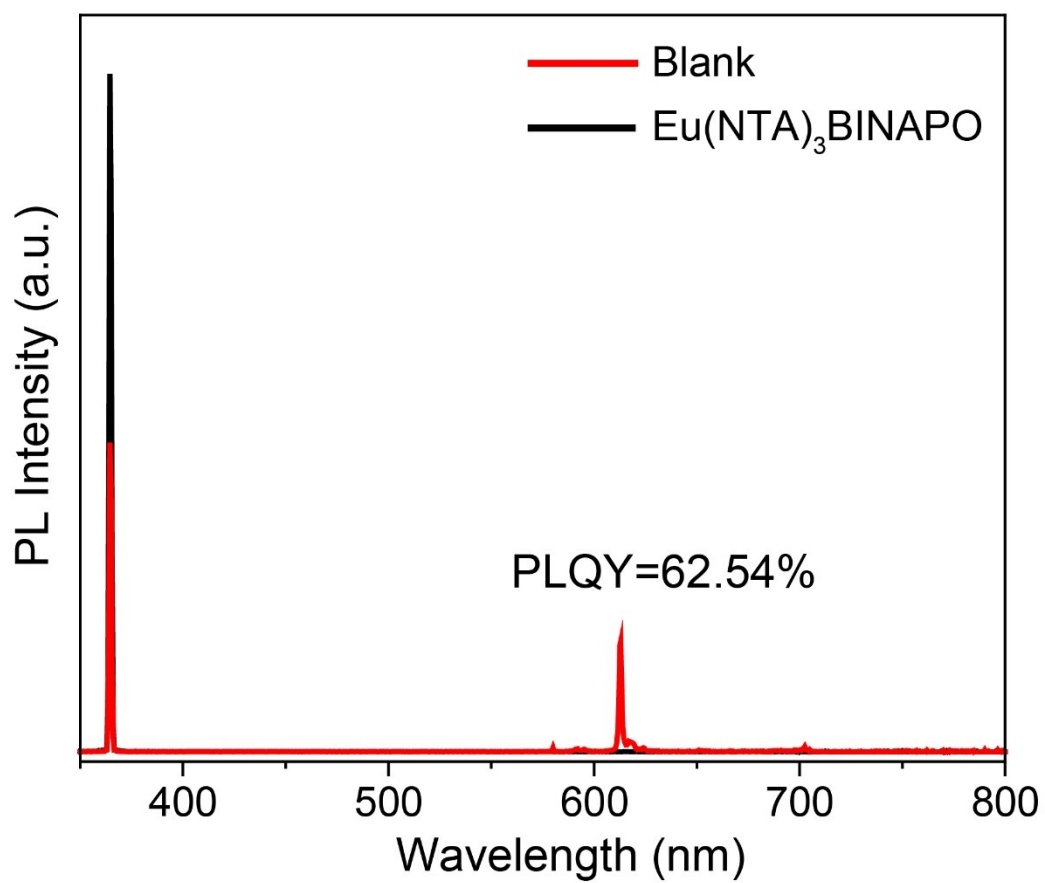


Figure S5. Photoluminescence quantum yield of Eu(NTA)₃BINAPO.

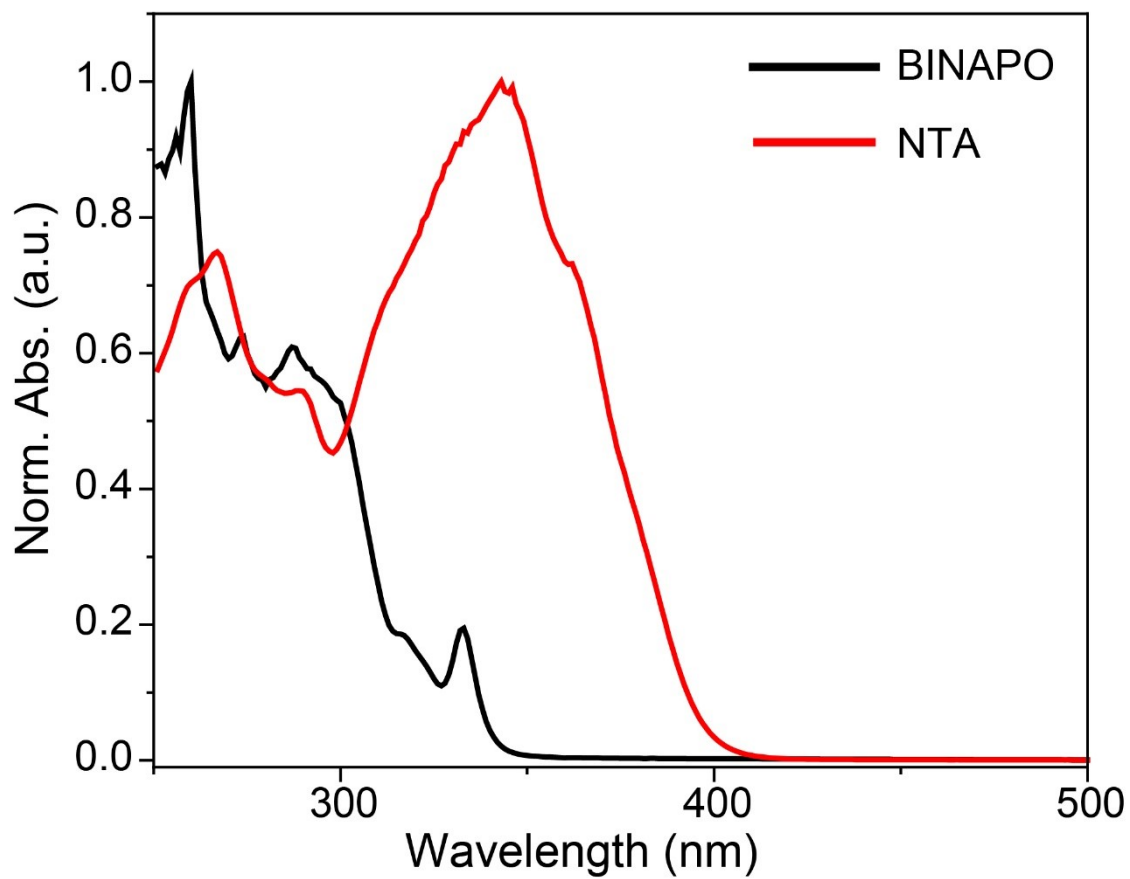


Figure S6. UV-Vis absorption spectra of NTA and BINAPO ligands.

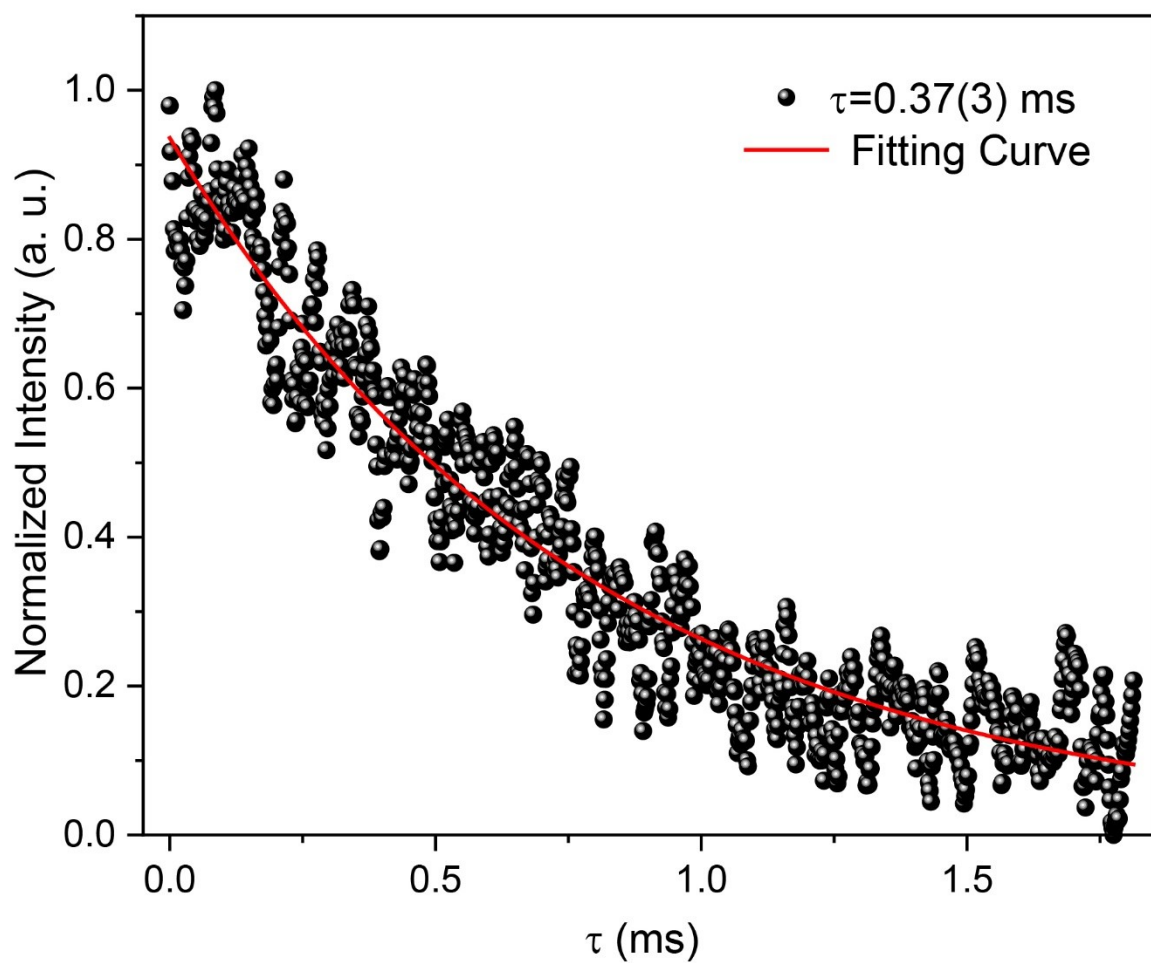


Figure S7. Photoluminescence decay spectra of $\text{Eu}(\text{NTA})_3(\text{BINAPO})$.

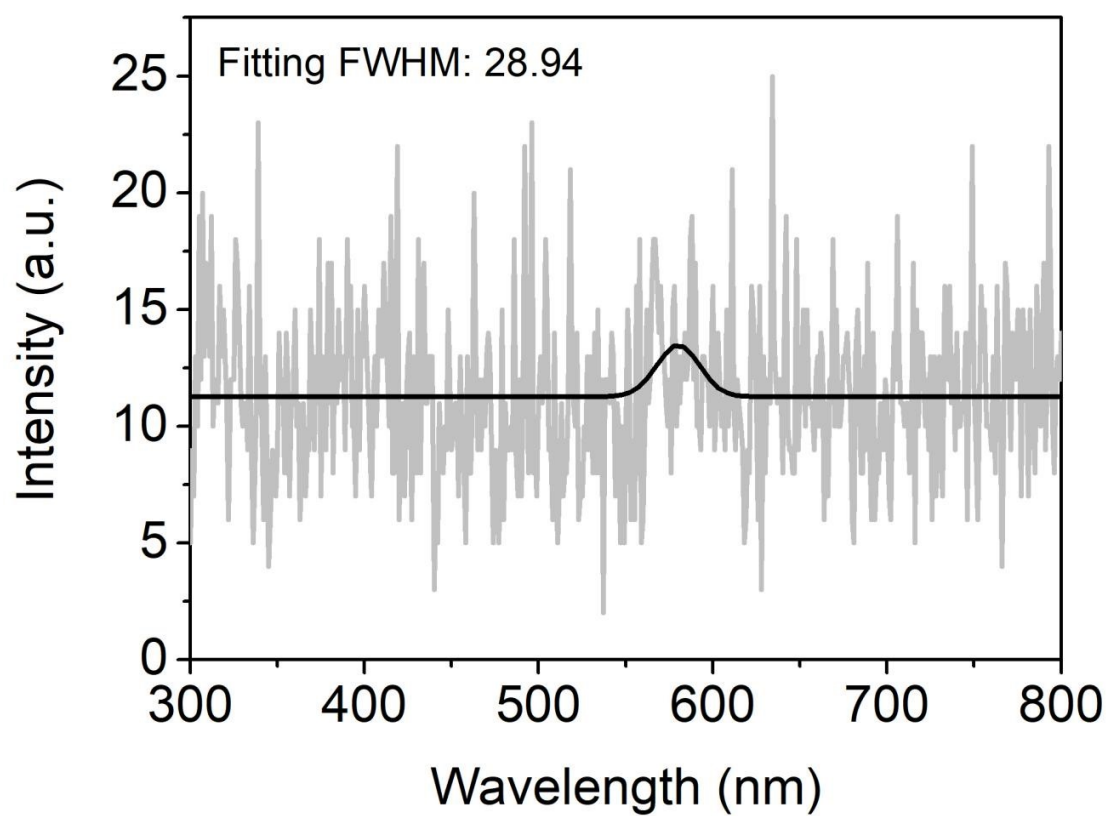


Figure S8. Backgrounds for calculating detection limit.

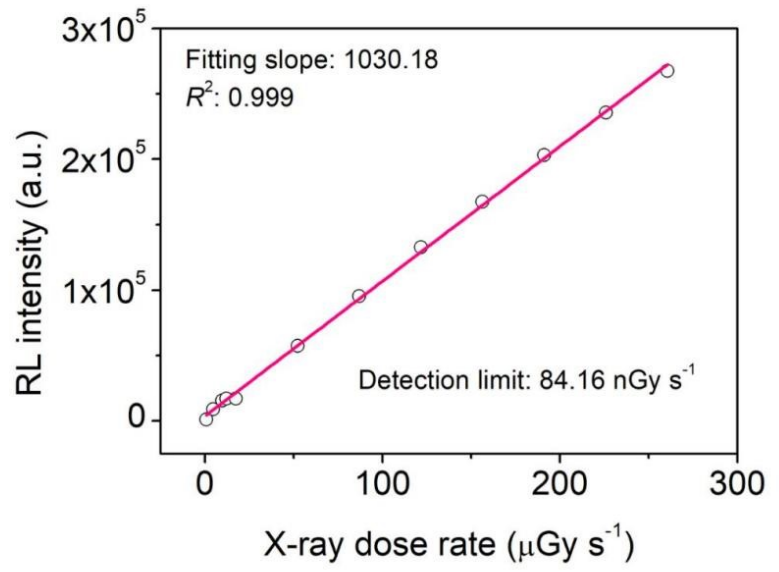
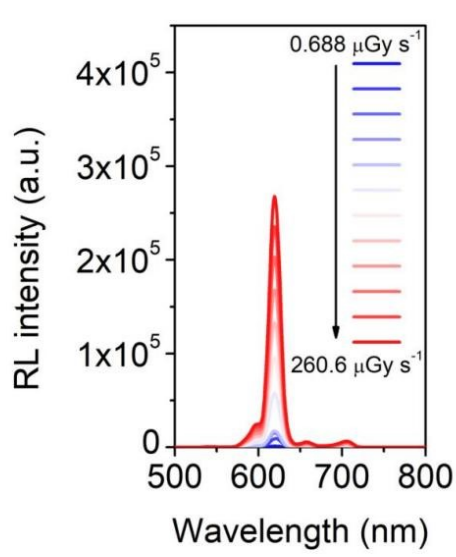


Figure S9. Detection limit of R-Eu.

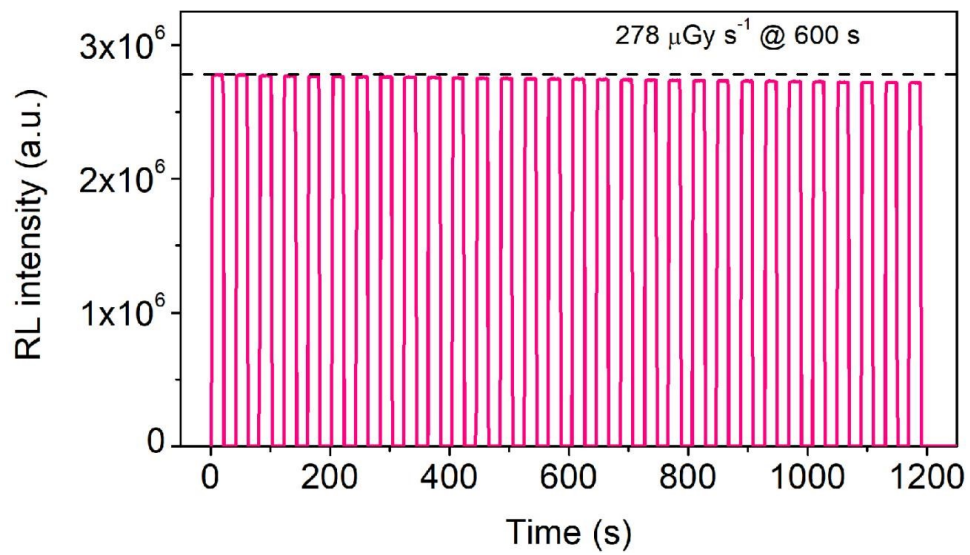


Figure S10. Stability against X-ray irradiation of *R*-Eu.

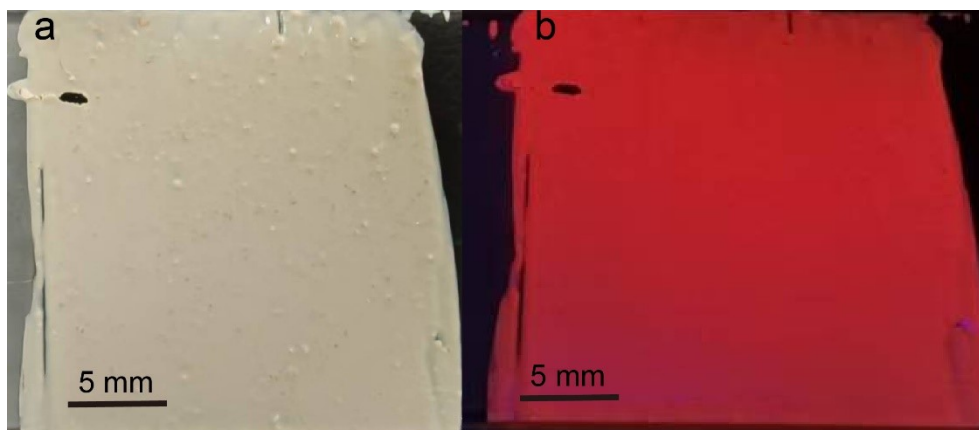


Figure S11. (a) Image of the scintillator film on a glass substrate and (b) the photograph of its luminescence under 365 nm excitation.

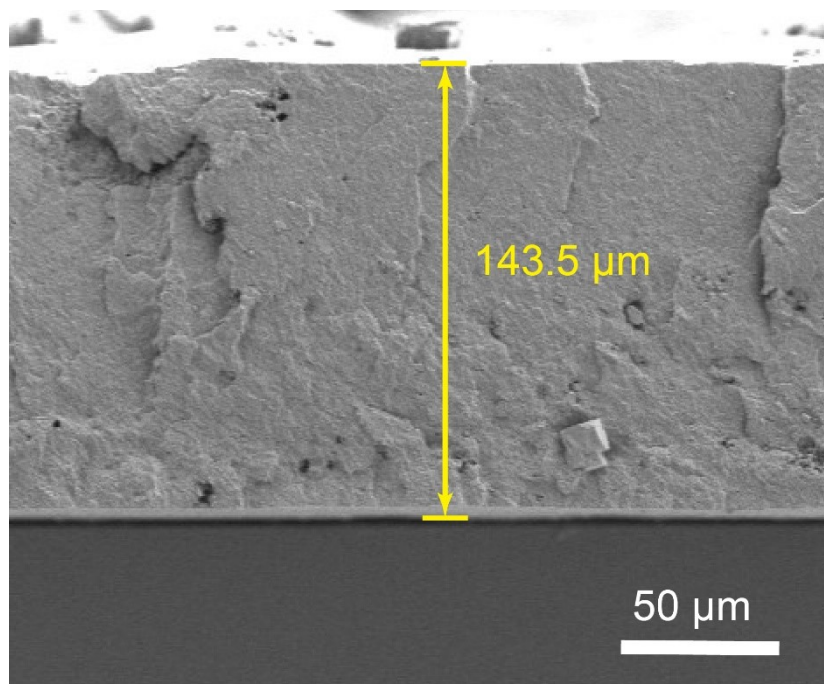


Figure S12. SEM cross-sectional image of the PDMS@Eu(NTA)₃BINAPO film.

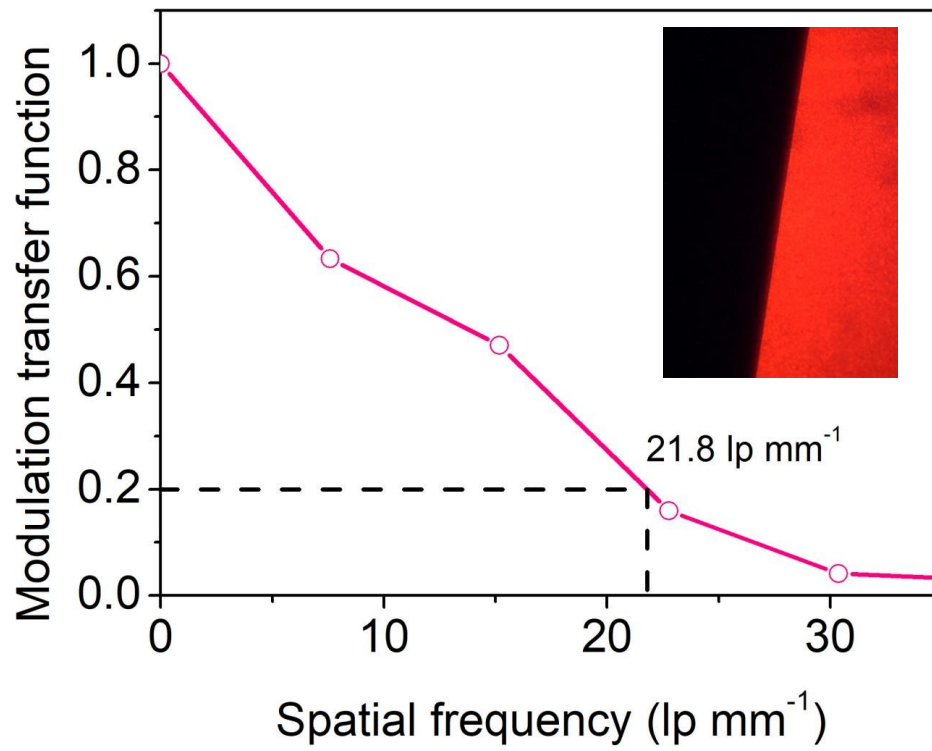


Figure S13. Modulation transfer function of *R-Eu*.

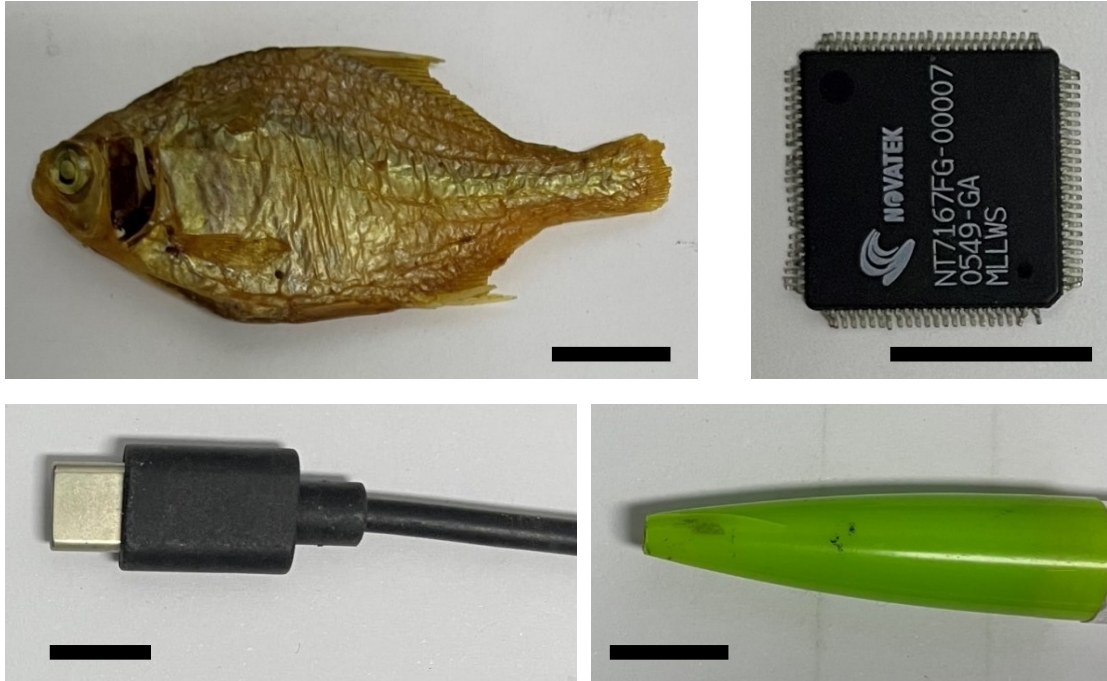


Figure S14. Optical photos of imaging objects. Scale bars: 1 cm.

Table S1. Comparison of asymmetric luminescence factors of different materials.

Material	$ g_{lum} $	Ref.
(<i>R/S</i> -atpp) ₂ MnBr ₄	5.8×10^{-2}	<i>Adv. Funct. Mater.</i> 2024, 2410219. DOI: 10.1002/adfm.202410219
(<i>R/S</i> -3AP)PbBr ₃ Cl·H ₂ O	4.0×10^{-2}	<i>Angew. Chem.</i> , 2022, 134, e202208440
<i>R/S</i> -3-aminopyrrolidinedihydrochloride) ₆ (Mn ₃ Cl ₁₂)(Cl) ₆	0.7×10^{-2}	<i>J. Mater. Chem. C</i> 2023, 11, 3206
(<i>R/S</i> -CIMBA) ₂ SnI ₄	2.0×10^{-2}	<i>Angew. Chem.</i> , 2024, 136, e202318557
(<i>R/S</i> -MPEA)PbBr ₃	2.3×10^{-3}	<i>Adv. Opt. Mater.</i> , 2023, 11, 2203125
(<i>R/S</i> -BINAPO)MAPbBr ₃	5.6×10^{-3}	<i>Adv. Funct. Mater.</i> , 2024, 34, 2310500
Mn(<i>R/S</i> -Binapo)Br ₂	5.1×10^{-3}	<i>Chem. Sci.</i> , 2024,15, 16698
(<i>L/D</i> -Ment)CAACCuCl	1.2×10^{-3}	<i>Angew. Chem. Int. Ed.</i> , 2020, 59, 1228
Eu(NTA) ₃ (<i>R/S</i> -BINAPO)	1.5×10^{-2}	Our work

References

- [1] J. S. McIndoe, K. L. Vikse, *J. Mass Spectrom.* **2019**, 54, 466.