Efficient Circularly Polarized Luminescence from Zero-Dimensional Terbium- and Europium-Based Hybrid Metal Halides

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Experimental procedures:

Materials. Terbium (III) chloride hexahydrate ($TbCl_3 \cdot 6H_2O$, 99.0%) was purchased from Leyan. Europium (III) chloride hexahydrate ($EuCl_3 \cdot 6H_2O$, 99.99%) was purchased from Aladdin Reagent Co. Ltd (Shanghai, China). (*S*)-3-Methylmorpholine (*S*-MOR, 97%) and (*R*)-3-Methylmorpholine (*R*-MOR, 98%) were purchased from BIDE. Hydrochloric acid (HCl, 36%-38wt. % in H_2O) was purchased from YongHua. All chemicals were used without any further purification.

Synthesis of *S*/*R*-TbCl and *S*/*R*-EuCl enantiomers: *S*/*R*-MOR (3 mmol) and $TbCl_3 \cdot 6H_2O$ (1 mmol) were mixed in a 20 mL glass vial. Then, 10 mL of HCl was added to the mixture. The solution was stirred at 110°C for 20 minutes, during which time the solution gradually became clarified. After obtaining a clear solution, the solvent was evaporated at 110°C. Colorless and transparent crystals of *S*/*R*-TbCl were formed upon evaporation.

The *S*/*R*-EuCl enantiomers were prepared using the same procedure, replacing $TbCl_3 \cdot 6H_2O$ with $EuCl_3 \cdot 6H_2O$ (1 mmol).

Synthesis of CP-LEDs based on *S*/*R*-TbCl and *S*/*R*-EuCl:

The luminescent layers were prepared by mixing the powder of *S*/*R*-TbCl and *S*/*R*-EuCl with a mixture of polydimethylsiloxane (1 ml) and methyltriethoxysilane (0.1 ml), respectively. Considering the difference in excitation wavelengths between *S*/*R*-TbCl and *S*/*R*-EuCl, the luminescent layers made from these two materials were coated onto commercial 275 nm and 395 nm chips, respectively, to fabricate the LED devices (*S*/*R*-Tb-LED and *S*/*R*-Eu-LED). The entire procedure was conducted inside a glove box to prevent performance degradation caused by moisture absorption. The LEDs were then placed in an oven for curing, maintaining a constant temperature of 80°C for approximately 12 hours. Once curing was completed, the devices were ready for testing.

Characterizations:

Single crystal X-ray diffraction (SCXRD) was conducted using a Bruker D8 Venture X-ray single crystal diffractometer. Data were collected with Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Data reduction, scaling, and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013), and the structures were solved and determined with Olex2 software.[1-2] The crystal structures were refined using ver. 2016/6 of ShelXL (Sheldrick, 2008) and visualized with VESTA[3-4].

Powder X-ray Diffraction (PXRD) patterns were collected on an X-ray diffractometer (Rigaku Smart Lab) with Cu Kα radiation (λ = 0.15418 nm) at a voltage of 45 kV and a current of 200 mA. The diffraction patterns were recorded over a range of 5° to 45° at room temperature to confirm the purity. Standard XRD patterns were exported using the Mercury 3.8 program.

Photoluminescence (PL) and Photoluminescence excitation (PLE) spectra were recorded using an Edinburgh Instrument FLS1000 spectrometer equipped with a xenon lamp (450 W) at room temperature. Temperature-independent PL spectra were obtained with a FLS1000 fluorescence spectrometer fitted with a cryogenic attachment. PL lifetime measurements were conducted using a microsecond flashlamp on the FLS1000 fluorescence spectrometer. Photoluminescence quantum yields (PLQYs) were measured directly using the FLS1000 spectrometer with an integrated sphere. X-ray photoelectron spectroscopy (XPS) data were acquired with an ULVAC PHI 5000 VersaProbe III spectrometer, utilizing the Al Kα (1489.6 eV) line as the excitation source. Data were analyzed using MultiPak software.

UV-Vis absorption spectra were measured on a UV-3600i Plus spectrophotometer with BaSO4 as the standard.

Transmission Circular Dichroism (CD) spectra were collected with a CD spectrometer (J810, JASCO) using "Standard" sensitivity (100 mdeg) at a scanning speed of 50 nm/min.

Circularly Polarized Luminescence (CPL) spectra were recorded using a JASCO CPL-300 instrument. The samples were dissolved in DMF, dropped onto quartz slides, and dried at 80°C to form uniform thin films. CPL spectra were scanned at a speed of 100 nm/min with two accumulations. The emission bandwidths were 5 nm for *S*/*R*-TbCl and 8 nm for *S*/*R*-EuCl.

Table S1. Single crystal X-ray diffraction data of ***S*/*R*-TbCl**.

Empirical formula	$C_{30}H_{72}Cl_{12}O_6N_6Tb_2$ **/*S*-TbCl**	$C_{30}H_{72}Cl_{12}O_6N_6Tb_2$ **/*R*-TbCl**
Formula weight	1356.17	1356.17
Temperature/K	100.00	100.00
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a/Å	13.2356(17)	13.2751(7)
b/Å	11.9576(15)	11.9418(7)
c/Å	16.874(2)	16.8205(10)
α/°	90	90
β/°	98.179(4)	97.982(2)
γ/°	90	90
Volume/Å^3	2643.4(6)	2640.7(3)
Z	2	2
ρ_{calc} g/cm^3	1.704	1.706
μ/mm^{-1}	3.302	3.305
F(000)	1352.0	1352.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.668 to 50.696	3.098 to 55.09
Index ranges	$-15 \le h \le 15$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-17 \le h \le 17$ $-15 \le k \le 15$ $-21 \le l \le 21$
Reflections collected	36291	73907
Independent reflections	9643 [R_{int} = 0.0637, R_{sigma} = 0.0596]	12139 [R_{int} = 0.0557, R_{sigma} = 0.0415]
Data/restraints/ parameters	9643/226/590	12139/451/574
Goodness-of-fit on F^2	1.048	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0735, wR_2 = 0.1879	R_1 = 0.0476, wR_2 = 0.0908
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.2028	R_1 = 0.0663 wR_2 = 0.1017
Largest diff. peak/hole / e Å^{-3}	1.91/-1.51	2.16/-1.71
Flack parameter	0.00(3)	0.015(6)
CCDC	**2364010**	**2364011**

$$R_1 = \frac{\sum||Fo| - |Fc||}{\sum|Fo|}, wR_2 = [\sum \frac{w(Fo^2 - Fc^2)^2}{\sum w(Fo^2)^2}]^{1/2}$$

Table S2. Single crystal X-ray diffraction data of ***S*/*R*-EuCl**.

Empirical formula	$C_{30}H_{72}Cl_{12}O_6N_6Eu_2$ **/*S*-EuCl**	$C_{30}H_{72}Cl_{12}O_6N_6Eu_2$ **/*R*-EuCl**
Formula weight	1342.25	1342.25
Temperature/K	100.00	100.00
Crystal system	Monoclinic	Monoclinic
Space group	*P2₁*	*P2₁*
a/Å	13.3233(6)	13.3330(5)
b/Å	11.9727(6)	11.9679(4)
c/Å	16.8005(8)	16.8004(6)
α/°	90	90
β/°	97.753(2)	97.7990(10)
γ/°	90	90
Volume/Å³	2655.4(2)	2656.01(16)
Z	2	2
ρ_{calc} g/cm³	1.679	1.678
μ/mm⁻¹	2.985	2.985
F(000)	1344.0	1344.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.67 to 55.022	3.666 to 54.994
Index ranges	-17 ≤ h ≤ 17 -15 ≤ k ≤ 15 -21≤ l ≤ 21	-17≤ h ≤ 17 -15 ≤ k ≤ 15 -21 ≤ l ≤ 21
Reflections collected	63859	74209
Independent reflections	12198[R_{int} = 0.0679, R_{sigma} = 0.0575]	12185 [R_{int} = 0.0613, R_{sigma} = 0.0451]
Data/restraints/ parameters	12198/415/603	12185/285/604
Goodness-of-fit on F²	1.049	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.0783	R_1 = 0.0446, wR_2 = 0.0809
Final R indexes [all data]	R_1 = 0.0734, wR_2 = 0.0881	R_1 = 0.0608 wR_2 = 0.0885
Largest diff. peak/hole / e Å⁻³	1.12/-1.23	2.35/-1.16
Flack parameter	0.015(8)	0.03(2)
CCDC	**2364012**	**2364013**

$$R_1 = \frac{\sum||Fo| - |Fc||}{\sum|Fo|}, wR_2 = [\sum \frac{w(Fo^2 - Fc^2)^2}{\sum w(Fo^2)^2}]^{1/2}$$

Table S3. Summary of Tb/Eu based luminescent materials.

Tb/Eu-based materials	**Lifetime**	**PLQY**	**$\|g_{lum}\|$**	**CIE**	**Reference**
Cs_3TbCl_6	5.53ms	36.85%	-	（0.30，0.66）	5
*m*CB-Tb	0.85ms	49.80%	-	（0.32，0.58）	6
[TbR(+)BnMeH$_{22}$IAM]	1.39ms	63.00%	0.044	-	7
[(R)-iPr-Pybox]$_8$(TbIII)$_8$(THP)$_8$	5.40μs	0.13%	0.25	-	8
L/D-Phe-Tb⊃UCNPs	0.11ms	6.48%	0.0029	(0.32, 0.55)	9
***S*/*R*-TbCl**	**4.62ms**	**(85.1-91.2)%**	**0.006**	**（0.33，0.62）**	**this work**
Cs_3EuCl_6	3.99ms	48.78%	-	（0.56，0.33）	5
*m*CB-Eu	0.74ms	20.50%	-	（0.62，0.38）	6
[EuR(+)BnMeH$_{22}$IAM]	0.88ms	2.30%	0.298	-	7
[(R)-iPr-Pybox]$_8$(EuIII)$_8$(THP)$_8$	0.86ms	14.50%	1.25	-	8
$TEA^+[Eu(+tfc)_4]^-$	0.371ms	17%	1.54	-	10
***S*/*R*-EuCl**	**2.27ms**	**(48.5-52.0)%**	**0.009**	**（0.64，0.35）**	**this work**

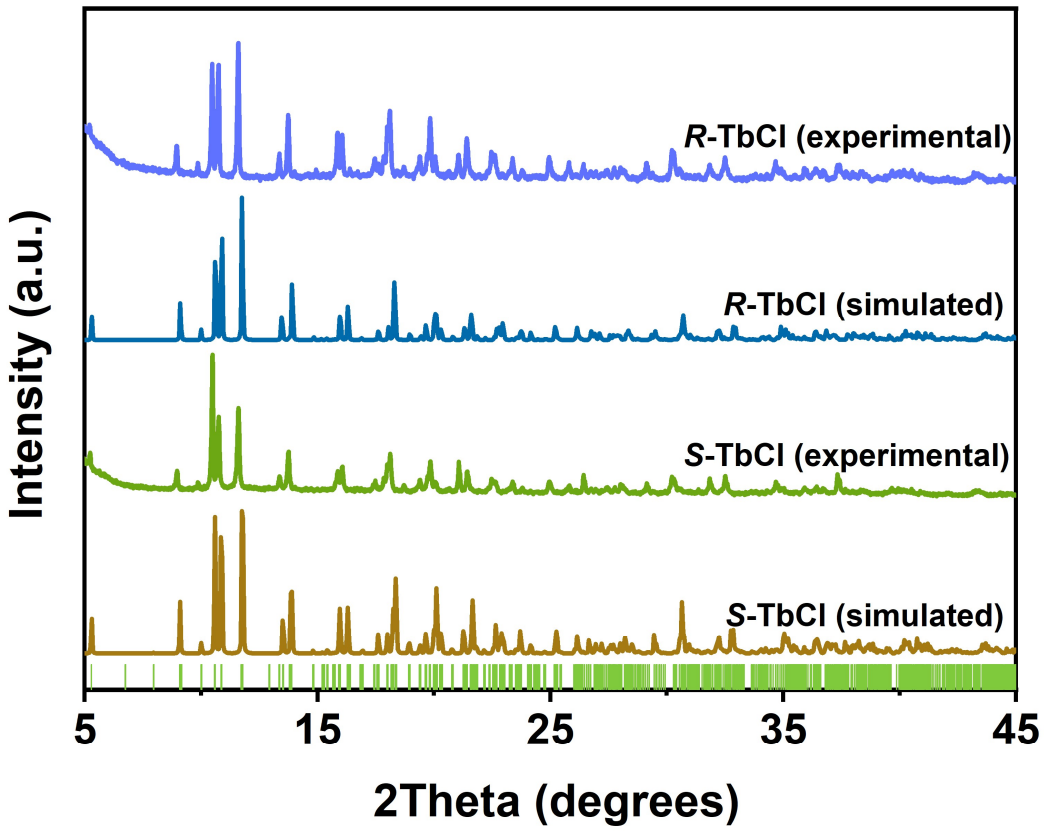

Fig. S1. PXRD patterns of *S*/*R*-TbCl with simulated and experimental curves.

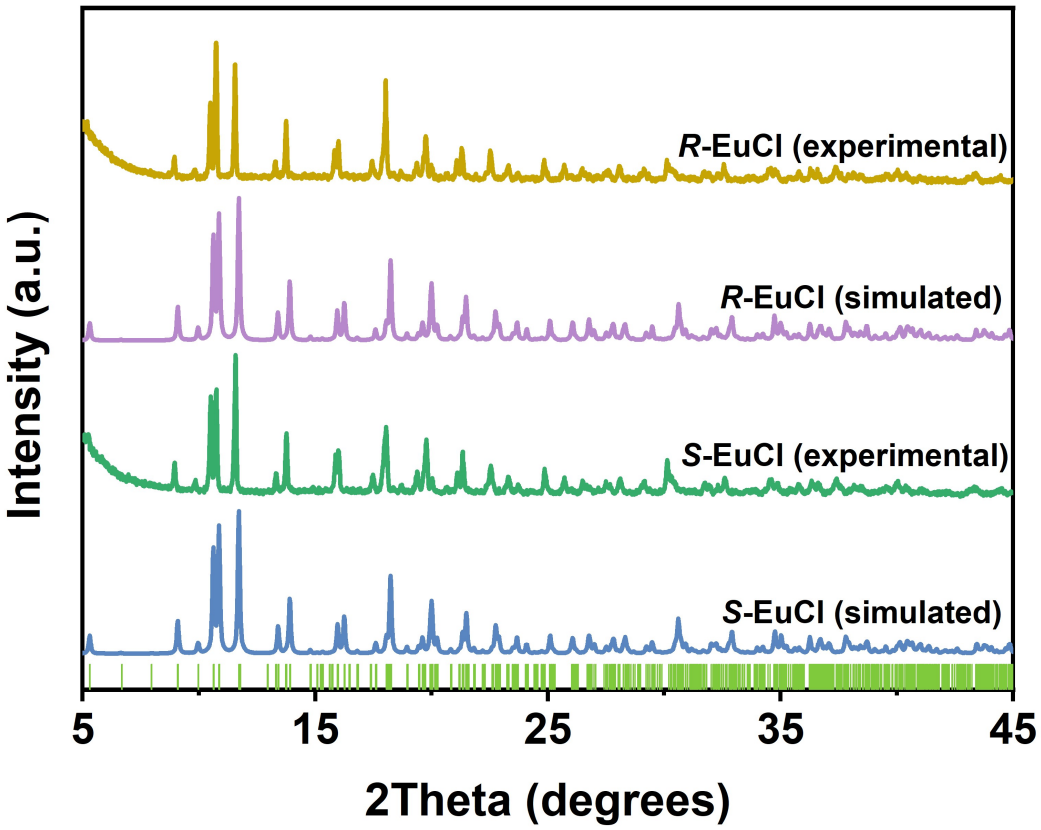

Fig. S2. PXRD patterns of *S*/*R*-EuCl with simulated and experimental curves.

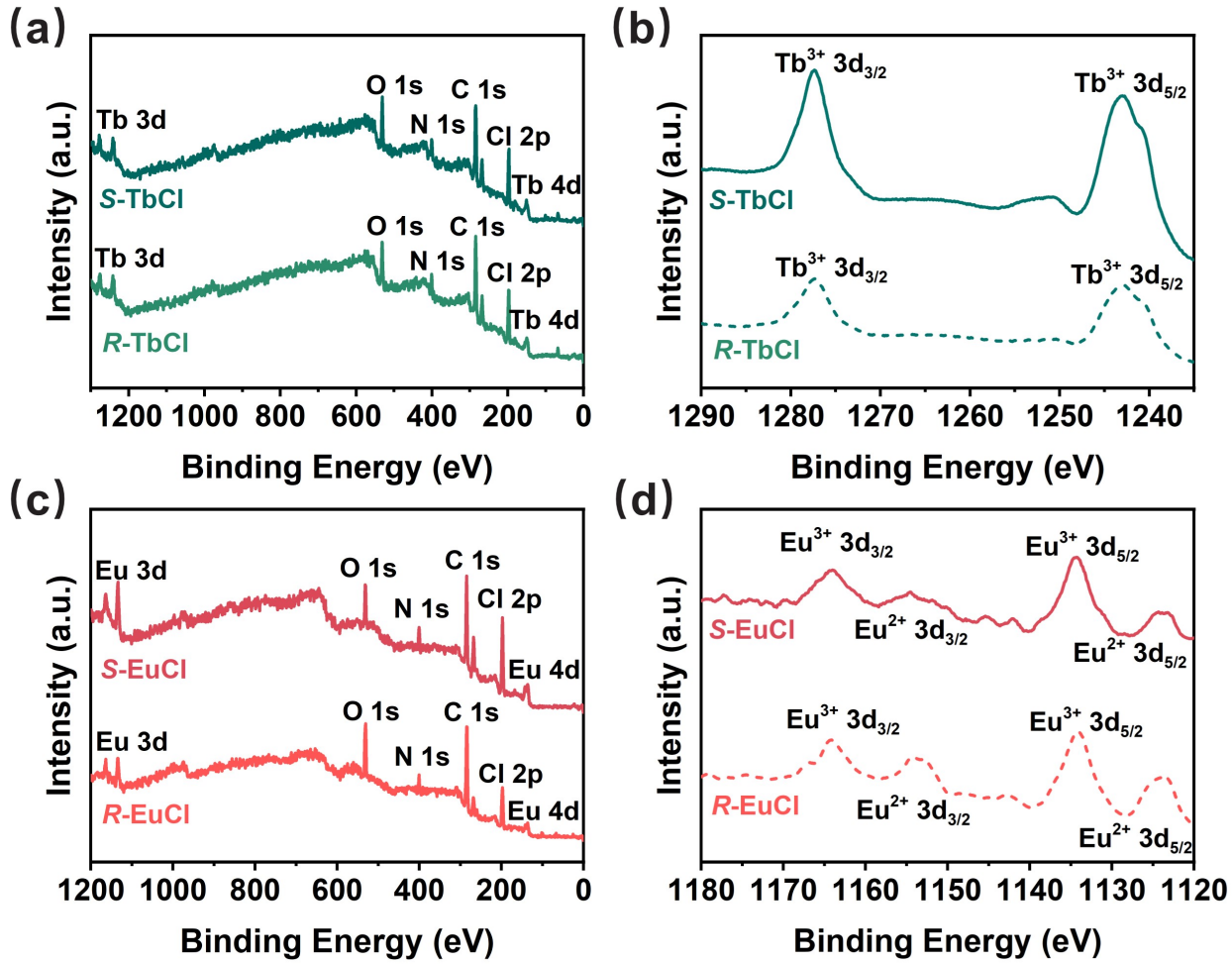

Fig. S3. (a) XPS survey spectra of *S*/*R*-TbCl. (b) High-resolution XPS spectra of Tb 3d. (c) XPS survey spectra of *S*/*R*-EuCl. (d) High-resolution XPS spectra of Eu 3d.

The binding energies of 1153.9 and 1123.9 eV correspond to $3d_{3/2}$ and $3d_{5/2}$ of Eu^{2+}, which may be attributed to the partial reduction during the XPS testing.[11]

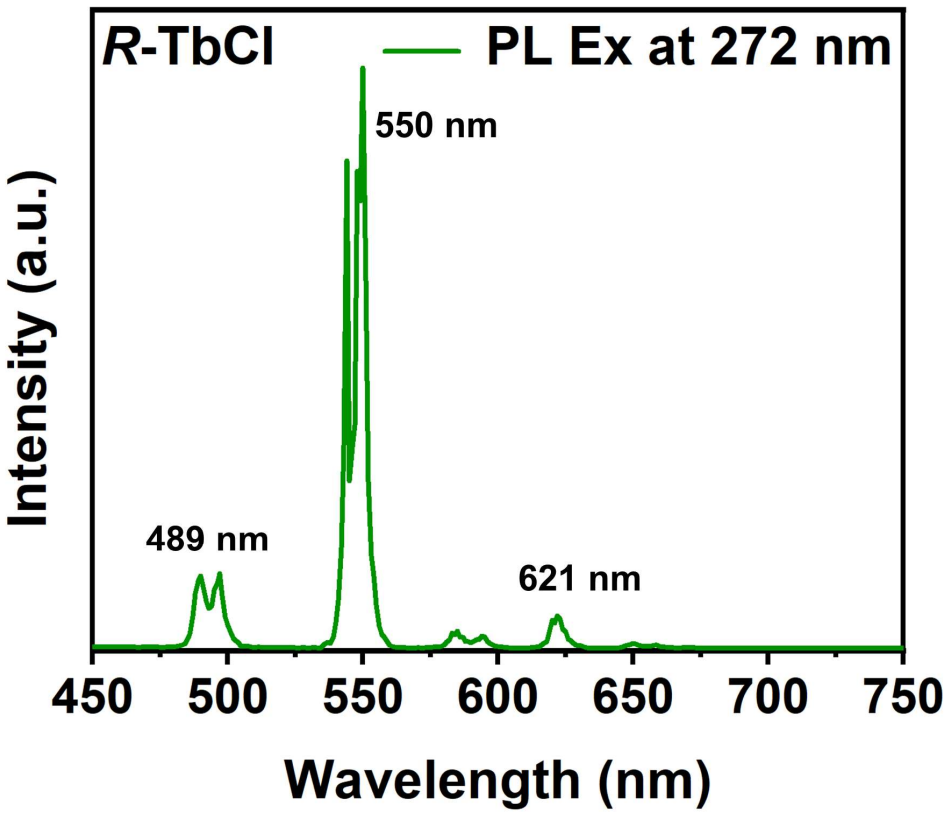

Fig. S4. PL spectrum of *R*-TbCl.

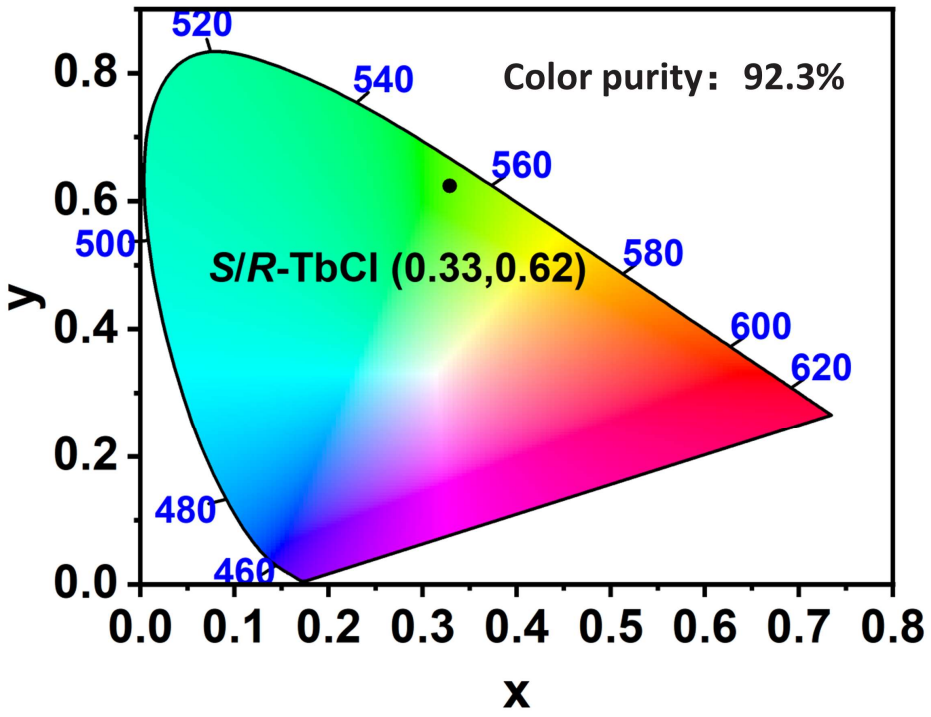

Fig. S5. CIE coordinates of *S*/*R*-TbCl.

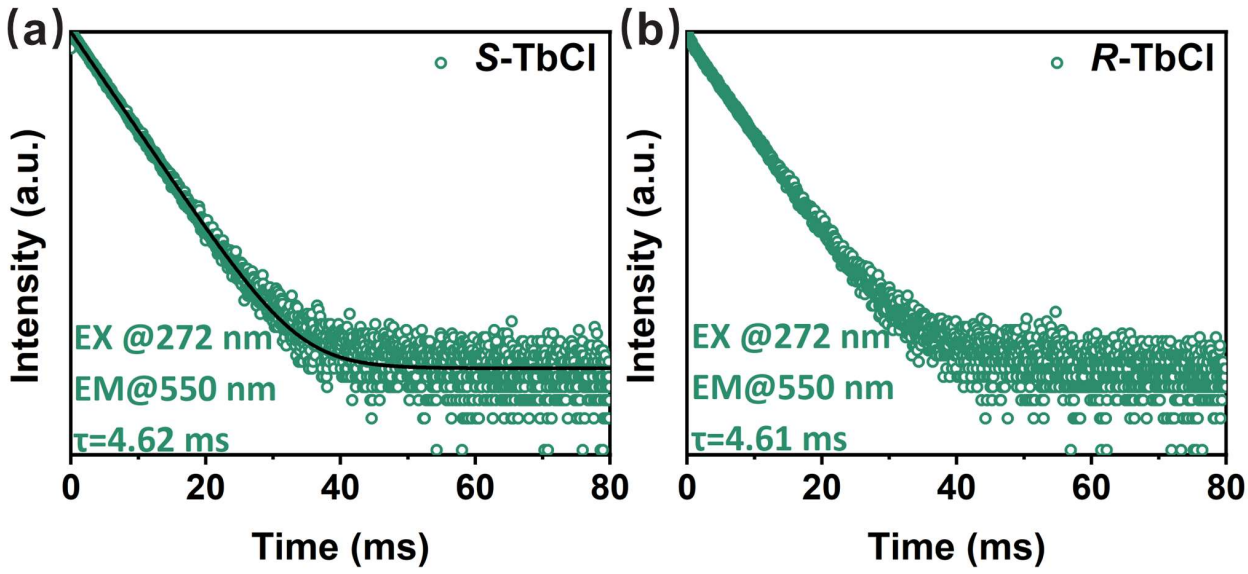

Fig. S6. PL decay curves of *S*-TbCl (a) and *R*-TbCl (b) under 272 nm excitation.

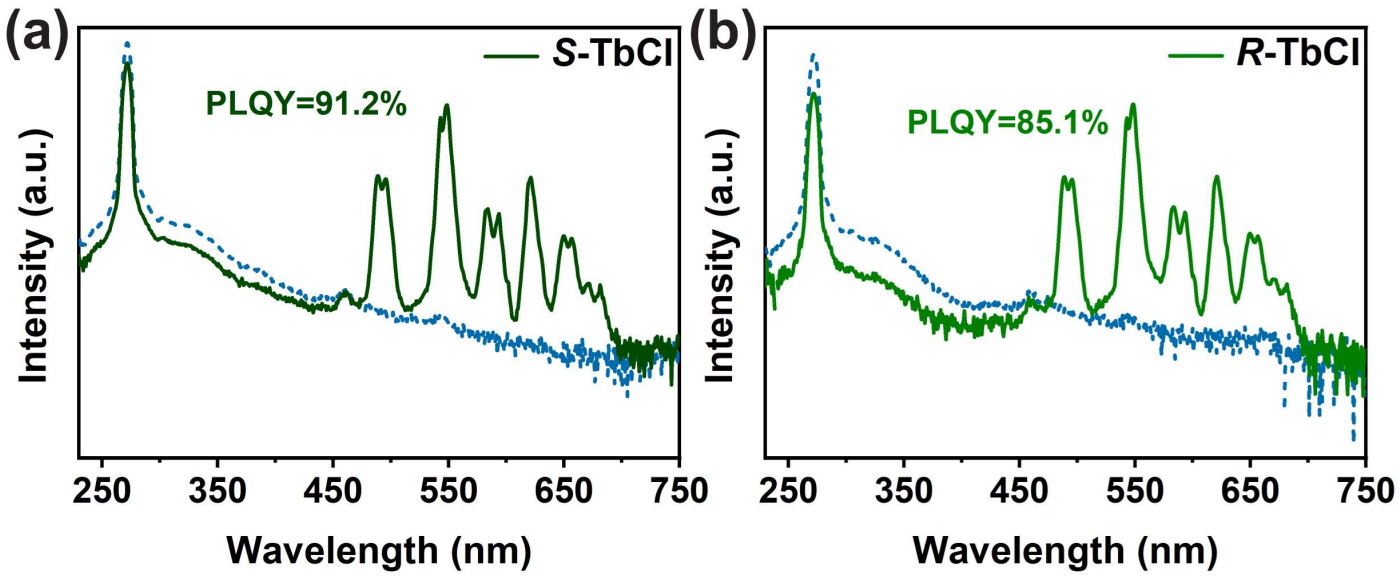

Fig. S7. PLQYs measurements of *S*-TbCl (a) and *R*-TbCl (b) at room temperature.

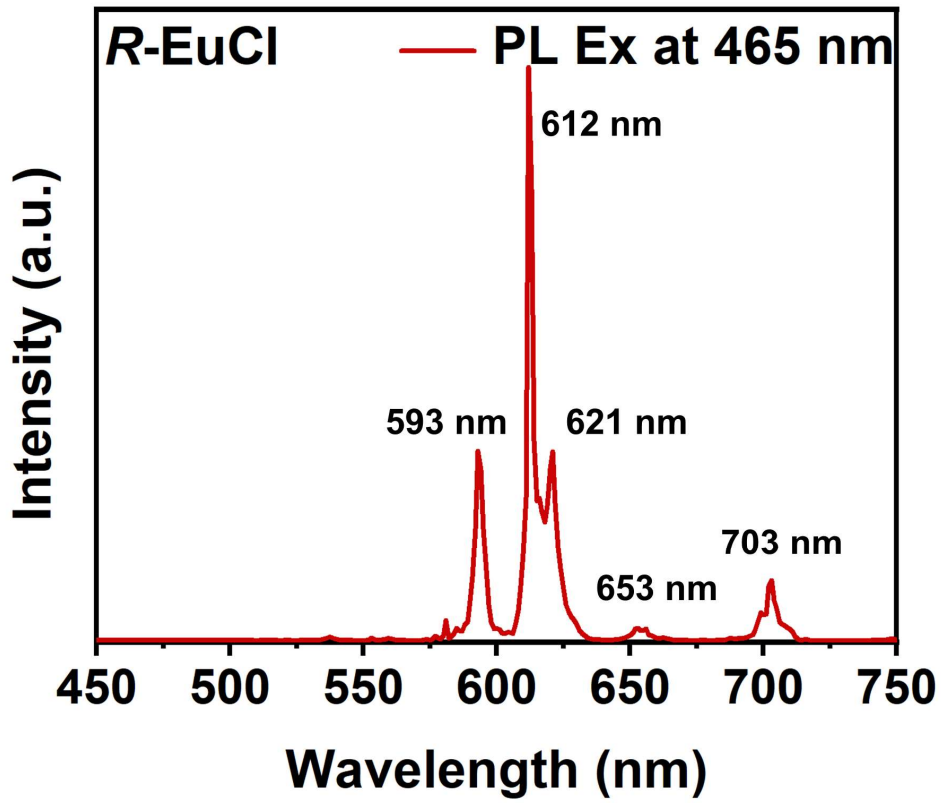

Fig. S8. PL spectrum of *R*-EuCl.

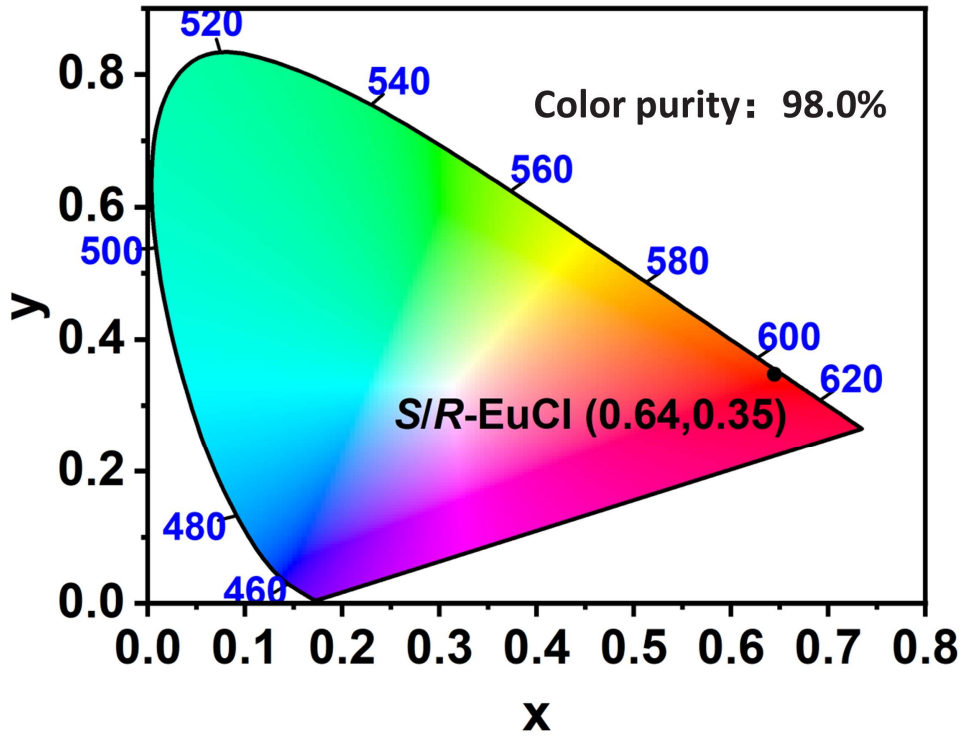

Fig. S9. CIE coordinates of *S*/*R*-EuCl.

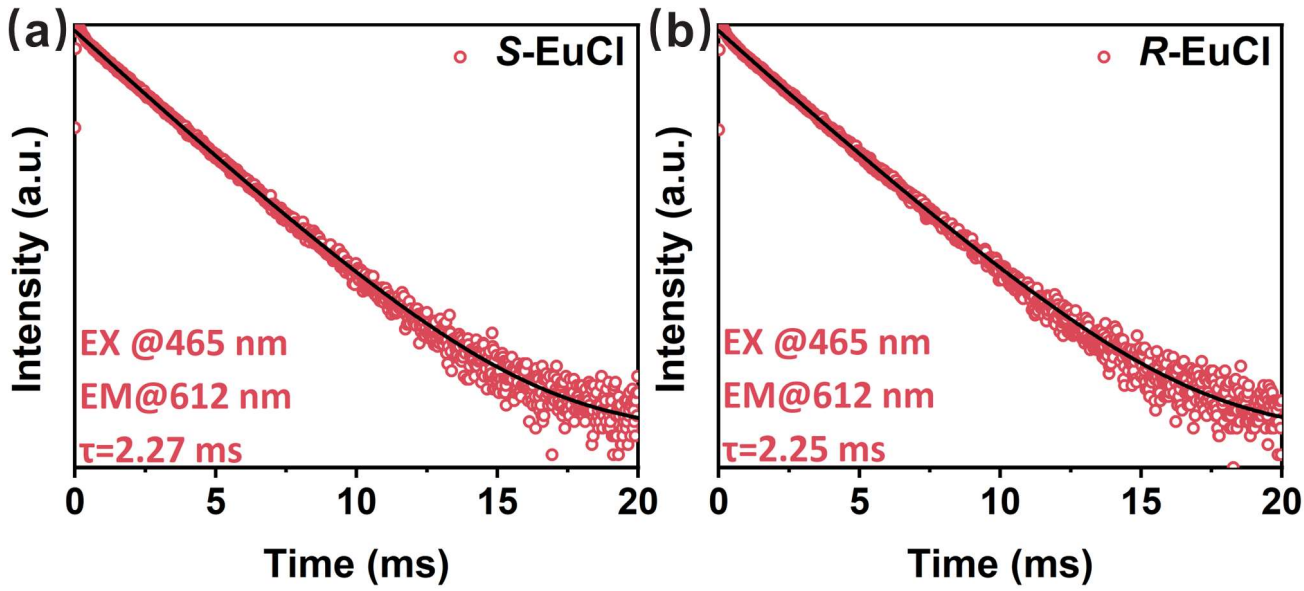

Fig. S10. PL decay curves of *S*-EuCl (a) and *R*-EuCl (b) under 465 nm excitation.

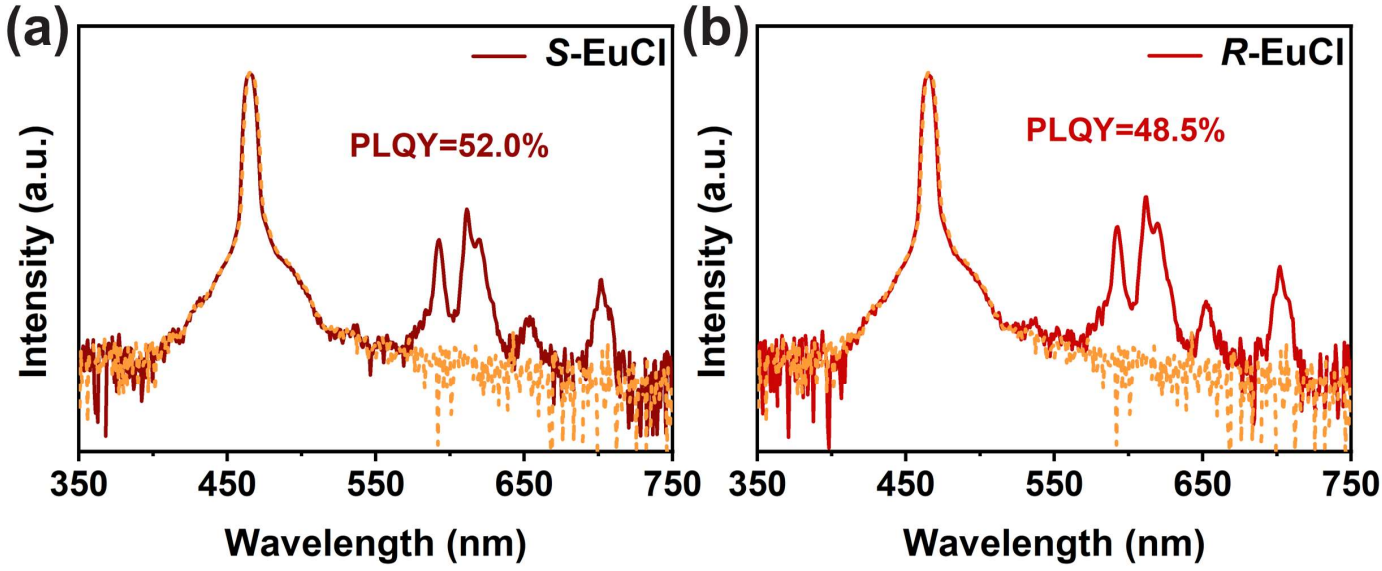

Fig. S11. PLQY measurements of *S*-EuCl (a) and *R*-EuCl (b) at room temperature.

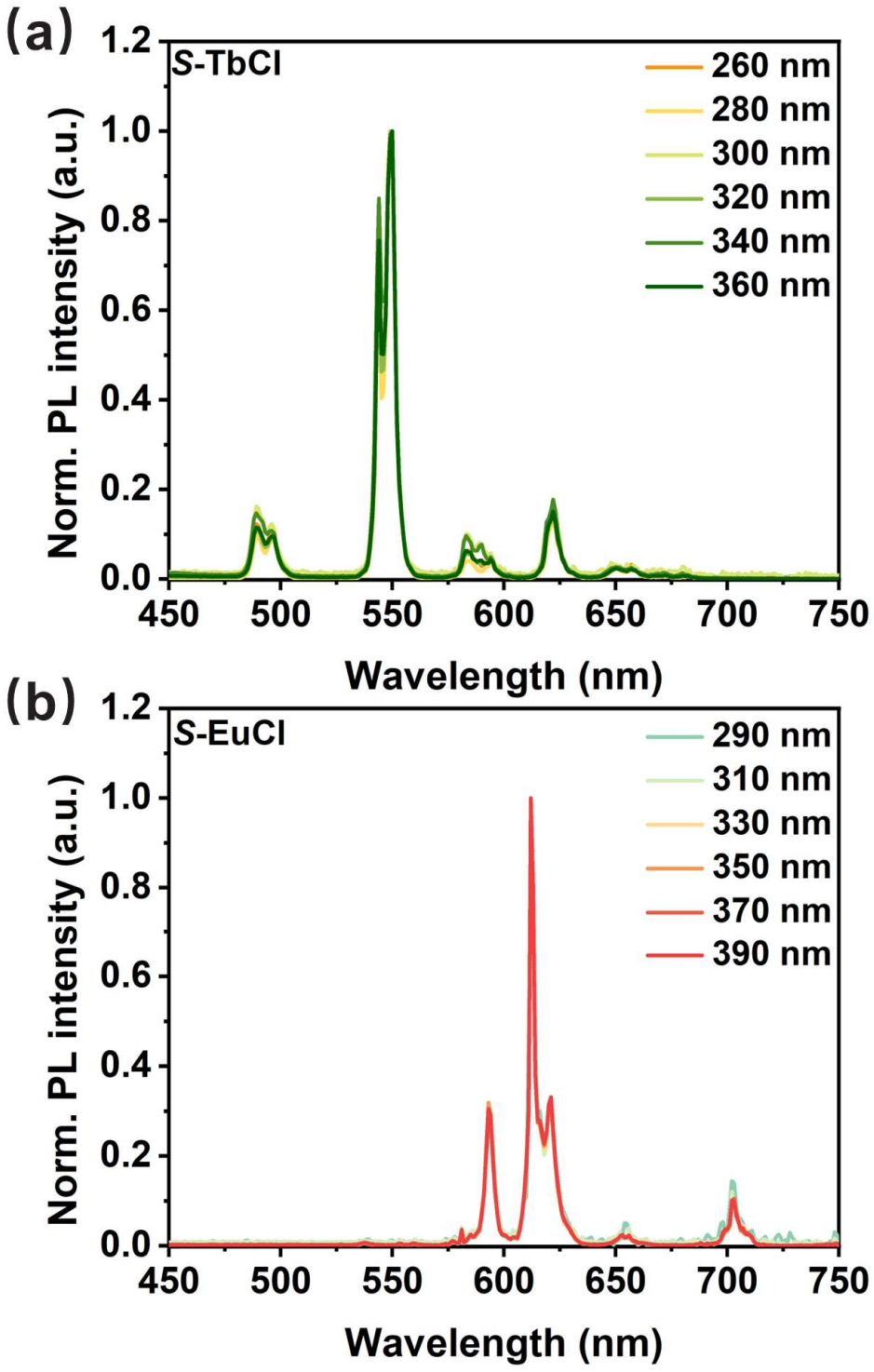

Fig. S12. Normalized PL spectra of *S*-TbCl (a) and *S*-EuCl (b) under different excitation wavelengths.

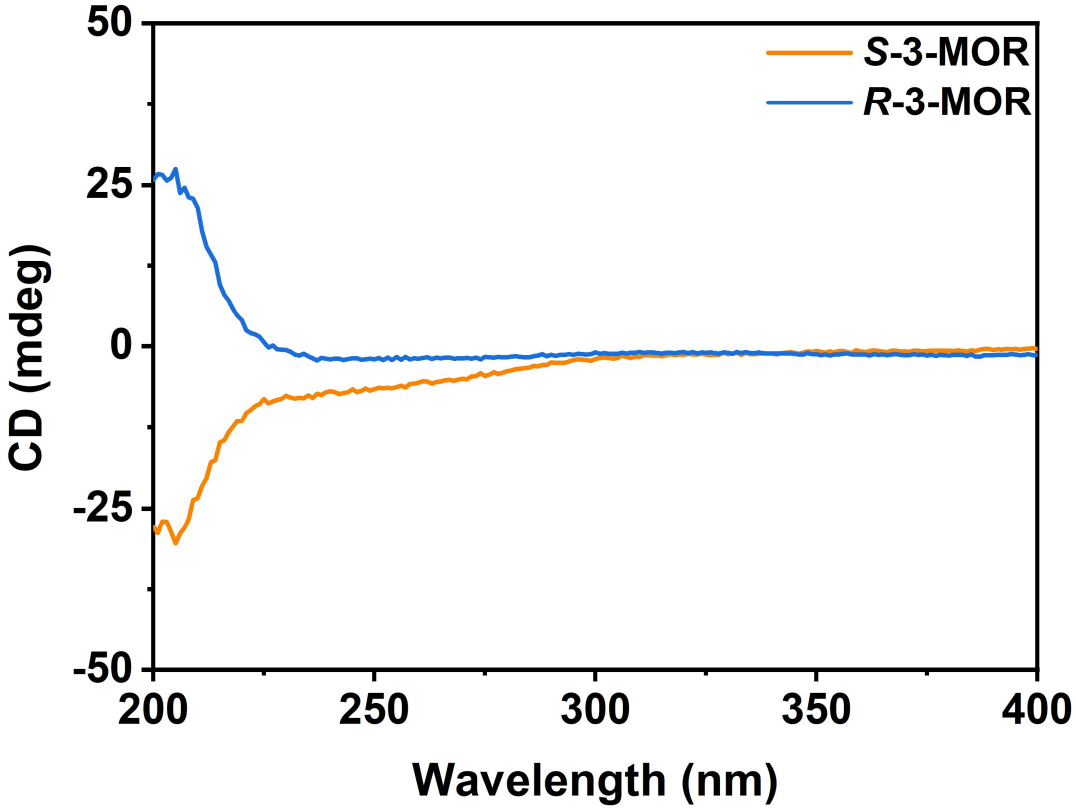

Fig. S13. CD spectra of *S*-3MOR and *R*-3MOR.

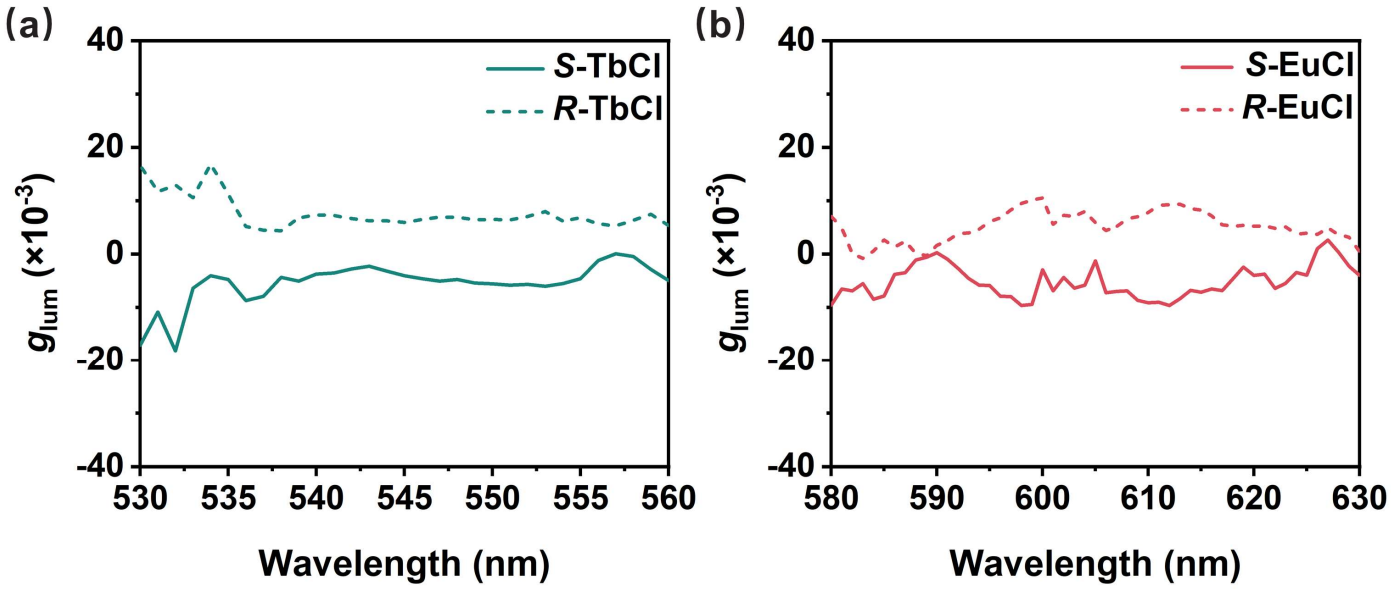

Fig. S14. g_{lum} of *S*/*R*-TbCl (a) and *S*/*R*-EuCl (b).

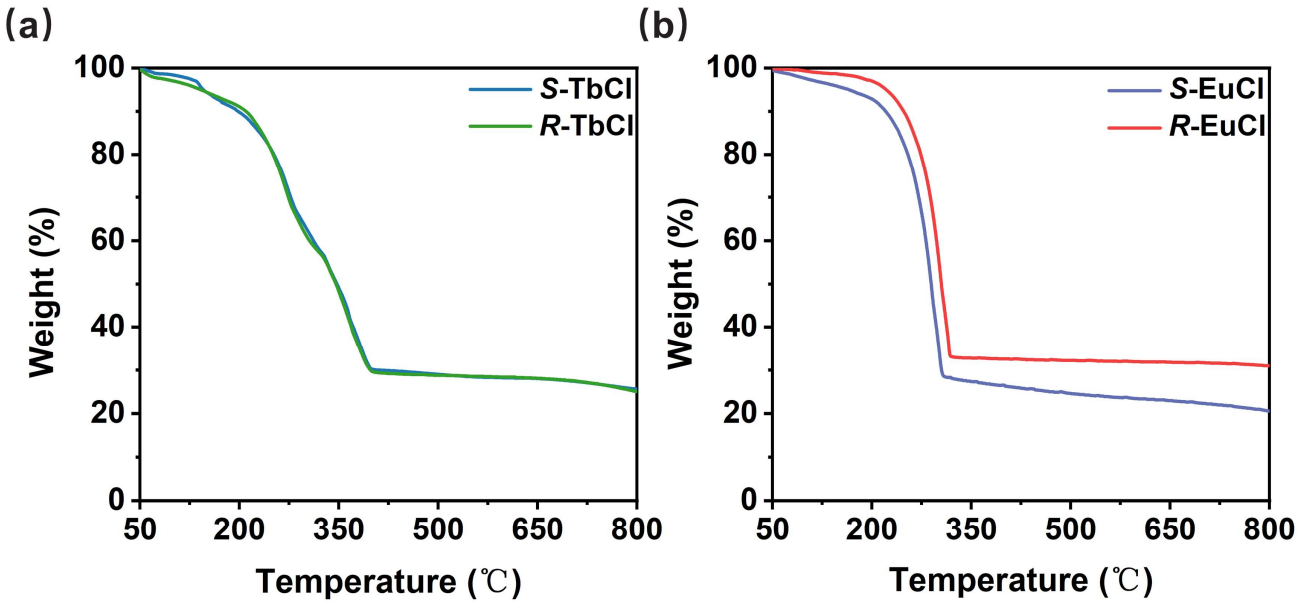

Fig. S15. TGA curves of *S*/*R*-TbCl (a) and *S*/*R*-EuCl (b) from 50 ℃ to 800 ℃.

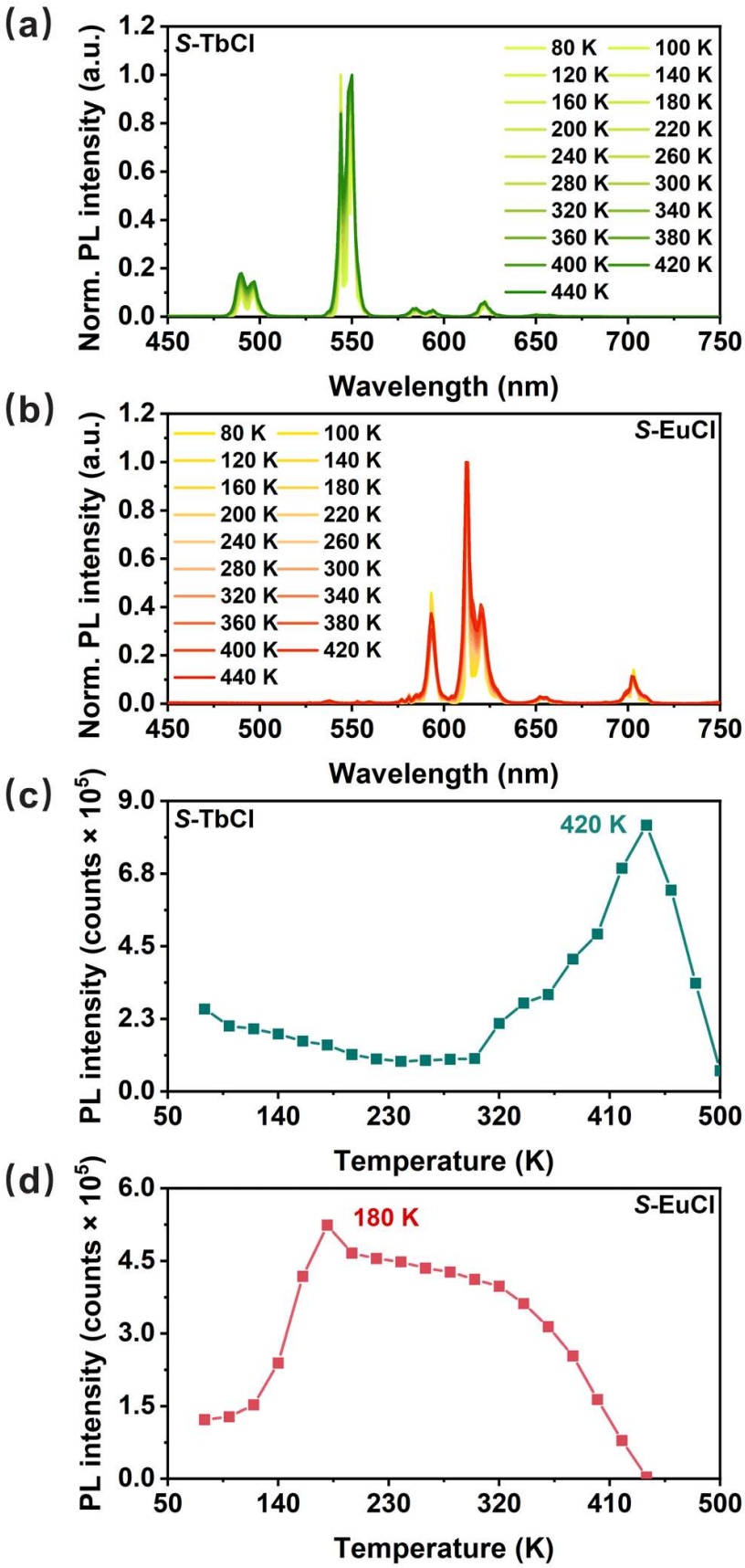

Fig. S16. Normalized PL spectra of *S*-TbCl (a) and *S*-EuCl (b) under different temperatures. PL intensities of *S*-TbCl (c) peaked at 550 nm and *S*-EuCl (d) peaked at 612 nm at various temperatures.

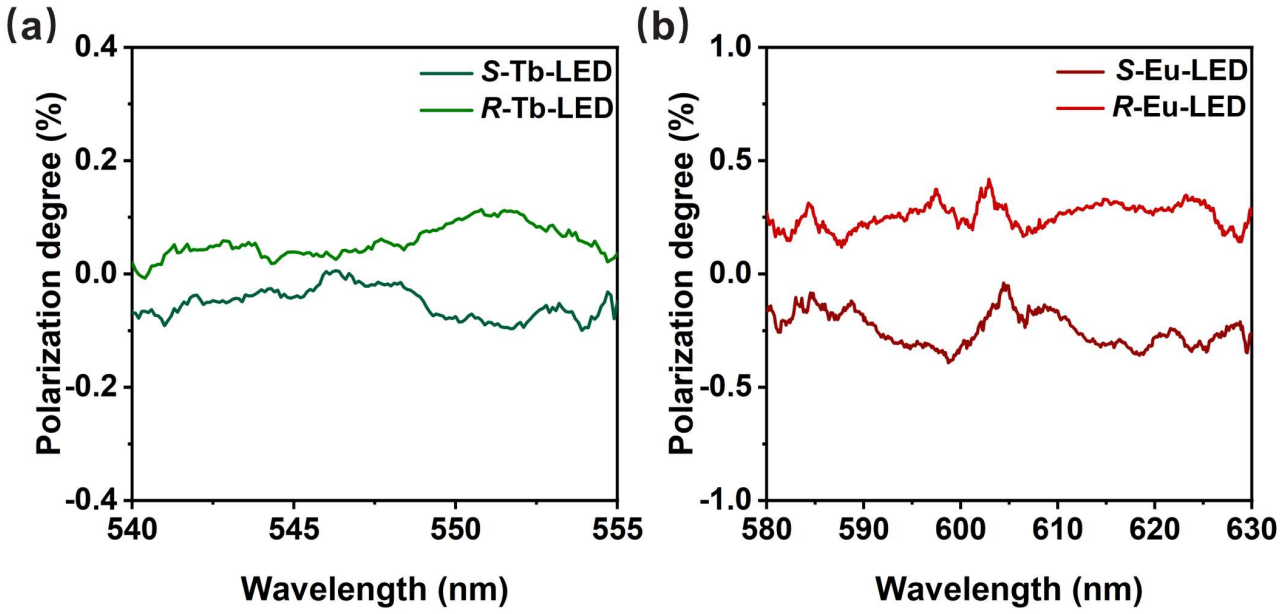

Fig. S17. Polarization degree curves of the CP-LEDs prepared by *S*/*R*-TbCl (a) and *S*/*R*-EuCl (b).

Reference:

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

2 G. Sheldrick, *Acta Crystallographica Section A*, 2015, **71**, 3-8.

3 A. Linden, *Acta Crystallographica Section C*, 2015, **71**, 1-2.

4 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272-1276.

5 M. Lee, H. Chung, S. V. Hong, H. Y. Woo, J.-Y. Chae, T. Y. Yoon, B. T. Diroll and T. Paik, *Nanoscale*, 2023, **15,** 1513-1521.

6 Z. Li, R. Núñez, M. E. Light, E. Ruiz, F. Teixidor, C. Viñas, D. Ruiz-Molina, C. Roscini and J. G. Planas, *Chem. Mater.*, 2022, **34**, 4795-4808.

7 S. Petoud, G. Muller, E. G. Moore, J. Xu, J. Sokolnicki, J. P. Riehl, U. N. Le, S. M. Cohen and K. N. Raymond, *J. Am. Chem. Soc.*, 2007, **129**, 77-83.

8 Y. B. Tan, Y. Okayasu, S. Katao, Y. Nishikawa, F. Asanoma, M. Yamada, J. Yuasa and T. Kawai, *J. Am. Chem. Soc.*, 2020, **142**, 17653-17661.

9 A. Zheng, T. Zhao, C. Xiao, X. Jin and P. Duan, *J. Mater. Chem. C,* 2022, **10,** 13084-13092.

10 M. Tsurui, R. Takizawa, Y. Kitagawa, M. Wang, M. Kobayashi, T. Taketsugu and Y. Hasegawa, *Angew. Chem. Int. Ed.,* 2024, **63,** e202405584.

11 J. Jin, M. C. Folgueras, M. Gao, S. Yu, S. Louisia, Y. Zhang, L. N. Quan, C. Chen, R. Zhang, F. Seeler, K. Schierle-Arndt and P. Yang, *Nano Lett.*, 2021, **21**, 5415-5421.