Supporting Information

Effect of Alkyl Substituent on the Amide of Bis-lactam-1,10-phenanthroline Ligands for Lanthanide Extraction

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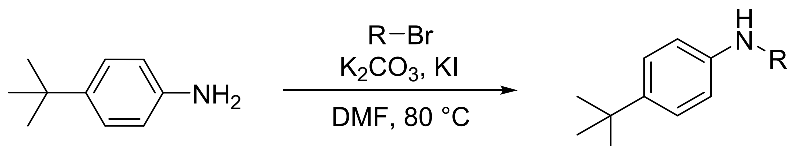
Content

1. Synthesis

1.1 Synthesis of 1.

A mixture of 4-tert-butylaniline (5.0 g, 33.5 mmol, 2 eq.), bromo-alkanes (25.1 mmol, 1.5 eq), K_2CO_3 (6.9 g, 50.3 mmol, 3 eq.), and KI (0.3 g, 1.6 mmol, 0.1 eq.) in DMF was stirred. The reaction mixture was heated to 80 °C for 16 hours. After finishing, the reaction was quenched with water, and the mixture was extracted with PE (15 mL × 3). The combined organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified *via* flash column chromatography (DCM: PE, 1:5 to 3:5) to afford intermediate **1**.



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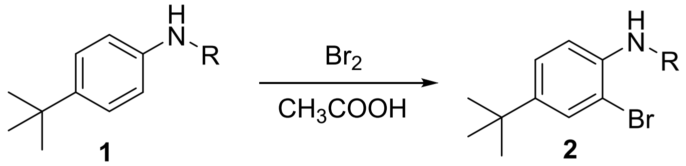
Scheme S1. Synthesis method of **1**.

R = n-butyl: Yield: 52%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.61 – 6.51 (m, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.47 – 1.39 (q, *J* = 7.4 Hz, 2H), 1.29 (s, 9H), 0.96 (t, *J* = 7.7 Hz, 3H). The test result is consistent with the reported results[1].
R = 2-ethylhexyl. Yield: 48%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 3.00 (d, *J* = 6.2 Hz, 2H), 1.58 – 1.51 (m, 1H), 1.48 – 1.29 (m, 8H), 1.28 (s, 9H), 0.93 – 0.87 (m, 6H). The test result is consistent with the reported results[1].
R = n-octyl: Yield: 46%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 6.68 (dd, *J* = 8.0 Hz, 3.18 (t, *J* = 7.2 Hz, 2H), 1.73 – 1.62 (m, 2H), 1.43 – 1.40 (m, 19H), 0.98 (t, *J* = 7.2 Hz, 3H). The test result is consistent with the reported results[2].
R = n-dodecane: Yield: 42%, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.43 – 1.24 (m, 27H), 0.88 (t, *J* = 6.9 Hz, 3H). The test result is consistent with the reported results[3].

1.2 Synthesis of 2.

The intermediate **1** (3.0 g, 14.6 mmol, 1.0 eq.) was added to 30 mL glacial acetic acid and then the solution was stirred. Bromine (0.5 mL, 1.0 eq.) solution in 15 mL glacial acetic acid was added dropwise over 20 minutes through a dropping funnel. The reaction mixture was stirred at room temperature for 4 hours. After finishing, sodium thiosulfate was added to quench excess bromine until the solution was colourless. It was diluted with 100 mL of water and extracted with DCM (3 × 40 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was purified *via* flash column chromatography (DCM: PE, 1:5) to afford intermediate **2**.



Scheme S2. Synthesis method of **2**.

R = n-butyl: Yield: 82%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.5, 2.2 Hz, 1H), 6.58 (d, J = 8.5 Hz, 1H), 4.12 (s, 1H), 3.13 (t, J = 7.0 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.49 – 1.40 (m, 2H), 1.26 (s, 9H),0.96 (t, J = 7.4 Hz, 3H). The test result is consistent with the reported results[1].

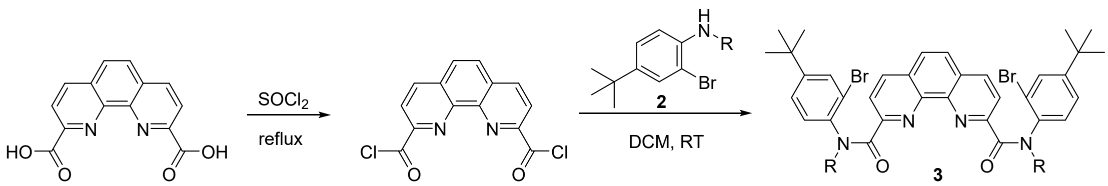
R = 2-ethylhexyl: Yield: 86%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.19 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 8.5 Hz, 2H), 3.04 (d, J = 6.0 Hz, 2H), 1.64 – 1.58 (m, 1H), 1.48 – 1.29 (m, 8H), 1.27 (s, 9H), 0.95 – 0.88 (m, 7H). The test result is consistent with the reported results[1].

R = n-octyl: Yield: 84%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.5, 2.2 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 4.13 (s, 1H), 3.12 (t, J = 7.2 Hz, 2H), 1.70 – 1.59 (m, 2H), 1.47 – 1.20 (m, 19H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.90, 140.64, 129.36, 125.31, 110. *m/z* calculated for $[C_{18}H_{30}NBr + Na]^+$ 362.1454, found 362.1478.

R = n-dodecane: Yield: 80%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.5, 2.2 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 4.13 (s, 1H), 3.12 (t, J = 7.1 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.46 – 1.20 (m, 27H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.89, 140.62, 129.35, 125.30, 110.94, 109.56, 44.08, 34.07, 33.90, 32.89, 31.96, 31.47, 29.68, 29.62, 29.40, 28.82, 28.23, 27.16, 22.74, 14.17. *m/z* calculated for $[C_{22}H_{37}NBr + Na]^+$ 417.2080, found 417.2087.

1.3 Synthesis of 3.

2,9-Dicarboxy-1,10-phenanthroline (1.0 g, 3.7 mmol, 1 eq.) was combined with sulfuryl chloride (15 mL) and refluxed under an Ar atmosphere for 5 hours. The sulfuryl chloride was subsequently evaporated under reduced pressure. Anhydrous DCM was added to the residue, and the resulting solution was placed in an ice-water bath. NEt_3 (2 mL) and intermediate **2** (8.8 mmol, 2.2 eq.) were then slowly introduced into the solution. The reaction mixture was stirred at room temperature for 3 hours. Upon completion, water was added, and the mixture was extracted with DCM (15 mL × 3). The organic phase was washed with brine and dried on $MgSO_4$. The residue was subjected to column chromatography (DCM: MeOH, 10:1), leading to the isolation of intermediate **3**.



Scheme S3. Synthesis method of **3**.

The introduction of the bromine atom adjacent to the amide resulted in an irregular split of the ^{1}H and ^{13}C spectra of the phenanthroline diamide (DAPhen) molecule due to the product including a mixture of s-*cis* and s-*trans* isomers of each amide moiety, making it impossible to fingerprint their H and C chemical shift. Considering that this reaction is a conventional nucleophilic substitution reaction, it can be confirmed that the desired target molecule has been obtained based on the mass spectrometry data.

R = n-butyl: Yield: 72%, white solid. *m/z* calculated for $[C_{42}H_{48}Br_2N_4O_2 + H]^+$ 799.2217, found 799.2009. The test result is consistent with the reported results[1].

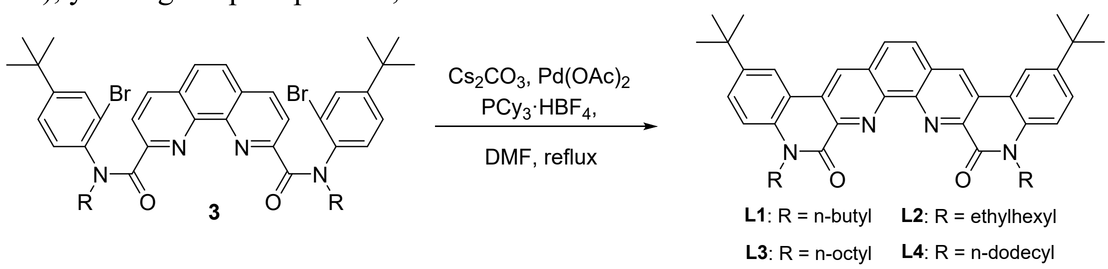
R = 2-ethylhexyl: Yield: 76%, white solid. *m/z* calculated for $[C_{50}H_{64}Br_2N_4O_2 + H]^+$ 911.3469, found 911.3321. The test result is consistent with the reported results[1].

R = n-octyl: Yield: 70%, white solid. *m/z* calculated for $[C_{50}H_{64}Br_2N_4O_2 + H]^+$ 911.3469, found 911.3491.

R = n-dodecane: Yield: 67%, white solid. *m/z* calculated for $[C_{58}H_{80}Br_2N_4O_2 + H]^+$ 1023.4721, found 1023.4944

1.4 Synthesis of ligands L1–L4.

Under an inert Ar atmosphere, intermediate **3** (0.5 g, 0.62 mmol, 1 eq.), $Cy_3P{\cdot}HBF_4$ (0.04 g, 0.13 mmol, 0.2 eq.), Cs_2CO_3 (0.8 g, 2.5 mmol, 4 eq.), and $Pd(OAc)_2$ (0.03 g, 0.13 mmol, 0.2 eq.) were dissolved in anhydrous DMF (25 mL). Then, the mixture solution was refluxed overnight. After the reaction mixture was cooled to room temperature, water was added dropwise to fully quench the reaction. Subsequently, the mixture was extracted with DCM (10 mL × 3). The organic phase obtained after extraction was dried over $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on Al_2O_3 (DCM:MeOH, 8:1), yielding the pure product, BLPhen.



Scheme S4. Synthesis method of ligands **L1**–**L4**.

R = n-butyl: Yield: 88%, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 2H), 8.36 (s, 2H), 8.05 (s, 2H), 7.69 (dd, J = 8.8, 1.9 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 4.37

(s, 4H), 1.84 – 1.75 (m, 4H), 1.51 (s, 22H), 0.98 (t, *J* = 7.3 Hz, 6H). FT-IR: $\nu_{max}(cm^{-1})$ 1657.5 (CO); 2867.2, 2903.7 (alkyl C-H stretching); 2955.9 (aromatic C-H stretching). *m/z* calculated for $[C_{42}H_{46}N_4O_2 + H]^+$ 639.3694, found 639.3771. The test result is consistent with the reported results[1].

R = 2-ethylhexyl: Yield: 89%, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 2H), 8.35 (s, 2H), 7.99 (s, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.34 (s, 2H), 4.33 (d, *J* = 145.4 Hz, 4H), 1.95 (s, 2H), 1.70 – 1.17 (m, 34H), 0.88 (s, 12H). FT-IR: $\nu_{max}(cm^{-1})$ 1658.9 (CO); 2867.2, 2929.9 (alkyl C-H stretching); 2955.2 (aromatic C-H stretching). *m/z* calculated for $[C_{50}H_{62}N_4O_2 + H]^+$ 751.4946, found 751.4954. The test result is consistent with the reported results[1].

R = n-octyl: Yield: 88%, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 2H), 8.35 (d, *J* = 2.3 Hz, 2H), 8.02 (s, 2H), 7.68 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 4.46 (s, 4H), 1.91 – 1.80 (m, 4H), 1.57 – 1.45 (m, 22H), 1.44 – 1.26 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.79, 146.30, 145.55, 141.35, 135.14, 130.51, 129.97, 129.01, 128.66, 128.53, 120.32, 117.03, 115.28, 43.35, 34.65, 31.86, 31.50, 29.45, 29.31, 27.37, 27.10, 22.67, 14.13. FT-IR: $\nu_{max}(cm^{-1})$ 1658.9 (CO); 2853.0, 2927.6 (alkyl C-H stretching); 2952.2 (aromatic C-H stretching). *m/z* calculated for $[C_{50}H_{62}N_4O_2 + H]^+$ 751.4946, found 751.4938.

R = n-dodecane: Yield: 90%, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 2H), 8.35 (d, *J* = 2.2 Hz, 2H), 8.02 (s, 2H), 7.67 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 4.46 (s, 4H), 1.91 – 1.79 (m, 4H), 1.57 – 1.45 (m, 22H), 1.43 – 1.22 (m, 32H), 0.88 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.70, 146.27, 145.40, 141.36, 135.17, 130.43, 129.86, 128.92, 128.56, 128.44, 120.25, 116.99, 115.20, 43.37, 34.60, 31.95, 31.48, 29.69, 29.67, 29.53, 29.39, 27.39, 27.13, 22.72, 14.15. FT-IR: $\nu_{max}(cm^{-1})$ 1659.7 (CO); 2853.0, 2924.6 (alkyl C-H stretching); 2953.7 (aromatic C-H stretching). *m/z* calculated for $[C_{58}H_{79}N_4O_2 + H]^+$ 863.6198, found 863.6191.

The purity of all ligands was confirmed to be 98–99%.

1.5 Characterization of ligand structures.

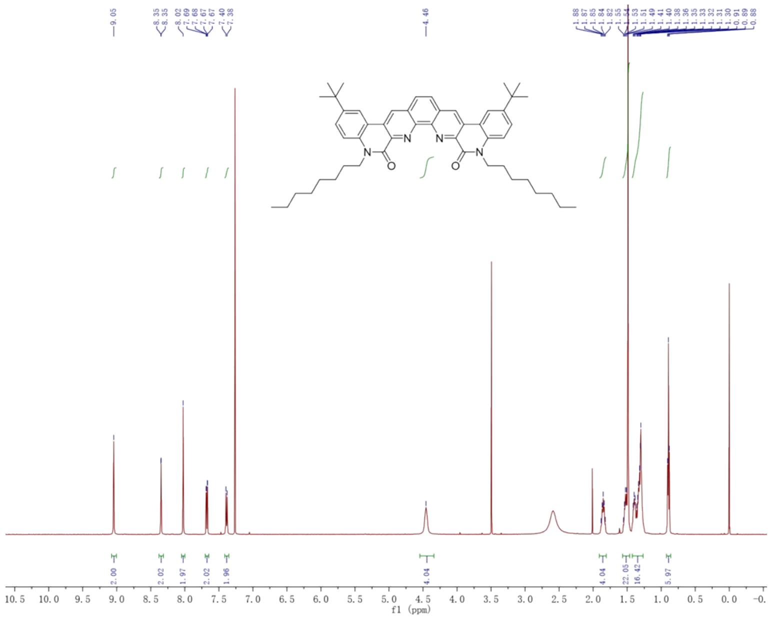


Fig. S1 ^{1}H NMR spectrum of **L3** in $CDCl_3$.

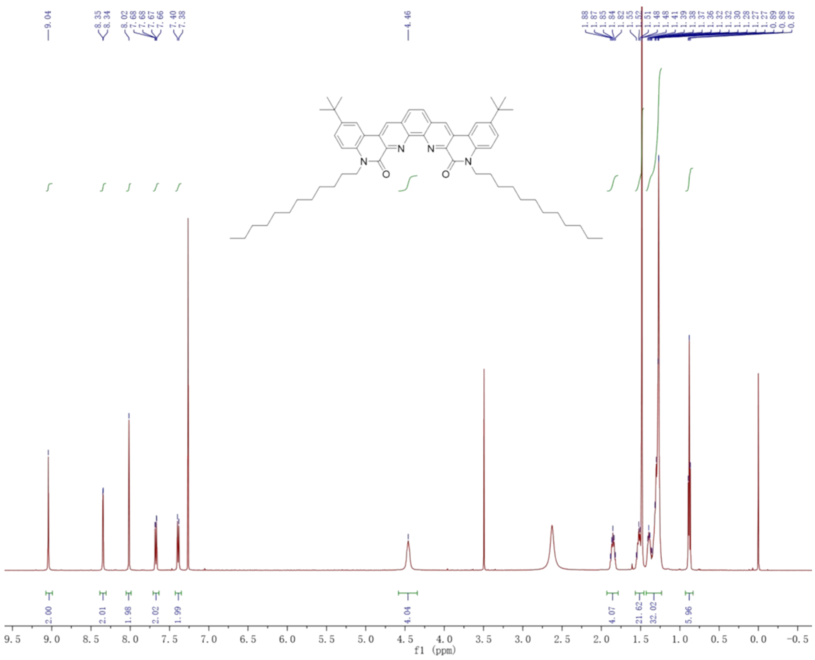


Fig. S2 ^{1}H NMR spectrum of **L4** in $CDCl_3$.

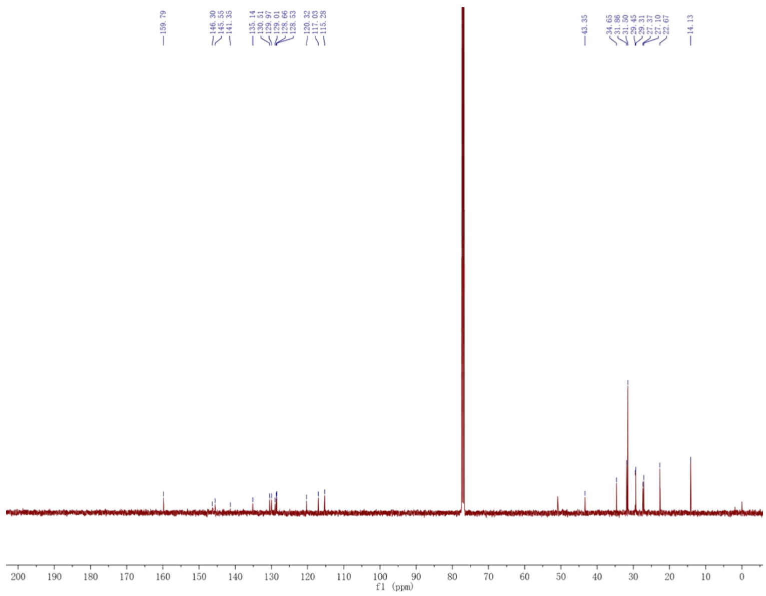


Fig. S3 ^{13}C NMR spectrum of **L3** in $CDCl_3$.

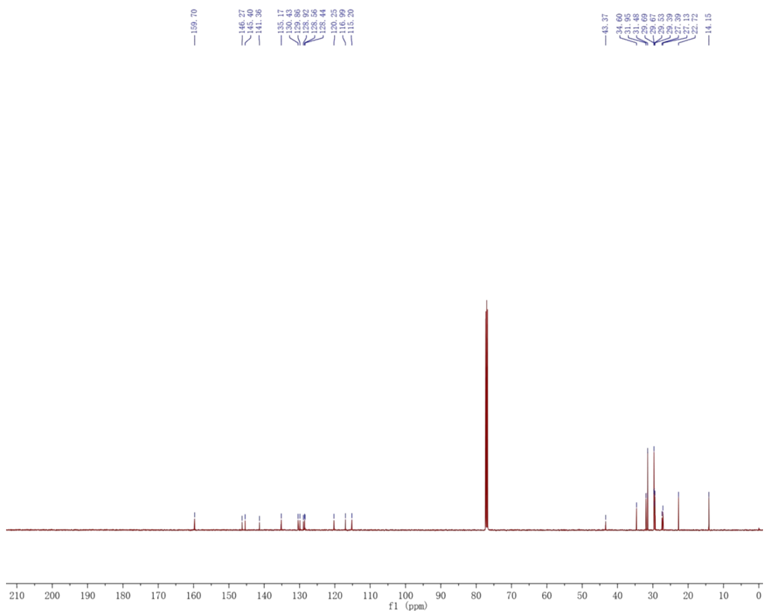


Fig. S4 ^{13}C NMR spectrum of **L4** in $CDCl_3$.

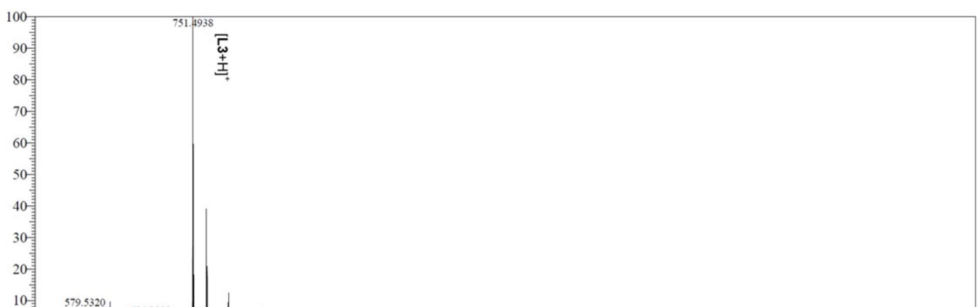


Fig. S5 The ESI-HRMS result of **L3**.

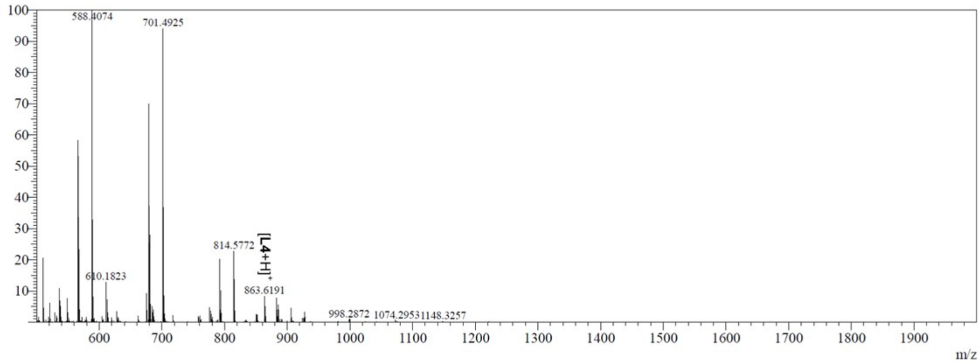


Fig. S6 The ESI-HRMS result of **L4**.

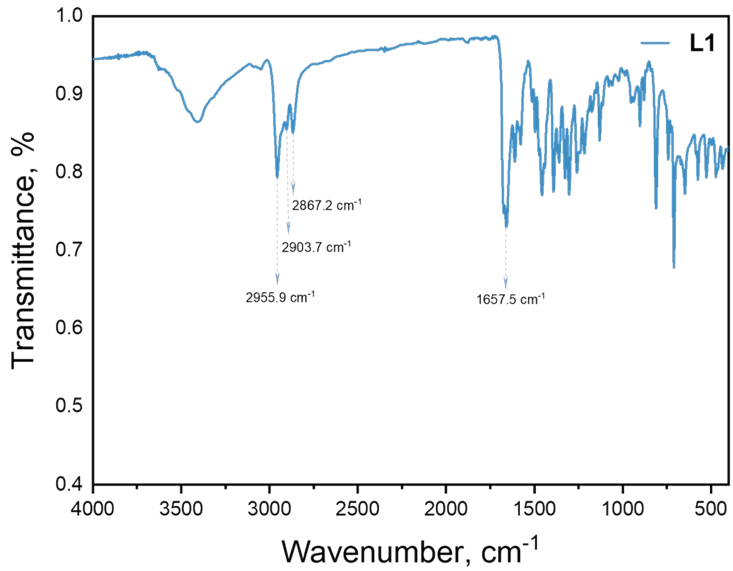


Fig. S7 The FT-IR spectrum of **L1**.

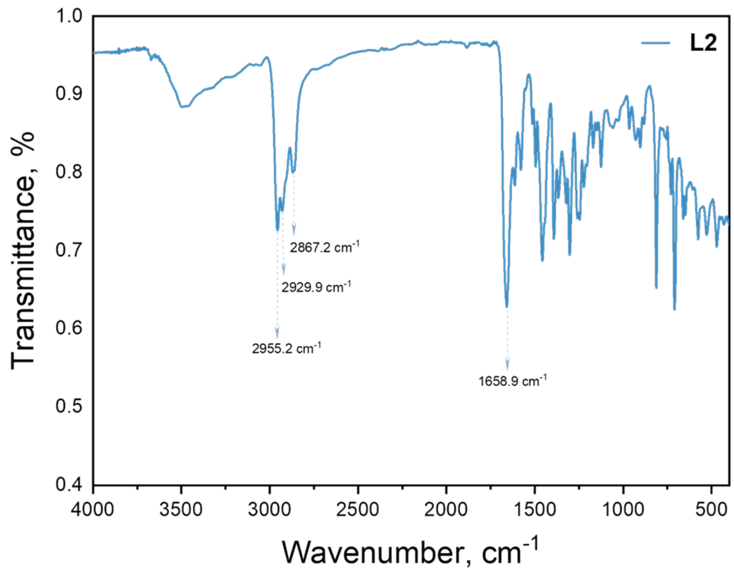


Fig. S8 The FT-IR spectrum of **L2**.

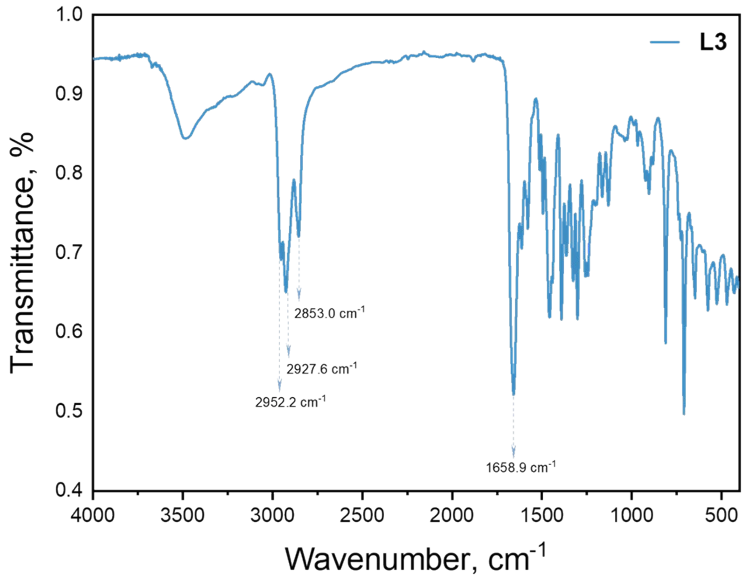


Fig. S9 The FT-IR spectrum of **L3**.

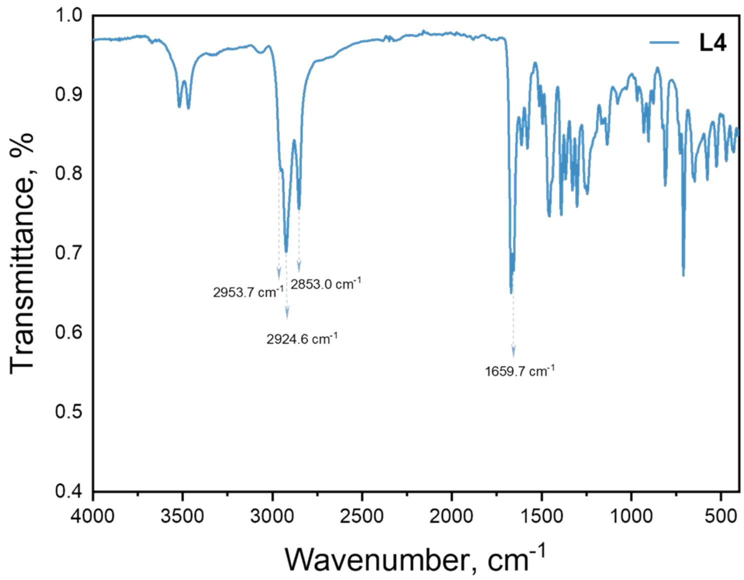


Fig. S10 The FT-IR spectrum of **L4**.

2. Solvent extraction

The distribution ratio (D) was determined according to Equation S1:

$$D = C_{org}/C_{aq} \qquad \text{S1}$$

The extraction efficiency (E) was determined according to Equation S2:

$$E\% = (D/(D+1))\times 100\% \qquad \text{S2}$$

The separation factor (SF) between any two metal ions was determined according to Equation S3:

$$SF_{\mathrm{M1/M2}} = D_{\mathrm{M1}}/D_{\mathrm{M2}} \qquad \text{S3}$$

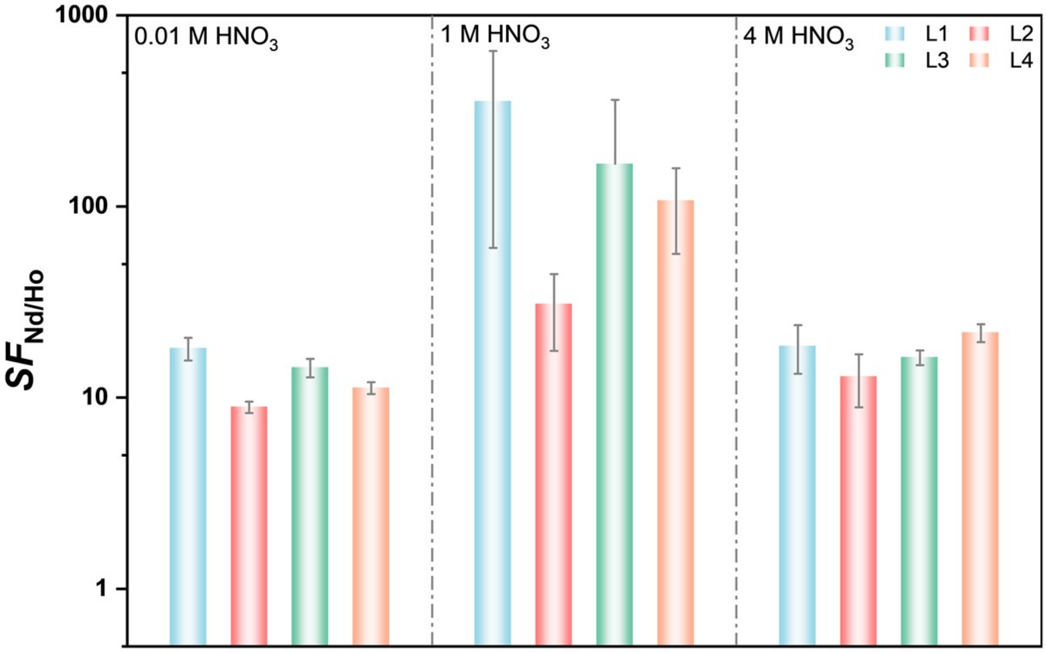


Fig. S11 Separation factors of Nd(III) over Ho(III) by four ligands under varying acidity conditions.

3. UV–vis spectroscopy titration

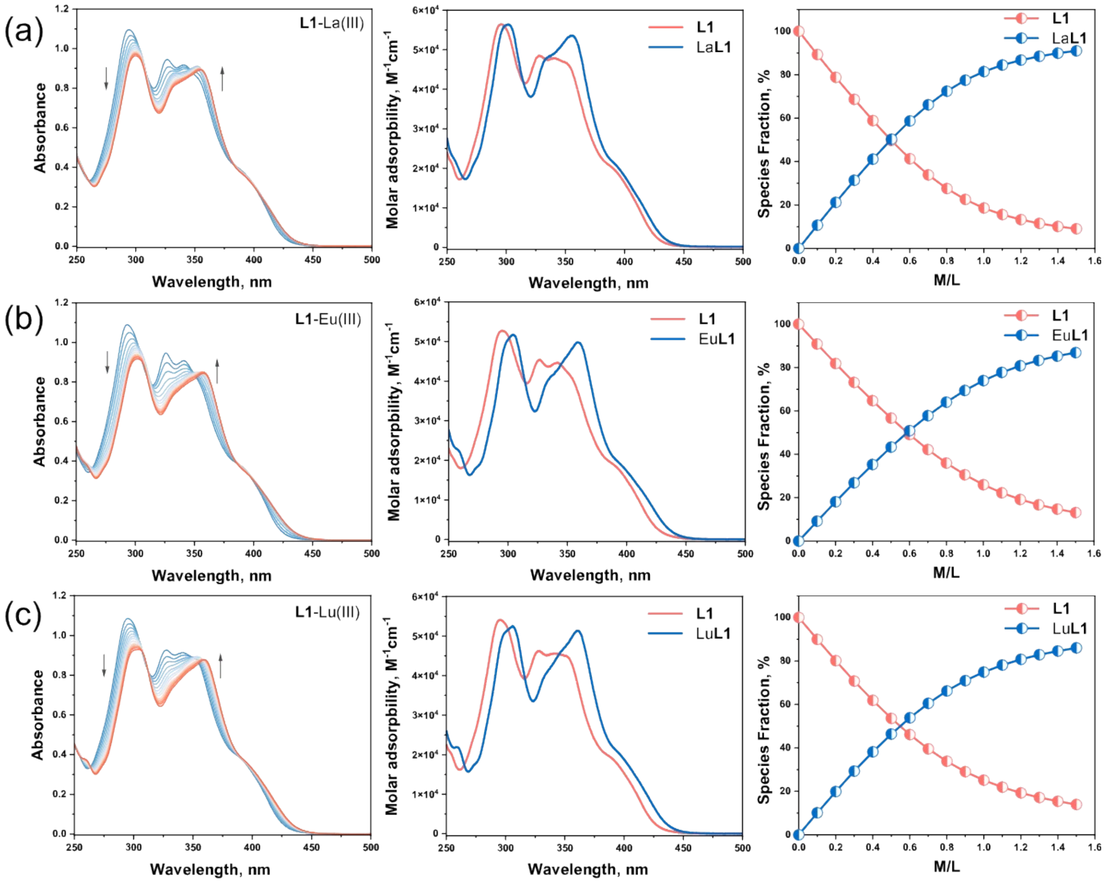


Fig. S12 UV–vis titration absorption spectra of ligands **L2**–**L4** with La(III), Eu(III), and Lu(III).

4. ESI-MS results

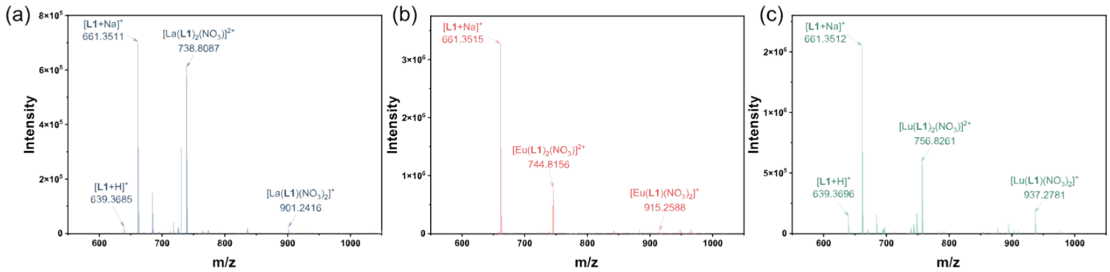


Fig. S13 ESI-MS spectrum of the complex solution.

Table S1. Exact and ChemDraw simulated values for the complex *m/z*.

complex	exact *m/z*	simulated *m/z*
$[La(\mathbf{L1})(NO_3)_2]^+$	901.2436	901.2416
$[La(\mathbf{L1})_2(NO_3)]^{2+}$	738.8086	738.8087
$[Eu(\mathbf{L1})(NO_3)_2]^+$	915.2585	915.2588
$[Eu(\mathbf{L1})_2(NO_3)]^{2+}$	745.8161	744.8156
$[Lu(\mathbf{L1})(NO_3)_2]^+$	937.2780	937.2781
$[Lu(\mathbf{L1})_2(NO_3)]^{2+}$	756.8259	756.8261
$[La(\mathbf{L2})(NO_3)_2]^+$	1013.3688	1013.3678
$[La(\mathbf{L2})_2(NO_3)]^{2+}$	851.4355	851.4352
$[Eu(\mathbf{L2})(NO_3)_2]^+$	1027.3837	1027.3824
$[Eu(\mathbf{L2})_2(NO_3)]^{2+}$	858.4430	858.4426
$[Lu(\mathbf{L2})(NO_3)_2]^+$	1049.4032	1049.4035
$[La(\mathbf{L3})(NO_3)_2]^+$	1013.3688	1013.3677
$[La(\mathbf{L3})_2(NO_3)]^{2+}$	851.4355	851.4353
$[Eu(\mathbf{L3})(NO_3)_2]^+$	1027.3837	1027.3834
$[Eu(\mathbf{L3})_2(NO_3)]^{2+}$	858.4430	858.4429
$[Lu(\mathbf{L3})(NO_3)_2]^+$	1049.4032	1049.4032
$[Lu(\mathbf{L3})_2(NO_3)]^{2+}$	869.4527	869.4527
$[La(\mathbf{L4})(NO_3)_2]^+$	1125.4940	1125.4938
$[La(\mathbf{L4})_2(NO_3)]^{2+}$	963.5607	963.5611
$[Eu(\mathbf{L4})(NO_3)_2]^+$	1139.5089	1139.5086
$[Eu(\mathbf{L4})_2(NO_3)]^{2+}$	970.5682	970.0673
$[Lu(\mathbf{L4})(NO_3)_2]^+$	1161.5284	1161.5289
$[Lu(\mathbf{L4})_2(NO_3)]^{2+}$	981.5779	981.5782

5. X-ray single crystal diffraction

Table S2. Structural refinement parameters for **L1** and complexes.

Identification code	**L1**	**Er(L1)(NO$_3$)$_3$**	**[Eu(L1)$_2$](ClO$_4$)$_3$**
CCDC number	2390588	2512427	2456431
Empirical formula	$C_{44}H_{50}Cl_6N_4O_3$	$C_{343}H_{384}Cl_{12}Er_8N_{556}O_{91}$	$C_{88}H_{116}Cl_3EuN_8O_{24}$
Formula weight	895.58	8510.52	1928.19
Temperature/K	302.0	240.0	240(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	16.465(10)	10.7123(3)	26.562(3)
b/Å	14.702(12)	34.4168(11)	18.3118(19)
c/Å	18.759(12)	24.4695(8)	20.898(2)
α/°	90	90	90
β/°	92.77(5)	94.404(2)	109.476(6)
γ/°	90	90	90
Volume/Å^3	4536(5)	8994.9(5)	9583.1(18)
Z	4	1	4
ρ_{calc}g/cm^3	1.311	1.571	1.336
μ/mm^{-1}	3.795	4.857	6.068
F(000)	1872.0	4310.0	4024.0
Crystal size/mm^3	0.18 × 0.15 × 0.12	0.05 × 0.02 × 0.01	0.23 × 0.2 × 0.18
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.644 to 137.31	4.44 to 109.996	9.76 to 137.7
Index ranges	-19 ⩽ h ⩽ 19, -16 ⩽ k ⩽ 17, -22 ⩽ l ⩽ 21	-8 ⩽ h ⩽ 11, -36 ⩽ k ⩽ 35, -24 ⩽ l ⩽ 25	-32 ⩽ h ⩽ 31, -22 ⩽ k ⩽ 22, -25 ⩽ l ⩽ 24
Reflections collected	42007	51709	69688
Independent reflections	8329 [R_{int} = 0.0905, R_{sigma} = 0.0629]	11250 [R_{int} = 0.1901, R_{sigma} = 0.1821]	8518 [R_{int} = 0.0740, R_{sigma} = 0.0441]
Data/restraints/parameters	8329/222/678	11250/391/1267	8518/423/652
Goodness-of-fit on F^2	1.027	1.015	0.972
Final R indexes [I>=2σ (I)]	R_1 = 0.0852, wR_2 = 0.2163	R_1 = 0.0746, wR_2 = 0.1682	R_1 = 0.0619, wR_2 = 0.1696
Final R indexes [all data]	R_1 = 0.1300, wR_2 = 0.2508	R_1 = 0.1486, wR_2 = 0.2188	R_1 = 0.0704, wR_2 = 0.1786

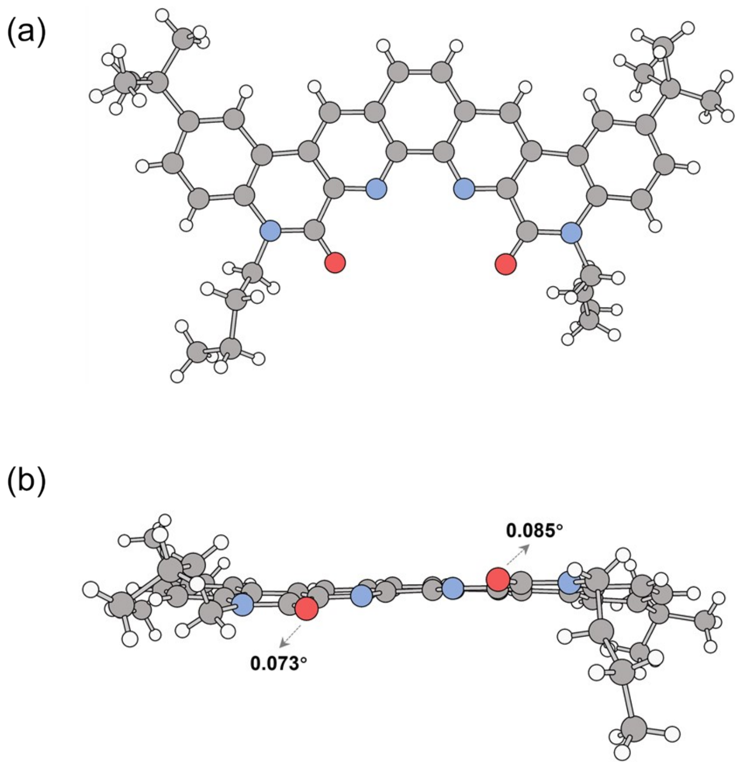


Fig. S14 Single crystal structure of **L1**. This structure has been reported in our previous work[1].

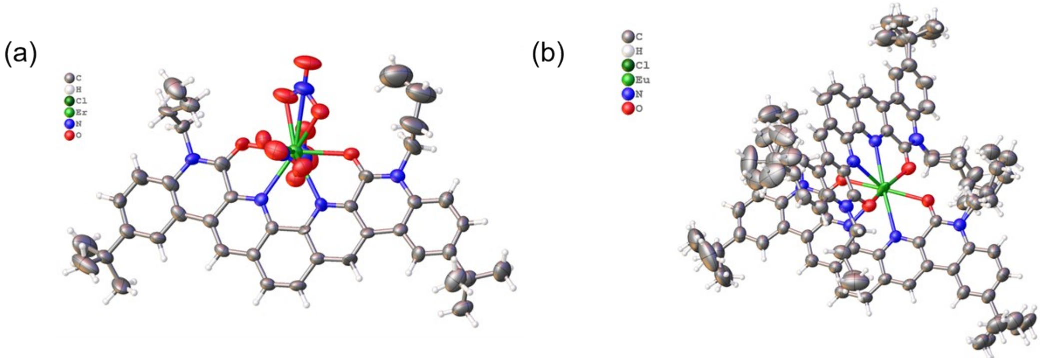


Fig. S15 Ortep style plots of (a) Er(**L1**)$(NO_3)_3$ and (b) [Eu(**L1**)$_2$]$(ClO_4)_3$.

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