Supporting Information

Subtle Adjustments for Constructing Multi-nuclear Luminescent Lanthanide Organic Polyhedra with Triazole-Based Chelates

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1. General

1.1 DOSY spectra

DOSY is a method of determining the rate of diffusion of molecules in solution. Stokes-Einstein equation was used for estimating the dynamic radius for assemblies:¹

$$\mathbf{r} = \frac{k_B T}{6\pi\eta D}$$

Where, r is spherical hydrodynamic radius of the molecule (m), k_B is Boltzmann constant, T is absolute temperature (K), D, is diffusion coefficient (m²·s⁻¹).

1.2 Luminescence quantum yield

The overall luminescence quantum yield was measured by using the FS5 spectrofluorometer from Edinburg Photonics (SC-30 Integrating Sphere). Firstly, the veracity of the instrument was carefully calibrated by two typical standard compounds ([Cs₃[Eu(dpa)₃] in Tris buffer 0.1 M, $\Phi = 24\pm2.5\%^2$ quinine sulfate in H₂SO₄ 0.1 M, $\Phi = 59\pm4\%)^3$. For liquid samples the reference would be a cuvette containing the solvent only.

2. Procedure

2.1 Synthesis of ligands



Scheme S1 Synthetic route of ligands.

2.1.1 Synthesis of 6-ethynyl-N-isopropylpicolinamide



The synthesis of 6-ethynyl-N-isopropylpicolinamide followed the literature procedure.⁴ ¹H NMR (400 MHz, CDCl₃, 298 K) $\delta = 8.15$ (d, J = 7.9 Hz, 1H), 7.79 (t, J = 7.8 Hz, 2H), 7.55 (d, J = 7.7 Hz, 1H), 4.29-4.19 (m, 1H), 3.21 (s, 1H), 1.25 (d, J = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃, 298 K): $\delta = 22.70$, 41.54, 77.80, 82.20, 122.10, 129.73, 137.62, 140.63, 150.51, 162.49; ESI-TOF-MS for C₁₁H₁₂N₂O [M + Na]⁺: calcd, m/z = 211.0842; found, 211.0843.

2.1.2 Synthesis of 2^{R/S}



6-bromopicolinic acid (5 g, 24.8 mmol), (1S)-1-naphthalen-1-ylethanamine (4.3 g, 24.8 mmol), HATU (18.8 g, 49.50 mmol, 2.0 equiv), DMF (30mL) and Et₃N (3 mL) were added into a 100 mL two-necked flask. Then the reaction was stirred under 0 °C for 36 h. The residual solvent was removed under vacuum distillation, and the residue was purified chromatographically (SiO₂, DCM/PE = 5/1) to afford 2^{S} as a colorless

grease (6.25 g, 71.0%). ¹H NMR (400 MHz, CDCl₃, 298 K) $\delta = 8.19$ (d, J = 7.7 Hz, 2H), 8.11 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.48 (dd, J = 10.2, 5.2 Hz, 2H), 6.15 (s, 1H), 1.79 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃, 298 K) $\delta = 161.77$, 150.97, 140.58, 139.64, 138.14, 133.97, 131.15, 130.79, 128.88, 128.44, 126.59, 125.85, 125.36, 123.33, 122.77, 121.51, 44.91, 21.16; ESI-TOF-MS for C₁₈H₁₅BrN₂O [M + Na]⁺: calcd, m/z = 377.0260; found, 377.0256.

 1^{R} was synthesized in the same procedure as above, starting from (1R)-1-naphthalen-1-ylethanamine.

2.1.3 Synthesis of 3^{R/S}



 $\mathbf{2^{S}}$ (5.0 g, 14.1 mmol, 1.0 equiv), CuI (537 mg, 2.82 mmol, 0.2 equiv) and Pd(PPh₃)₄ (815 mg, 0.71 mmol, 0.05 equiv) were added into a three-necked flask, and the reaction mixture was stirred in anhydrous THF/TEA (80 mL, v/v = 1/1) under nitrogen atmosphere. Then TMSA (1.5 g, 15.5 mmol, 1.1 equiv, TMSA) was added dropwise into the mixture and the suspension was stirred at room temperature for 16 h. The residue was filtered off with kieselguhr, and the filtrate was concentrated under vacuum distillation. Then, the crude product was purified chromatographically (DCM/PE = 2/1) to afford 3^s as a white powder (3.6 g, 68.3%). ¹H NMR (400 MHz, *DMSO-d*₆, 298 K) $\delta = 8.97$ (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.3 Hz, 1H), 8.04 (d, J =6.8 Hz, 1H), 7.97 (t, J = 7.8 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.0 Hz, 1H), 7.55 (t, J = 6.8 Hz, 1H), 7.53 -7.44 (m, 2H), 6.00 (p, J = 6.9 Hz, 1H), 1.66 (d, J = 6.9 Hz, 3H), 0.22 (s, 9H); ¹³C NMR (101 MHz, *DMSO-d*₆, 298 K) $\delta = 162.38$, 150.52, 140.78, 139.34, 138.39, 133.32, 130.46, 130.18, 128.66, 127.45, 126.23, 125.55, 125.39, 123.00, 122.11, 103.48, 95.32, 44.39, 20.93, -0.50; ESI-TOF-MS for $C_{23}H_{24}N_2OSi [M + Na]^+$: calcd, m/z = 395.1550; found: 395.1545.

 3^{R} was synthesized in the same procedure as above, starting from 2^{R} .

2.1.4 Synthesis of 4^{R/S}



To a solution of 3^{s} (3.6 g, 9.7 mmol, 1 equiv) in MeOH (80 mL) was added KF (620.0 mg, 10.7 mmol, 1.1 equiv). The solution was further stirred for 6 h at room temperature. The organic solvent was removed under vacuum distillation, and the crude product was purified chromatographically (SiO₂, DCM) to afford 4^{s} as

colourless grease (2.8 g, 96.6%). ¹H NMR (400 MHz, CDCl₃, 298 K) $\delta = 8.24$ (t, J = 8.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.81 (t, J = 7.8 Hz, 2H), 7.62 (d, J = 7.1 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.54 – 7.50 (m, 1H), 7.50 – 7.45 (m, 2H), 6.14 (m, J = 13.9, 6.9 Hz, 1H), 3.16 (s, 1H), 1.78 (d, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃, 298 K) $\delta = 162.39$, 150.25, 140.75, 138.23, 137.65, 133.96, 131.19, 129.97, 128.71, 128.37, 126.53, 125.79, 125.31, 123.39, 122.76, 122.32, 82.19, 77.87, 44.79, 21.10. ESI-TOF-MS for C₂₀H₁₆N₂O [M + Na]⁺: calcd, m/z 323.1155; found, 323.1154.

 4^{R} was synthesized in the same procedure as above, starting from 3^{R} .

2.1.5 Synthesis of 1,4-diazidobenzene

Aqueous sodium nitrite (2.73 g, 39.6 mmol, for a 3:1 ratio of nitrite to amino group) was added to a cooled solution of *p*-phenylenediamine (500 mg, 6.6 mmol, 1.0 equiv) in dilute hydrochloric acid (2 M, 30 mL) to synthesize the diazonium salt in an ice bath. After stirring for 2 h, an aqueous solution of sodium azide (1.72 g, 26.4 mmol, 4.0 equiv) was added dropwise to the diazonium salt. The mixture was stirred for another 2 h. The precipitate was recovered by filtration and further purified by column chromatography on silica gel with petroleum ether. Off-white powder was obtained after dried in vacuum (264 mg, 25.0%). ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.05 (s, 4 H).¹³C NMR (151 MHz, CDCl₃, 298 K) δ = 136.68, 120.41. ESI-TOF-MS for C₆H₄N₆ [M + Na]⁺: calcd, m/z = 161.0570; found, 161.0542.

2.1.6 Synthesis of 4,4'-diazidobiphenyl

Aqueous sodium nitrite (1.65 g, 24 mmol, for a 3:1 ratio of nitrite to amino group) was added to a cooled solution of benzidine (1.0 g, 4 mmol, 1.0 equiv) in dilute hydrochloric acid (2 M, 30 mL) to create the diazonium salt in an ice bath. After stirring for 2 h, an aqueous solution of sodium azide (1.04 g, 10 mmol, 4.0 equiv) was added dropwise to the diazonium salt. The mixture was stirred for another 2 h. The precipitate was recovered by filtration and further purified by column chromatography on silica gel with petroleum ether. Off-white powder was obtained after dried in vacuum (976 mg, 78.1%). ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.58 (d, *J* = 9.0 Hz, 8H), 7.07 (d, *J* = 8.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃, 298 K) δ = 128.31, 127.29, 119.49. ESI-TOF-MS for C₁₈H₁₂N₆ [M + Na]⁺: calcd, m/z = 335.1041; found, 335.1039.

2.1.7 Synthesis of 1,4-bis(4-azidophenyl)benzene

Aqueous sodium nitrite (5 g, 24 mmol, for a 3:1 ratio of nitrite to amino group) was added to a cooled solution of 4,4"-diamino-*p*-terphenyl (1.0 g, 4 mmol, 1.0 equiv) in dilute hydrochloric acid (2 M, 30 mL) to create the diazonium salt in an ice bath. After stirring for 0.5 h, an aqueous solution of sodium azide (1.04 g, 10 mmol, 4.0 equiv.) was added dropwise to the diazonium salt. The mixture was stirred for another 2 h. The precipitate was recovered by filtration and further purified by column chromatography on silica gel with petroleum ether. Off-white powder was obtained after dried in vacuum (976 mg, 78.1%). ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 7.58

(d, J = 9.0 Hz, 8H), 7.07 (d, J = 8.6 Hz, 4H).¹³C NMR (101 MHz, CDCl₃, 298 K) $\delta = 128.31, 127.29, 119.49$. ESI-TOF-MS for C₁₈H₁₂N₆ [M + Na]⁺: calcd, m/z = 335.1041; found, 335.1039.

2.2 NMR spectra



Figure S1 ¹H NMR spectrum of 2^S (400 MHz, CDCl₃, 298 K).



Figure S2 1 H- 1 H COSY NMR spectrum of 2^S (400 MHz, CDCl₃, 298 K).





Figure S3 13 C NMR spectrum of 2^S (101 MHz, CDCl₃, 298 K).



Figure S4 1 H- 1 H COSY spectrum of 2^S (400 MHz, CDCl₃, 298 K).



Figure S5 ¹H NMR spectrum of 3° (400 MHz, DMSO- d_6 , 298 K).









Figure S7 ¹H NMR spectrum of 4^S (400 MHz, CDCl₃, 298 K).



Figure S8 13 C NMR spectrum of 4⁸ (101 MHz, CDCl₃, 298 K).



Figure S9 ¹H-¹H COSY NMR spectrum of 4^S (400 MHz, CDCl₃, 298 K).



Figure S10 ¹H-¹H COSY spectrum of **4**⁸ (400 MHz, CDCl₃, 298 K).



Figure S11 ¹H NMR spectrum of L_1^{SS} (400 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S12 ¹³C NMR spectrum of L_1^{SS} (101 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S13 1 H- 1 H COSY spectrum of L₁^{SS} (400 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S15 13 C NMR spectrum of L_2^{SS} (101 MHz, CDCl₃, 298 K).



Figure S16 1 H- 1 H COSY spectrum of L_{2}^{SS} (400 MHz, CDCl₃, 298 K).



Figure S17 1 H- 1 H COSY spectrum of L_{2}^{SS} (400 MHz, CDCl₃, 298 K).

7.870 8.396 7.870 8.352 7.810 8.260 7.810 8.260 7.810 8.260 7.810 8.260 7.719 7.798 7.703 7.967 7.703 7.966 7.703 7.965 7.538 7.953 7.524 7.563 7.523 7.564 7.524 7.564 7.523 7.564 7.544 6.156 7.447 6.156 7.446 6.156 7.447 6.156 7.446 6.156 7.447 6.156 7.446 6.156 7.447 6.156 7.447 6.156 7.441 6.156 7.441 6.156



1.841

Figure S18 ¹H NMR spectrum of L_3 ^{SS} (400 MHz, CDCl₃, 298 K).



Figure S19 ¹³C NMR spectrum of L₃^{SS} (101 MHz, CDCl₃, 298 K).



Figure S20 1 H- 1 H COSY NMR spectrum of L₃^{SS} (400 MHz, CDCl₃, 298 K).



Figure S21 1 H- 1 H COSY spectrum of L₃^{SS} (400 MHz, CDCl₃, 298 K).



Figure S22 ¹H NMR spectrum of L_1^{AC} (600 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S23 1 H- 1 H COSY NMR spectrum of L₁^{AC} (600 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S24 13 C NMR spectrum of L_1^{AC} (151 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S25 ¹H NMR spectrum of L_2^{AC} (400 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S26 ¹³C NMR spectrum of L_2^{AC} (101 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S27 ¹H-¹H COSY NMR spectrum of L_2^{AC} (400 MHz, CDCl₃/CD₃OD v/v 5/1, 298 K).



Figure S28 ¹H NMR spectra of the self-assembly complexes of L_1^{SS} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S29 ¹H-¹H COSY spectra of the self-assembly complexes of L_1^{SS} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S30 ¹³C NMR spectra of the self-assembly complexes of L_1^{SS} and Eu(OTf)₃ (101 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S31 ¹H DOSY spectra of the self-assembly complexes of L_1^{SS} and $Eu(OTf)_3$ (logD = -9.251, r = 11.3 Å, 400 MHz, CD₃CN/CD₃OD 4/1, 298 K).



Figure S32 ¹H NMR spectra of the self-assembly complexes of L_2^{SS} (4.8×10⁻³ M) and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S33 ¹H DOSY spectra of the self-assembly complexes of L_2^{SS} (4.8×10⁻³ M) and Eu(OTf)₃ (log D_1 = -9.290, log D_2 = -9.181, r₁ = 12.4 Å, r₂ = 9.6 Å, 400 MHz,



Figure S34 ¹H NMR spectra of the self-assembly complexes of L_2^{SS} (1.2×10⁻² M) and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S35 ¹H-¹H COSY spectra of the self-assembly complexes of L_2^{SS} (1.2×10⁻² M) and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S36 ¹³C NMR spectra of the self-assembly complexes of L_2^{SS} (1.2×10⁻² M) and Eu(OTf)₃ (101 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S37 ¹H DOSY spectra of the self-assembly complexes of L_2^{SS} (1.2×10⁻² M) and Eu(OTf)₃ (log*D* = -9.320, r = 13.3 Å, 400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S38 ¹H NMR spectra of the self-assembly complexes of L_3 ^{SS} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S39 ¹H-¹H COSY spectra of the self-assembly complexes of L_3 ^{SS} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S40 ¹³C NMR spectra of the self-assembly complexes of L_3^{SS} and Eu(OTf)₃ (101 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S41 ¹H DOSY spectra of the self-assembly complexes of L_3 ^{SS} and Eu(OTf)₃ (logD = -9.251, r = 11.3 Å, 400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S42 ¹H NMR spectrum of the self-assembly complex of L_1^{AC} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S43 ¹H-¹H COSY spectrum of the self-assembly complex of L_1^{AC} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S44 ¹³C NMR spectrum of the self-assembly complex of L_1^{AC} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S45 ¹H DOSY spectrum of the self-assembly complex of L_1^{AC} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K, Diffusion Coefficient $D = 5.72 \times 10^{-10} \text{ m}^2/\text{s}$,



Figure S46 ¹H NMR spectrum of the self-assembly complex of L_2^{AC} and Eu(OTf)₃ ([L_2^{AC}] = 3.7 mM, 400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S47 ¹H-¹H COSY spectrum of the self-assembly complex of L_2^{AC} and Eu(OTf)₃ ([L_2^{AC}] = 3.7 mM, 400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S48 ¹H DOSY spectrum of the self-assembly complex of L_2^{AC} and Eu(OTf)₃ (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K, Diffusion Coefficient $D = 1.02 \times 10^{-9} \text{ m}^2/\text{s}$, d = 1.3 nm).



Figure S49 ¹H NMR spectrum of the self-assembly complex of L_2^{AC} and Eu(OTf)₃

 $([L_2^{AC}] = 13.2 \text{ mM}, 400 \text{ MHz}, CD_3CN/CD_3OD \text{ v/v} 4/1, 298 \text{ K}).$



Figure S50 ¹H-¹H COSY spectrum of the self-assembly complex of L_2^{AC} and Eu(OTf)₃ ([L_2^{AC}] = 13.2 mM, 400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K).



Figure S51 ¹H DOSY spectrum of the self-assembly complex of L_2^{AC} and Eu(OTf)₃ $[L_2^{AC}] = 32.6$ mM, 400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K, Diffusion Coefficient $D_1 = 9.95 \times 10^{-10}$ m²/S, $d_1 = 1.3$ nm, $D_2 = 5.81 \times 10^{-10}$ m²/s, $d_2 = 2.3$ nm).

3. Concentration-Dependent Interconversion



3.1 Structural transformation from $Eu_2(L_2^{SS})_3$ to $Eu_4(L_2^{SS})_6$

Figure S52 ¹H NMR spectra (400 MHz, 298 K) for the concentration-dependent self-assembly of L_2^{SS} with Eu(OTf)₃ in mixed CD₃CN/CD₃OD (v/v 4/1) solution.



Figure S53 (A, C) NMR-tracking (400 MHz, 298 K, CD₃CN/CD₃OD v/v 4/1) the reversible conversion from tetrahedra to helicates under dilution conditions ($[L_2^{SS}]$ = 4.8 mM). (B, D) Corresponding plots of helicate content vs. time.



Figure S54 Comparison of the ¹H NMR spectra (400 MHz, CD₃CN/CD₃OD v/v 4/1, 298 K) for the assembly of L_2^{AC} or L_2^{SS} with Eu(OTf)₃ under the same ligand concentration (7.2 mM). For L_2^{AC} , the content of triple helicate Eu₂(L_2^{AC})₃ is 89.8%, while 82.9% for Eu₄(L_2^{SS})₆ was observed for L_2^{SS} .

3.2 Determination of apparent equilibrium (*K*) and Gibbs free energy (ΔG)



Figure S55 ¹H NMR spectra (400 MHz, 298 K) of the self-assembly complexes of L_2^{ss} (4.8 mM) with Eu(OTf)₃ in mixed CH₃CN/CH₃OH (v/v 4/1) solution.

Based on dynamic equilibrium of two species $2Eu_2(L_2^{SS})_3 \stackrel{\scriptstyle{>}}{=} Eu_4(L_2^{SS})_6$ and ratio of integration of ¹H NMR, two equations can be given as follows:

$$3[Eu_2(L_2^{SS})_3] + 6[Eu_4(L_2^{SS})_6] = [L_2^{SS}]$$
(1)

$$3[Eu_2(L_2^{SS})_3] / 6[Eu_4(L_2^{SS})_6] = 1/2.19$$
(2)

Hence, the concentration calculation results of $Eu_2(L_2^{SS})_3$ and $Eu_4(L_2^{SS})_6$ are 0.50

mM and 0.55 mM, respectively. Hence, the apparent equilibrium (*K*, 298 K) can be calculated as 2200 M⁻¹ ($K = [Eu_4(L_2^{SS})_6]/[Eu_2(L_2^{SS})_3]^2$). The corresponding Gibbs free energy (ΔG) can be determined as -19.1 kJ·mol⁻¹ ($\Delta G = -RTlnK$).



Figure S56 ¹H NMR spectra (400 MHz, 298K) of the self-assembly complexes of L_2^{AC} (7.2 mM) with Eu(OTf)₃ in mixed CH₃CN/CH₃OH (v/v 4/1) solution.

Similarly, the apparent equilibrium (*K*, 298 K) for $2\text{Eu}_2(\mathbf{L_2}^{AC})_3 \stackrel{\text{\tiny{\leftarrow}}}{=} \text{Eu}_4(\mathbf{L_2}^{AC})_6$ can be calculated as 39.4 M⁻¹ (*K* = $[\text{Eu}_4(\mathbf{L_2}^{AC})_6]/[\text{Eu}_2(\mathbf{L_2}^{AC})_3]^2$). The corresponding Gibbs free energy (ΔG) can be determined as -8.9 kJ·mol⁻¹ (ΔG = -RTln*K*).

3.3 VT-NMR experiments for the equilibrium $2Eu_2L_3 \Rightarrow Eu_4L_6$ (L = L_2^{AC} or L_2^{SS})



Figure S57. VT-NMR stack plot (600 MHz, CD₃CN/MeOD v/v 4/1) showing the effect of temperature on the equilibrium of $2Eu_2(L_2^{AC})_3 \rightleftharpoons Eu_4(L_2^{AC})_6$. ($[L_2^{AC}] = 4.7$ mM). The pyridine region of $Eu_2(L_2^{AC})_3$ (\blacklozenge) and $Eu_4(L_2^{AC})_6$ (\bullet) were labeled. It can be observed that decrease in temperature is conducive to the formation of $Eu_4(L_2^{AC})_6$.



Figure S58. Distribution plots (left) and table (right) of $Eu_2(L_2^{AC})_3$ and $Eu_4(L_2^{AC})_6$ at various temperatures. The molar fractions at each temperature were calculated by ¹H NMR integral ratios for the pyridine regions.



Figure S59. VT-NMR stack plot (600 MHz, CD₃CN/MeOD v/v 4/1) showing the effect of temperature on the equilibrium of $2\text{Eu}_2(\mathbf{L}_2^{SS})_3 \approx \text{Eu}_4(\mathbf{L}_2^{SS})_6$. ([\mathbf{L}_2^{SS}] = 7.8 mM). The pyridine region of $\text{Eu}_2(\mathbf{L}_2^{SS})_3$ (\blacklozenge) and $\text{Eu}_4(\mathbf{L}_2^{SS})_6$ (\bullet) were labeled. It can be observed that decrease in temperature is conducive to the formation of $\text{Eu}_4(\mathbf{L}_2^{SS})_6$.



Figure S60. Distribution plots (left) and table (right) of $Eu_2(L_2^{SS})_3$ and $Eu_4(L_2^{SS})_6$ at various temperatures. The molar fractions at each temperature were calculated by ¹H NMR integral ratios for the pyridine regions.

The thermodynamic parameters for the equilibrium of $2Eu_2L_3 \rightleftharpoons Eu_4L_6$ (L = L_2^{AC} or L_2^{SS}) can be obtained based upon van't Hoff equation:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$
(3)

According to VT-NMR spectra, the values of equilibrium constant (K) at various temperature can be calculated by integral ratios. There is a linear relationship between 1/T and $\ln K$ in equation 1. Therefore, the slope and intercept of the line can be obtained by linear fitting, and then corresponding thermodynamic parameters for encapsulation equilibrium are calculated as follows.



Figure S61. Left: Data for the equilibrium of $2Eu_2(L_2^{AC})_3 \stackrel{\scriptstyle{\diamond}}{=} Eu_4(L_2^{AC})_6$ from VT-NMR. Right: The linear fitting of 1/T vs. ln*K* based on the van't Hoff equation and the calculated thermodynamic parameters of ΔH° , ΔS° and ΔG° (298 K).



Figure S62. Left: Data for the equilibrium of $2Eu_2(L_2^{SS})_3 \stackrel{=}{=} Eu_4(L_2^{SS})_6$ from VT-NMR. Right: The linear fitting of 1/T vs. ln*K* based on the van't Hoff equation and the calculated thermodynamic parameters of ΔH° , ΔS° and ΔG° (298 K).

3.4 Driving force analysis for the equilibrium $2Eu_2L_3 \Rightarrow Eu_4L_6$ (L = L_2^{AC} or L_2^{SS})

The dimerization equilibrium of $2[Eu_2(L_2^{AC})_3]^{6+} \approx [Eu_4(L_2^{AC})_6]^{12+}$: $\beta_{dim}^{Eu,L_2^{AC}}(1)$ can be considered as the combination of equilibria (3) and (4) (Figure S63). Corresponding rotational statistical factors $\omega_{2,3}^{Eu,L_2^{AC}} = 24$ and $\omega_{4,6}^{Eu,L_2^{AC}} = 864$ can be obtained by using eqn (5) for the general complexation process (6).⁵

$$\omega_{m,n}^{\mathrm{M,L}} = \frac{(\sigma_{\mathrm{tot}}^{\mathrm{M}})^m (\sigma_{\mathrm{tot}}^{\mathrm{L}})^n}{(\sigma_{\mathrm{tot}}^{\mathrm{MmLn}}) (\sigma_{\mathrm{tot}}^{\mathrm{ion}})^x}$$
(5)

$$m[\mathrm{M}(\mathrm{ion})_x] + n\mathrm{L} \rightleftharpoons [\mathrm{M}_m\mathrm{L}_n] + x(\mathrm{ion}): \beta_{m,n}^{\mathrm{M},\mathrm{L}}:$$
(6)

Whereby M = metal and L = ligand. Thus, the statistical factor for equilibrium (1) $\omega_{dim}^{Eu,L_2^{AC}} = \omega_{4,6}^{Eu,L_2^{AC}} / (\omega_{2,3}^{Eu,L_2^{AC}})^2 = 3/2$ was determined. Eventually, the contribution of the rotational degeneracy to the overall energetic balance of the dimerization process are evaluated by the expression $\Delta G_{dim}^{Eu,L_2^{AC}} = -RT \ln \left(\omega_{dim}^{Eu,L_2^{AC}} \right) =$ -1.0 kJ mol^{-1} . For the complexation of chiral L_2^{SS} with Eu(CF₃SO₃)₃, we further computed the statistical factors $\omega_{2,3}^{Eu,L_2^{SS}} = 12$ and $\omega_{4,6}^{Eu,L_2^{SS}} = 432$ for equilibria (7) and (8) (Figure S64). The statistical factor and its corresponding free energy contribution to the equilibrium of $2[Eu_2(L_2^{SS})_3]^{6+} \neq [Eu_4(L_2^{SS})_6]^{12+}$: $\beta_{dim}^{Eu,L_2^{SC}}$ (2) are calculated as $\omega_{dim}^{Eu,L_2^{SS}} = \omega_{4,6}^{Eu,L_2^{SS}} / (\omega_{2,3}^{Eu,L_3^{SS}})^2 = 3$ and $\Delta G_{dim}^{Eu,L_3^{SS}} =$ $-RT ln \left(\omega_{dim}^{Eu,L_2^{SS}} \right) = -2.7 \text{ kJ mol}^{-1}$, respectively.



Figure S63 Calculated symmetry numbers (σ) and rotational statistical factors ($\omega_{2,3}^{\text{Eu},\text{L}_2^{\text{AC}}}$ and $\omega_{4,6}^{\text{Eu},\text{L}_2^{\text{AC}}}$) for equilibria (3) and (4) by using the symmetry number method.^{6,7} For clarity, the symmetry for metal source Eu(CF₃SO₃)₃ in equilibria (3, 4, 7, 8) is considered to be the ideal $C_{3\nu}$.



Figure S64 Calculated symmetry numbers (σ) and rotational statistical factors ($\omega_{2,3}^{\text{Eu},\text{L}_2^{\text{SS}}}$ and $\omega_{4,6}^{\text{Eu},\text{L}_2^{\text{SS}}}$) for equilibria (7) and (8) by using the symmetry number method.

To quantitatively analyze the contribution of enthalpic/entropic driving force to the dimerization process, eqn: $\beta_{dim}^{Eu,L_2^{AC}} = \alpha \frac{(EM_{4,6}^{Eu,L_2^{AC}})^3}{(EM_{2,3}^{Eu,L_2^{AC}})^4}$ (9) ($\alpha = 3/2$ for equilibrium 1; $\alpha = 3$ for equilibrium 2) was used. Whereby the first 3/2 term corresponds to the ratio of the statistical factors. The second ratio can be used to estimate the steric constraints accompanying the intramolecular macrocyclization processes from two triple-stranded helicates with macrobicyclic structures to a tetrahedron with a macrotricyclic structure (Figure S65). Among them, the separation of binding metal sites is measured as $a_{2,3}^{Eu,L_2^{AC}} = 16.5$ Å in $[Eu_2(L_2^{AC})_3]^{6+}$ and $a_{4,6}^{Eu,L_2^{AC}} = 18.5$ Å in $[Eu_4(L_2^{AC})_6]^{12+}$, respectively. According to eqn:

$$EM(r=a)_{\max} = \frac{1}{N_{Av}a^3} \left(\frac{3}{2\pi}\right)^{3/2} \exp\left(-3/2\right)$$
(10)

the ratio of $EM_{4,6}^{\text{Eu},\text{L}_2^{\text{AC}}}/EM_{2,3}^{\text{Eu},\text{L}_2^{\text{AC}}}$ can be calculated as $EM_{4,6}^{\text{Eu},\text{L}_2^{\text{AC}}}/EM_{2,3}^{\text{Eu},\text{L}_2^{\text{AC}}} = \left(a_{2,3}^{\text{Eu},\text{L}_2^{\text{AC}}}/a_{4,6}^{\text{Eu},\text{L}_2^{\text{AC}}}\right)^3 = (16.5/18.5)^3 = 0.71$. Therefore, by introducing this ratio, eqn (9) can be simplified as

$$\beta_{\rm dim}^{\rm Eu, L_2^{\rm AC}} = \frac{3}{2} (0.71)^3 \frac{1}{{}_{EM_{2,3}^{\rm Eu, L_2^{\rm AC}}}} = \frac{0.54}{{}_{EM_{2,3}^{\rm Eu, L_2^{\rm AC}}}}$$
(11)

Similarly, for equilibrium (8), eqn (9) can be simplified as

$$\beta_{\rm dim}^{\rm Eu, L_2^{\rm SS}} = 3(0.75)^3 \frac{1}{EM_{2,3}^{\rm Eu, L_2^{\rm SS}}} = \frac{1.27}{EM_{2,3}^{\rm Eu, L_2^{\rm SS}}}$$
(12)



Figure S65 Stick representation of the structures for the dimerization process in equilibria $2[Eu_2(L_2^{AC})_3]^{6+} \approx [Eu_4(L_2^{AC})_6]^{12+}$ (a) and $2[Eu_2(L_2^{SS})_3]^{6+} \approx [Eu_4(L_2^{SS})_6]^{12+}$ (b) highlighting the intramolecular connection processes. The distances between the binding metal sites are measured based on the optimized structures $[Eu_2(L_2^{AC})_3, Eu_2(L_2^{SS})_3, and Eu_4(L_2^{SS})_6]$ by Material Studio 8.0 and the crystal structure of $Eu_4(L_2^{AC})_6$.

Table S1 Experimental *EM* for equilibria (1) and (2) at different temperatures.

	-				-	
T (K)	238	258	278	298	318	338
$\beta_{\dim}^{\operatorname{Eu},\mathrm{L}_{2}^{\operatorname{AC}}}(\mathrm{M}^{-1})^{a}$	55.6	47.4	41.8	39.0	33.6	28.2
$EM_{2,3}^{\operatorname{Eu},\operatorname{L}_2^{\operatorname{AC}}}(\operatorname{M})$	9.71×10 ⁻³	1.14×10 ⁻²	1.29×10 ⁻²	1.38×10 ⁻²	1.61×10 ⁻²	1.91×10 ⁻²
$\beta_{\dim}^{\operatorname{Eu}, \mathrm{L}_{2}^{\mathrm{SS}}}(\mathrm{M}^{-1})^{a}$	5292	3968	2613	2200	1614	1262
$EM_{2,3}^{\operatorname{Eu}, \operatorname{L}_2^{\operatorname{SS}}}(\operatorname{M})$	2.40×10 ⁻⁴	3.20×10 ⁻⁴	4.86×10 ⁻⁴	5.77×10 ⁻⁴	2.40×10 ⁻⁴	7.87×10 ⁻⁴

^{*a*} The dimerization constants at various temperature can be calculated by NMR integral ratios.

Given the high charge state of the complexes and the use of polar solvents, the solvation energies may play an important role in the dimerization process. The solvation energies for triple-stranded helicates and tetrahedra can be calculated using the Born equation $(13)^8$

$$\Delta_{\text{solv}}G^0 = -\frac{N_{\text{Av}}Z^2 e^2}{8\pi\varepsilon_0 R} \left(1 - \frac{1}{\varepsilon_r}\right)$$
(13)

Whereby $N_{\rm Av}$ is Avogadro's number (6.023 × 10²³ mol⁻¹), Z is the charge of the complex, *e* is the elementary charge (1.602 × 10⁻¹⁹ C), ε_0 is the vacuum permittivity constant (8.859 × 10⁻¹² C N⁻¹ m⁻²), *R* is the pseudo-spherical hydrodynamic radii of the complex determined by diffusional NMR, $\varepsilon_{\rm r}$ is the relative dielectric permittivity of the medium.

For equilibrium of $2[Eu_2(L_2^{AC})_3]^{6+} \approx [Eu_4(L_2^{AC})_6]^{12+}$ (1), the contribution of solvation energies can be expressed by $\Delta_{solv} G_{4,6}^{Eu,L_2^{AC}} - 2\Delta_{solv} G_{2,3}^{Eu,L_2^{AC}}$.

$$\begin{split} \Delta_{\text{solv}} G_{4,6}^{\text{Eu},\text{L}_{2}^{\text{AC}}} &- 2\Delta_{\text{solv}} G_{2,3}^{\text{Eu},\text{L}_{2}^{\text{AC}}} \\ &= -\frac{12^{2} N_{\text{Av}} e^{2}}{8\pi\varepsilon_{0} R_{4,6}^{\text{L}_{2}^{\text{AC}}}} \Big(1 - \frac{1}{\varepsilon_{\text{r}}}\Big) - \left[-2\frac{6^{2} N_{\text{Av}} e^{2}}{8\pi\varepsilon_{0} R_{2,3}^{\text{L}_{2}^{\text{AC}}}} \Big(1 - \frac{1}{\varepsilon_{\text{r}}}\Big)\right] \\ &= -976 \text{ kJ mol}^{-1} \end{split}$$

Whereby $\varepsilon_r = 35.8$ for mixed CH₃CN/CH₃OH (v/v 4/1) is the weighted average of the mixture components by assuming a simple additive function of the concentration of the solvents.⁹ $R_{2,3}^{L_2^{AC}} = 6.5 \times 10^{-10}$ m and $R_{4,6}^{L_2^{AC}} = 1.15 \times 10^{-9}$ m.

Similarly, for equilibrium of $2[Eu_2(L_2^{SS})_3]^{6+} \approx [Eu_4(L_2^{SS})_6]^{12+}$ (2), the contribution of solvation energies can be expressed by $\Delta_{solv}G_{4,6}^{Eu,L_2^{SS}} - 2\Delta_{solv}G_{2,3}^{Eu,L_2^{SS}}$.

$$\Delta_{\text{solv}} G_{4,6}^{\text{Eu},\text{L}_{2}^{\text{SS}}} - 2\Delta_{\text{solv}} G_{2,3}^{\text{Eu},\text{L}_{2}^{\text{SS}}}$$

$$= -\frac{12^2 N_{\text{Av}} e^2}{8\pi\varepsilon_0 R_{4,6}^{\text{L}_{2}^{\text{SS}}}} \left(1 - \frac{1}{\varepsilon_{\text{r}}}\right) - \left[-2\frac{6^2 N_{\text{Av}} e^2}{8\pi\varepsilon_0 R_{2,3}^{\text{L}_{2}^{\text{SS}}}} \left(1 - \frac{1}{\varepsilon_{\text{r}}}\right)\right]$$

$$= -2777 \text{ kJ mol}^{-1}$$
Whereby $R_{2,3}^{\text{L}_{2}^{\text{SS}}} = 9.6 \times 10^{-10} \text{ m and } R_{4,6}^{\text{L}_{2}^{\text{SS}}} = 1.24 \times 10^{-9} \text{ m.}$

4. Comparison of the Linear Ligand Length



Figure S66 Comparison of $N \cdots N$ distances (pyridine nitrogen atom) between APA-L and APT-L ligands.

5. Single Crystal X-ray Diffraction

 $Eu_4(L_1^{AC})_6(OTf)_{12}, Eu_4(L_1^{RR})_6(OTf)_{12}$ for Suitable single crystals $Eu_4(L_2^{AC})_6(OTf)_{12}$, and $Eu_2(L_3^{SS})_6(OTf)_6$ were obtained through the slow diffusion of a poor solvent vapor, dichloromethane (DCM), into the corresponding assembly solution at room temperature for one to two weeks. Diffraction data for $Eu_4(L_1^{AC})_6(OTf)_{12}$, $Eu_4(L_1^{RR})_6(OTf)_{12}$, and $Eu_2(L_3^{SS})_6(OTf)_6$ were collected using a Bruker D8 VENTURE photon II diffractometer with I_{us} 3.0 microfocus X-ray source using APEX III program. Data reduction was performed with the saint and SADABS package. Due to the very weak diffraction signals of the giant supramolecular assembly in nature, the X-ray diffraction studies for the complex $Eu_4(L_2^{AC})_6(OTf)_{12}$ were carried out on the BL17B macromolecular crystallography beamline in Shanghai Synchrotron Facility (SSRF). Raw diffraction data in the "filename.mccd" format were converted to "filename.sfrm" using the APEX III program. Data reduction was performed with the SAINT and SADABS package. Both structures were solved by direct methods and refined with full-matrix least-squares on F^2 , using anisotropic displacement and the SHELXTL software package.¹⁰ Because of the large amount of amorphous solvents and highly-disordered counterions existing in the unit cell, which occupy as much as 64.8% for $Eu_4(L_1^{AC})_6(OTf)_{12}$, 59.1% for $Eu_4(L_1^{RR})_6(OTf)_{12}$, 67.1% for Eu₄(L₂^{AC})₆(OTf)₁₂ and 43.5% for Eu₂(L₃^{SS})₃(OTf)₆ of the unit cell based on PLATON/SOLV calculation,¹¹ the final R factors were slightly high. These residual electron intensities were removed by the PLATON/SQUEEZE routine. Details on crystal data collection and refinement were summarized in Tables S3-S6.

Crystal data for Eu₄(L_1^{AC})₆(OTf)₁₂: Tetragonal space group $P4_12_12$, a = 31.093(2) Å, b = 31.093(2) Å, c = 44.345(3) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 42871(6) Å³, Z = 4, T = 298(2) K. Anisotropic least-squares refinement for the framework atoms and isotropic refinement for the other atoms on 30953 independent merged reflections ($R_{int} = 0.1200$) converged at residual $wR_2 = 0.2694$ for all data; residual $R_1 = 0.0797$ for 19961 observed data [I > 2 σ (I)], and goodness of fit (GOF) = 0.999.

Crystal data for Eu₄(L_1^{RR})₆(OTf)₁₂: Orthorhombic space group *C222₁*, a = 21.6885(9) Å, b = 51.788(2) Å, c = 42.6164(18) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 47866(3) Å³, Z = 4, T = 293(2) K. Anisotropic least-squares refinement for the framework atoms and isotropic refinement for the other atoms on 38422 independent merged reflections ($R_{int} = 0.0781$) converged at residual $wR_2 = 0.2044$ for all data; residual $R_1 = 0.0679$ for 27636 observed data [I > 2 σ (I)], and goodness of fit (GOF) = 1.021.

Crystal data for Eu₄(L_2^{AC})₆(OTf)₁₂: Monoclinic space group *C*2/*c*, a = 109.88(2) Å, b = 21.340(4) Å, c = 42.920(9) Å, $\alpha = 90^{\circ}$, $\beta = 108.98(3)^{\circ}$, $\gamma = 90^{\circ}$, V = 95172(37) Å³, Z = 8, T = 293(2) K. Anisotropic least-squares refinement for the framework atoms and isotropic refinement for the other atoms on 95690 independent merged reflections ($R_{int} = 0.0747$) converged at residual $wR_2 = 0.2879$ for all data; residual $R_I = 0.0802$ for 49499 observed data [I > 2 σ (I)], and goodness of fit (GOF) = 1.006.

Crystal data for Eu₂(L_3^{RR})₃(OTf)₆: Monoclinic space group $P2_1$, a = 14.336(3) Å, b = 22.784(5) Å, c = 34.552(6) Å, $\alpha = \gamma = 90^{\circ} \beta = 100.957(5)^{\circ}$, V = 11080(4) Å³, Z =

2, T = 293(2) K. Anisotropic least-squares refinement for the framework atoms and isotropic refinement for the other atoms on 11544 independent merged reflections ($R_{int} = 0.0636$) converged at residual $wR_2 = 0.2620$ for all data; residual $R_1 = 0.0884$ for 7386 observed data [I > 2 σ (I)], and goodness of fit (GOF) = 1.009.

CCDC 2304348-2304351 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



Figure S67 Ortep-drawing of the asymmetric unit in the crystal structure of $Eu_4(L_1^{AC})_6(OTf)_{12}$ at 30% probability level.



Figure S68 Ortep-drawing of the asymmetric unit in the crystal structure of $Eu_4(L_1^{RR})_6(OTf)_{12}$ at 30% probability level.



Figure S69 Ortep-drawing of the asymmetric unit in the crystal structure of $Eu_4(L_2^{AC})_6(OTf)_{12}$ at 30% probability level.



Figure S70 Ortep-drawing of the asymmetric unit in the crystal structure of $Eu_2(L_3^{SS})_3(OTf)_6$ at 30% probability level.



Figure S71 Cartoon drawing for crystal structures of $Eu_4(L_1^{RR})_6(OTf)_{12}$, $Eu_4(L_2^{AC})_6(OTf)_{12}$ and $Eu_2(L_3^{SS})_3(OTf)_6$.

6. Photophysical Property

6.1 UV-Vis absorption spectroscopy



Figure S72 UV-Vis absorption spectra of (A) ligands L_n^{SS} in CH₂Cl₂ (1×10⁻⁵ M, n = 1-3) and (B) corresponding LOPs in CH₃CN (1×10⁻⁵ M).

6.2 Luminescence spectroscopy



Figure S73 (A) Excitation and emission spectra of Eu₄(\mathbf{L}_1^{SS})₆ (CH₃CN, 1.0×10⁻⁵ M, $\lambda_{ex} = 314$ nm). (B) Excited state decay curve of Eu₄(\mathbf{L}_1^{SS})₆ ($\tau = 0.93$ ms). (C) Excitation and emission spectra of Eu₄(\mathbf{L}_2^{SS})₆ (CH₃CN, 1.0×10⁻⁵ M, $\lambda_{ex} = 331$ nm). (D) Excited state decay curve of Eu₄(\mathbf{L}_2^{SS})₆ ($\tau = 1.09$ ms). (E) Excitation and emission spectra of Eu₄(\mathbf{L}_2^{SS})₆ ($\tau = 344$ nm). (F) Excited state decay curve of Eu₂(\mathbf{L}_3^{SS})₃ ($\tau = 0.49$ ms).

6.3 Calculation of photophysical parameters for europium complexes

The sensitization efficiency of ligands (η_{sens}) and intrinsic quantum yield of europium (Q_{Ln}^{Ln}) are calculated as following equations:

$$\eta_{sens} = \frac{Q_{Ln}^L}{Q_{Ln}^{Ln}} \tag{4}$$

$$Q_{Ln}^{Ln} = \frac{\tau_{obs}}{\tau_{rad}} \tag{5}$$

Where, τ_{obs} and τ_{rad} are observed and radiative lifetimes, respectively. The τ_{obs} can be obtained by spectrofluorometer, while τ_{rad} can be determined by the equation:¹²

$$\frac{1}{\tau_{rad}} = A_{\rm MD,0} \cdot n^3 (\frac{I_{\rm tot}}{I_{\rm MD}}) \tag{6}$$

With $A_{MD,0}$ being a constant equal to 14.65 s⁻¹ and (I_{tot}/I_{MD}) the ratio of the total integrated emission from the Eu(⁵D₀) level to the ⁷F_J manifold (*J*=0-6) to the integrated intensity of the MD transition ⁵D₀ \rightarrow ⁷F₁. *n* is the refractive index of the medium. The detailed photophysical parameters are summarized in Table S1.

	λ_{abs}	3	λ_{ex}	τ_{obs}^{1}	τ_{rad}^{2}	η_{sens}^{3}	$Q_{Ln}^{Ln\ 4}$	Q_{Ln}^{L} ⁵	
Complexes	nm	$M^{-1}cm^{-1}$	nm	ms	ms	%	%	%	
$Eu_4(L_1^{SS})_6$	284	2.7×10 ⁵	320	2.68	6.32	4	42.4	1.7	
$Eu_4(L_2^{SS})_6$	300	3.3×10 ⁵	334	2.65	6.12	85.9	43.3	37.2	
$Eu_2(L_3^{SS})_3$	310	2.9×10 ⁵	347	1.92	4.55	~100	42.2	42.4	

Table S2. Summarized photophysical parameters for europium complexes.

¹ Observed lifetime monitored at 615 nm; ² Radiative lifetimes of the europium complexes; ³ Sensitization efficiency of ligand; ⁴ Intrinsic quantum yield of europium; ⁵ Overall luminescence quantum yield.



Figure S74 Low temperature (77 K) emission spectra of $Cd_4(L_1^{SS})_6$ (A, $\lambda_{ex} = 330$ nm, 0.83 mM, N₂), $Cd_4(L_2^{SS})_6$ (B, $\lambda_{ex} = 334$ nm, 0.83 mM, N₂), and $Cd_2(L_3^{SS})_3$ (C, $\lambda_{ex} = 347$ nm, 1.70 mM, N₂).



Figure S75 CD spectra of L_n^{SS} and L_n^{RR} in MeCN (n = 1-3, 1×10⁻⁵ M).



Figure S76 CD spectra of $[Eu_4(L_1^{SS/RR})_6](OTf)_{12}$, $[Eu_4(L_2^{SS/RR})_6](OTf)_{12}$, and $[Eu_2(L_3^{SS/RR})_3](OTf)_6$ in MeCN $(1 \times 10^{-5} \text{ M})$.

6.5 CPL spectroscopy



Figure S77 CPL spectra of $[Eu_4(L_1^{SS/RR})_6](OTf)_{12}$, $[Eu_4(L_2^{SS/RR})_6](OTf)_{12}$, and $[Eu_2(L_3^{SS/RR})_3](OTf)_6$ in MeCN (1×10⁻⁵ M).



Figure S78 Luminescence dissymmetry ratio (g_{lum}) of $[Eu_4(L_1^{SS/RR})_6](OTf)_{12}$, $[Eu_4(L_2^{SS/RR})_6](OTf)_{12}$, and $[Eu_2(L_3^{SS/RR})_3](OTf)_6$ in MeCN $(1 \times 10^{-5} \text{ M})$.

8. ESI-TOF-MS



Figure S79 ESI-TOF-MS of $Eu_4(L_1^{AC})_6(OTf)_{12}$ with the observed and calculated isotopic patterns of the +5 peak.



Figure S80 ESI-TOF-MS of the equilibrium between $Eu_2(L_2^{AC})_3(OTf)_6$ and $Eu_4(L_2^{AC})_6(OTf)_{12}$ with the observed and calculated isotopic patterns of the +2 peak of $[Eu_2(L_2^{AC})_3]$ and the +4 peak of $[Eu_4(L_2^{AC})_6]$.



Figure S81 ESI-TOF-MS of $Eu_4(L_1^{SS})_6(OTf)_{12}$ with the observed and calculated isotopic patterns of the peak +7.



Figure S82 ESI-TOF-MS of the mixed $\text{Eu}_2(\mathbf{L}_2^{SS})_3(\text{OTf})_6$ and $\text{Eu}_4(\mathbf{L}_2^{SS})_6(\text{OTf})_{12}$ with the observed and calculated isotopic patterns of the +7 peak of $\text{Eu}_4(\mathbf{L}_2^{SS})_6(\text{OTf})_{12}$.



Figure S83 ESI-TOF-MS of $Eu_2(L_3^{SS})_3(OTf)_6$ with the observed and calculated isotopic patterns of the +5 peak.



Figure S84. ESI-TOF-MS of $Gd_4(L_1^{SS})_6(OTf)_{12}$ with the observed and calculated isotopic patterns of the peak +5.



Figure S85. ESI-TOF-MS of the mixed $Gd_2(L_2^{SS})_3(OTf)_6$ and $Gd_4(L_2^{SS})_6(OTf)_{12}$ with the observed and calculated isotopic patterns of the +6 peak of $[Gd_4(L_2^{SS})_6(OTf)_6]^{6+}$ and $[Gd_2(L_2^{SS})_6(OTf)_3]^{3+}$. Under the dilution condition $([L_2^{SS}] < 0.2 \text{ mg/ml})$ of mass spectrometry, $Gd_4(L_2^{SS})_6(OTf)_{12}$ is inevitably partially converted into $Gd_2(L_2^{SS})_3(OTf)_6$.



Figure S86. ESI-TOF-MS of $Gd_2(L_3^{SS})_3(OTf)_6$ with the observed and calculated isotopic patterns of the peak +5.

	$(-1)_{12}$
Identification code	$\operatorname{Eu}_4(\mathbf{L_1^{AC}})_6(\operatorname{OTf})_{12}$
Empirical formula	$C_{217}H_{242}Cl_{74}Eu_4F_{36}N_{60}O_{48}S_{12}$
Formula weight	8758.55
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P41212
Unit cell dimensions	$a = 31.093(2) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 31.093(2) \text{ Å} \qquad \beta = 90^{\circ}$
	$c = 44.345(3) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	42871(6) Å ³
Z	4
Density (calculated)	1.357 Mg/m ³
Absorption coefficient	1.170 mm^{-1}
F(000)	17496
Crystal size	$0.2 \ge 0.15 \ge 0.1 \text{ mm}^3$
Theta range for data collection	2.122 to 23.313°
Index ranges	-32<=h<=34, -34<=k<=31, -49<=l<=48
Reflections collected	252333
Independent reflections	30953 [R(int) = 0.1200]
Completeness to theta = 20.863°	99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	30953 / 1286 / 1117
Goodness-of-fit on F^2	0.999
Final R indices [I>2sigma(I)]	$R_1 = 0.0797, wR_2 = 0.2220$
R indices (all data)	$R_1 = 0.1280, wR_2 = 0.2694$
Absolute structure parameter	0.191(6)
Extinction coefficient	n/a
Largest diff. peak and hole	1.093 and -0.863 $e.\text{Å}^{-3}$

Table S3. Crystal data and structure refinement for $Eu_4(L_1^{AC})_6(OTf)_{12}$.

Identification code	$Eu_4(L_1^{RR})_6(OTf)_{12}$
Empirical formula	$C_{316}H_{272}Cl_{56}Eu_4F_{36}N_{60}O_{48}S_{12}\\$
Formula weight	9339.68
Temperature	273(2) K
Wavelength	0.62298 Å
Crystal system	Orthorhombic
Space group	C222 ₁
Unit cell dimensions	$a = 21.6885(9) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 51.788(2) \text{ Å} \qquad \beta = 90^{\circ}$
	$c = 42.6164(18) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	47866(3) Å ³
Z	4
Density (calculated)	1.296 Mg/m ³
Absorption coefficient	0.765 mm ⁻¹
F(000)	18768
Crystal size	0.3 x 0.2 x 0.1 mm ³
Theta range for data collection	0.689 to 22.042°.
Index ranges	-24<=h<=25, -61<=k<=61, -45<=l<=43
Reflections collected	120143
Independent reflections	38422 [R(int) = 0.0781]
Completeness to theta = 21.765°	91.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	38422 / 1642 / 1357
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	$R_1 = 0.0679$, wR ₂ = 0.1911
R indices (all data)	$R_1 = 0.0875, wR_2 = 0.2044$
Absolute structure parameter	0.205(8)
Extinction coefficient	n/a
Largest diff. peak and hole	1.217 and -0.964 e.Å ⁻³

Table S4. Crystal data and structure refinement for $Eu_4(L_1^{RR})_6(OTf)_{12}$.

	1(2)0()12
Identification code	$\operatorname{Eu}_4(\mathbf{L_2^{AC}})_6(\operatorname{OTf})_{12}$
Empirical formula	$C_{228.88}H_{217.75}Cl_{25.75}Eu_4F_{36}N_{60}O_{48}S_{12}$
Formula weight	7166.27
Temperature	293(2) K
Wavelength	0.62298 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 109.88(2) \text{ Å} \qquad \alpha = 90^{\circ}$
	$b = 21.340(4) \text{ Å} \qquad \beta = 108.98(3)^{\circ}$
	$c = 42.920(9) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	95172(37) Å ³
Z	8
Density (calculated)	1.000 Mg/m ³
Absorption coefficient	0.590 mm ⁻¹
F(000)	28806
Crystal size	0.4 x 0.3 x 0.2 mm ³
Theta range for data collection	0.854 to 22.860°
Index ranges	-136<=h<=136,-26<=k<=26, -49<=l<=53
Reflections collected	351692
Independent reflections	95690 [R(int) = 0.0747]
Completeness to theta = 21.949°	99.3%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	95690 / 4655 / 2473
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	$R_1 = 0.0802, wR_2 = 0.2431$
R indices (all data)	$R_1 = 0.1282, wR_2 = 0.2879$
Extinction coefficient	n/a
Largest diff. peak and hole	$0.678 \text{ and } -0.643 \text{ e.Å}^{-3}$

Table S5. Crystal data and structure refinement for $Eu_4(L_2^{AC})_6(OTf)_{12}$.

Identification code	$\operatorname{Eu}_2(\mathbf{L_3}^{SS})_3(\operatorname{OTf})_6$
Empirical formula	$C_{190}H_{151}Cl_{20}Eu_{2}F_{6}N_{30}O_{24}S_{6}$
Formula weight	4557.68
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	$a = 14.336(3) \text{ Å} \qquad \alpha = 90^{\circ}$
	b = 22.784(5) Å β = 100.957(5)°
	$c = 34.552(6) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	11080(4) Å ³
Z	2
Density (calculated)	1.366 Mg/m ³
Absorption coefficient	0.930 mm ⁻¹
F(000)	4618
Crystal size	0.3 x 0.25 x 0.2 mm ³
Theta range for data collection	2.235 to 20.878°.
Index ranges	-14<=h<=14, -22<=k<=22, -34<=l<=34
Reflections collected	11544
Independent reflections	11544 [R(int) = 0.0636]
Completeness to theta = 20.878°	95.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11544 / 2043 / 1531
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	$R_1 = 0.0884, wR_2 = 0.2423$
R indices (all data)	$R_1 = 0.1139, wR_2 = 0.2620$
Absolute structure parameter	0.02(3)
Extinction coefficient	n/a
Largest diff. peak and hole	2.868 and -0.926 e.Å ⁻³

Table S6. Crystal data and structure refinement for $Eu_2(L_3^{SS})_3(OTf)_6$.

9. References

(1) Wu, D. H.; Chen, A. D.; Johnson, C. S. Journal of Magnetic Resonance, Series A 1995, 115, 260-264.

(2) (a) Spectroscopy Letters 2007, 40, 193-193. (b) Chauvin, A. S.; Gumy, F.; Imbert, D.; Bünzli, J. C.
G. Spectroscopy Letters 2004, 37, 517-532.

(3) (a) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. Analytical Chemistry 2011, 83,

3431-3439. (b) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. *Nature Protocols* 2013, 8, 1535.

(4) Guo, X.-Q.; Zhou, L.-P.; Cai, L.-X.; Sun, Q.-F. *Chemistry-a European Journal* **2018**, *24*, 6936-6940.

(5) Piguet, C. Chem. Commun., 2010, 46, 6209-6231.

(6) Benson, S. W. J. Am. Chem. Soc., 1958, 80, 5151.

(7) Bailey, W. F.; Monahan, A. S. J. Chem. Educ., 1978, 55, 489.

(8) Atkins, P. W.; MacDermott, A. J. J. Chem. Educ., 1982, 59, 359.

(9) Prakongpan, S.; Nagai, T. Chem. Pharm. Bull., 1984, 32, 340.

(10) Sheldrick, G. A short history of SHELX. Acta Crystallogr. Sect. C, 2015, 71, 3-8.

(11) Spek, A. L. Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **2003**, *36*, 7.

(12) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. Phys. Chem. Phys. 2002, 4, 1542.