

Lanthanide Supramolecular Transformers Induced by K⁺ and CO₂

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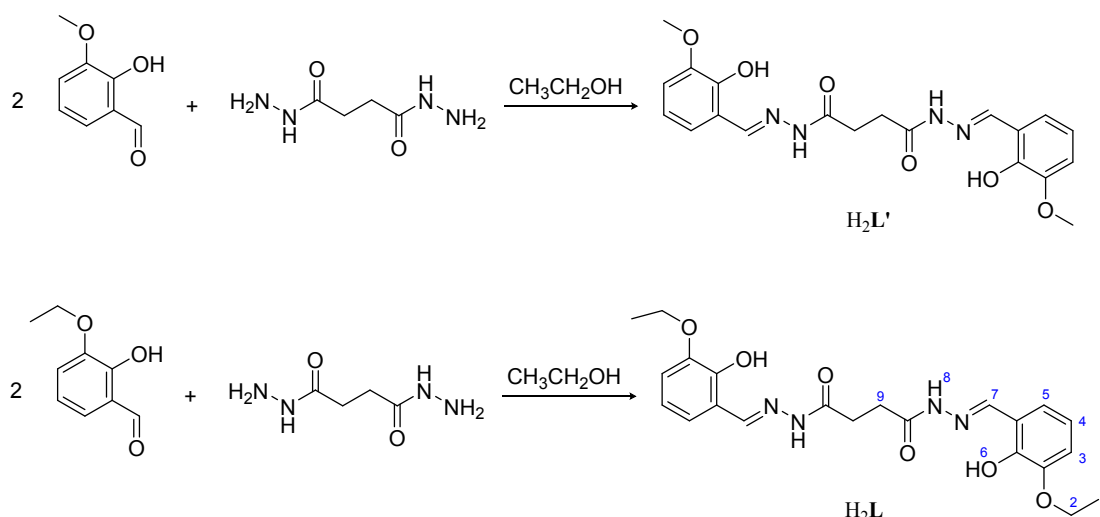
Supporting Information

Experimental Section

General Materials and Methods.

The 3-methoxysalicylaldehyde and 3-ethoxysalicylaldehyde were purchased from Alfa Aesar and used without further purification. All solvents and other reagents were reagent grade quality. Elemental analyses were tested by an Elementar Vario El instrument. HRESI-MS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer, Bruker Apex IV FTMS and Agilent 6210 ESI/TOF mass spectrometer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument. ¹H NMR (400 MHz) and ¹H NMR (600 MHz) were recorded on a JNM-ECS 400M NMR spectrometer and a Varian Mercury Plus 400 respectively. Solid-state ¹³C NMR spectra were performed on a Bruker AV400 spectrometer.

Ligand Synthesis.



Scheme S1. Synthesis of H_2L' and H_2L

Butanedihydrazide-bridged bis(3-ethoxysalicylaldehyde) ligand (H_2L)

Butanedihydrazide (1.46 g, 0.010 mol) was added to a 20 mL refluxing ethanol solution of 3-ethoxysalicylaldehyde (4.15 g, 0.025 mmol). The mixture was refluxed for 4 hours and the precipitate was filtered off and washed several times with ethanol and then dried over vacuum to get pure H_2L as a white solid (3.54 g, 80 %). M.p.: 247-249 °C. 1H NMR (400 MHz, DMSO- d_6 , ppm): δ 11.69 (d, 1H, J = 10.8 Hz, H^6), 11.30 (d, 1H, J = 4.4 Hz, H^6), 10.89 (d, 1H, J = 18 Hz, H^8), 9.46 (d, 1H, J = 15.6 Hz, H^8), 8.35(s, 1H, H^7), 8.30(s, 1H, H^7), 6.77-7.22 (m, 6H, Ph-H), 4.02-4.08 (m, 4H, H^2), 2.91 (m, 2H, H^9), 2.56 (m, 2H, H^9), 1.34 (m, 6H, H^1). ^{13}C NMR (100 MHz, Solid-state, ppm), δ 175.42(CO), 148.10(CO, CN), 123.92(CH), 121.04(CH), 117.71(C), 112.16(CH), 62.55(CH_2), 26.74(CH_2), 16.74(CH_3); ESI-MS: m/z 443.2 $[M + H]^+$. (We reported this ligand in our early work *Angew. Chem. Int. Ed.* **2013**, 52, 3756-3759.)

Butanedihydrazide-bridged bis(3-methoxysalicylaldehyde) ligand (H_2L')

The preparation of the ligands H_2L' is as same as the procedure of H_2L (see Scheme S1). M.p.: 248.7 – 249.9 °C. 1H NMR (400 MHz, DMSO- d_6 , ppm): δ 11.69 (d, 1H, OH), 11.30 (d, 1H, OH), 10.89 (d, 1H, NH), 9.52 (d, 1H, NH), 8.35(s, 1H, NCH), 8.30(s, 1H, NCH), 6.78 – 7.27 (m, 6H, Ar), 2.91 (m, 2H, CH_2CO), 3.81 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 2.56 (m, 2H, CH_2CO). ESI-MS: m/z 413.5 $[M - H]^+$.

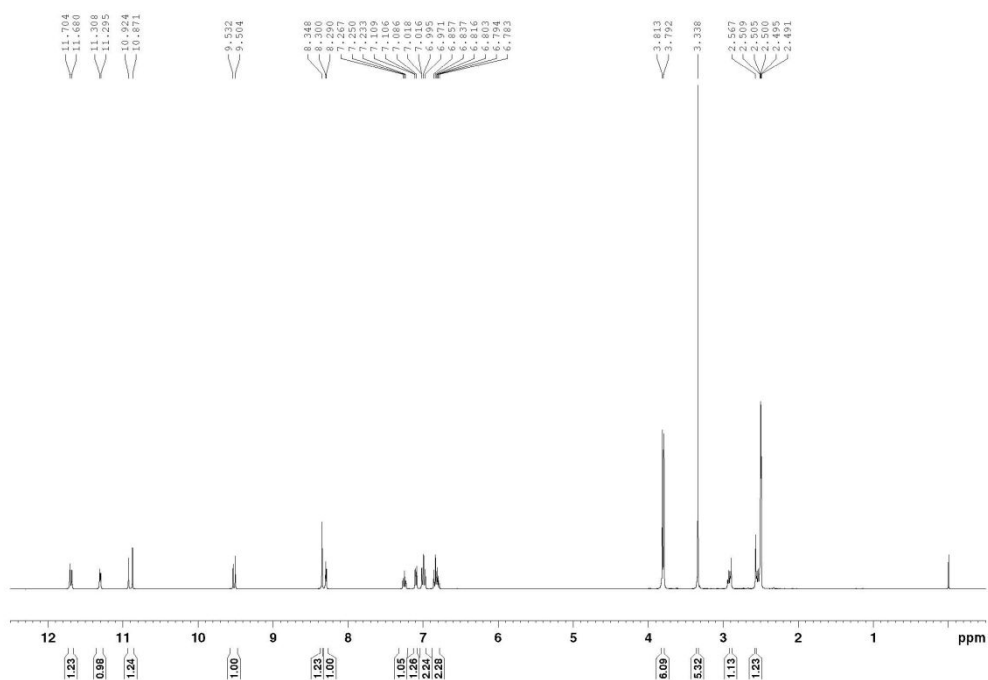


Figure S1. ^1H NMR (400 MHz) spectrum of $\text{H}_2\text{L}'$ in $[\text{D}_6]$ DMSO.

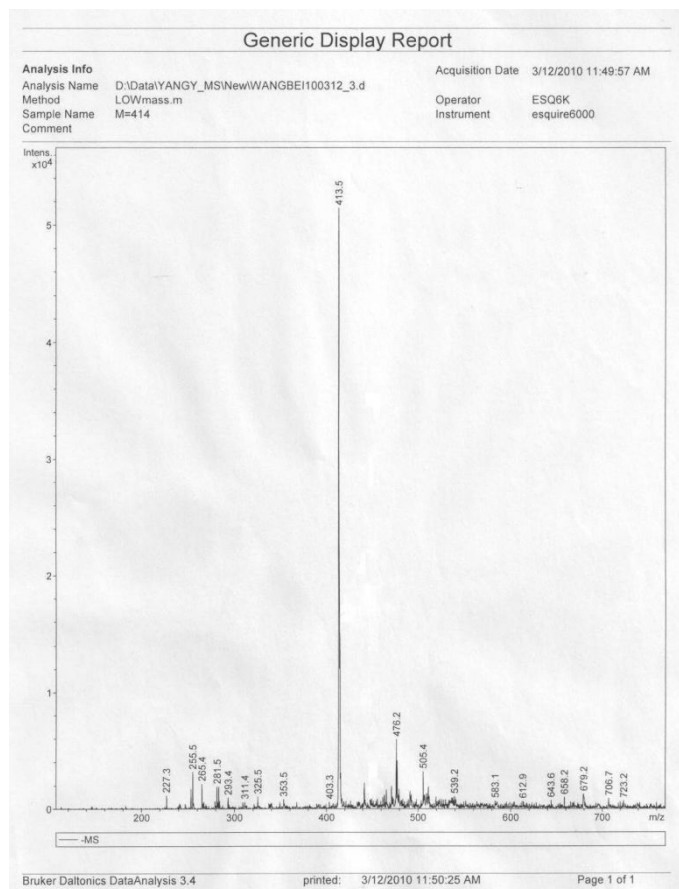


Figure S2. ESI-MS spectrum of $\text{H}_2\text{L}'$

Synthesis of complex 3.

2 mL methanol containing 0.1 mmol $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (37.3 mg) was added in batches to a stirred 5 mL DMF of 0.1 mmol $\text{H}_2\text{L}'$ (41.4 mg). The mixture was stirred in air for 4h at room temperature, then a black solution was formed. The solution was filtered and kept in air then. Black block single crystals of $\text{Ce}_2\text{L}'_3$ which are suitable for X-ray crystallography were obtained on slow evaporation over 1 month. Elemental analysis calcd (%) for **3** $\text{C}_{60}\text{H}_{60}\text{Ce}_2\text{Cl}_2\text{N}_{12}\text{O}_{18}$ (non-coordinated solvent molecules were lost upon drying process): C, 45.39; H, 3.78; N, 10.59. Found: C, 45.40; H, 3.75; N, 10.58. High-resolution electrospray ionization mass spectrometry (HRESI-MS): $m/z = 758.1103$ [$\text{Ce}_2\text{L}'_3$] $^{2+}$ (calcd for $\text{C}_{60}\text{H}_{60}\text{N}_{12}\text{O}_{18}\text{Ce}_2$, 758.1129), FT-IR (KBr pellet) (cm^{-1}): 3440.0(br), 1600.0(vs), 1557.5(m), 1442.9(s), 1396.0(m), 1365.5(w), 1292.7(s), 1248.4(s), 1073.3(w), 854.9(w), 739.9(m), 567.3(w) (Figure S5).

Synthesis of complexes 4a and 4b.

A solution of 0.1 mmol rare earth halide salt in 2 mL methanol was added into a light yellow and transparent solution of H_2L (44.2 mg, 0.1 mmol) with KOH (5.6 mg, 0.2 mmol) after mixing in 8 mL methanol along with 0.5 mL DMF. Tetranuclear dimetallic triple-stranded helicates, $[\text{K}_2\text{La}_2\text{L}_3(\text{H}_2\text{O})_2]\text{Br}_2$ (**4a**) and $[\text{K}_2\text{Nd}_2\text{L}_3(\text{DMF})_2]\text{Cl}_2$ (**4b**) were formed by evaporation in air at room temperature over 4 weeks (yield: 50%). Elemental analysis calcd (%) for **4a** $\text{C}_{66}\text{H}_{76}\text{Br}_2\text{K}_2\text{La}_2\text{N}_{12}\text{O}_{20}$ (non-coordinated solvent molecules were lost upon evaporation): C, 42.28; H, 4.06; N, 8.97. Found: C, 42.31; H, 4.01; N, 8.88. High-resolution electrospray ionization mass spectrometry (HRESI-MS): $m/z = 856.1344$ [$\text{K}_2\text{La}_2\text{L}_3(\text{H}_2\text{O})_2$] $^{2+}$ (calcd for [$\text{C}_{66}\text{H}_{72}\text{K}_2\text{La}_2\text{N}_{12}\text{O}_{18}$] $^{2+}$, 856.1350); Elemental analysis calcd (%) for **4b** $\text{C}_{72}\text{H}_{86}\text{Cl}_2\text{K}_2\text{Nd}_2\text{N}_{14}\text{O}_{20}$ (noncoordinated solvent molecules were lost upon drying): C, 45.47; H, 4.53; N, 10.31. Found: C, 45.31; H, 4.41; N, 10.28. High-resolution electrospray ionization mass spectrometry (HRESI-MS): $m/z = 843.1322$ [$\text{K}_2\text{Nd}_2\text{L}_3$] $^{2+}$ (calcd for [$\text{C}_{66}\text{H}_{72}\text{K}_2\text{Nd}_2\text{N}_{12}\text{O}_{18}$] $^{2+}$, 843.1285); FT-IR for **4a** and **4b** (KBr pellet) (cm^{-1}): 3428.11 (br), 2958.88 (br), 1603.67 (vs), 1453.10 (s), 1395.30(m), 1365.64 (m), 1310.15 (m), 1220.38 (s), 1175.51 (w), 1068.28(m), 1017.33(w), 972.46(w), 888.05(w), 850.5(w), 741.27(s), 656.86(w), 566.36(w) (Figure S9).

Synthesis of complexes 5a and 5b.

0.2 mmol $\text{LiOH} \cdot \text{H}_2\text{O}$ or 0.2 mmol NaOH and 0.1 mmol H_2L (44.2 mg) were added into a mixing solvent containing 8 mL methanol and 0.5 mL DMF, and then the solution was stirred for 10 min. After that, a solution of 0.1 mmol $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ in 2 mL methanol was added. The mixture was rapidly stirred for 10 min. Then the solution was filtered and kept in air. Rhombohedral crystals of $[\text{La}_4\text{L}_4(\text{CO}_3)]\text{Cl}_2$ (**5a**) and $[\text{Nd}_4\text{L}_4(\text{CO}_3)]\text{Cl}_2$ (**5b**) suitable for X-ray analysis were obtained by slow evaporation over several weeks at room temperature in air (yield: 60%). CO_2 molecules from air are efficiently captured and fixed by these clusters. Elemental analysis calcd (%) for **5a** $\text{C}_{89}\text{H}_{96}\text{Cl}_2\text{La}_4\text{N}_{16}\text{O}_{27}$ (non-coordinated solvent molecules were lost upon drying process): C, 44.94; H, 4.04; N, 9.43. Found: C, 44.71; H, 4.01;

N, 9.21. HRESI-MS: $m/z = 1188.14244$ $[\text{La}_4\text{L}_4(\text{CO}_3)]^{2+}$ (calcd for $[\text{C}_{89}\text{H}_{96}\text{La}_4\text{N}_{16}\text{O}_{27}]^{2+}$, 1188.14369); Elemental analysis calcd (%) for **5b** $\text{C}_{89}\text{H}_{96}\text{Cl}_2\text{Nd}_4\text{N}_{16}\text{O}_{27}$ (non-coordinated solvent molecules were lost upon drying): C, 43.34; H, 3.90; N, 9.09. Found: C, 43.61; H, 3.98; N, 9.13. HRESI-MS: $m/z = 1197.1517$ $[\text{Nd}_4\text{L}_4(\text{CO}_3)]^{2+}$ (calcd for $[\text{C}_{89}\text{H}_{96}\text{Nd}_4\text{N}_{16}\text{O}_{27}]^{2+}$, 1197.1509); FT-IR for **5a** and **5b** (KBr pellet) (cm^{-1}): 3402.00(br), 3180.44(br), 2974.75(br), 1642.97(vs), 1610.00(vs), 1552.44(m), 1500.00(w), 1450.00(s), 1392.02(m), 1308.63(w), 1218.10(s), 1070.39(m), 973.50(w), 883.77(w), 844.85(w), 742.40(w), 651.87(w), 562.13(w) (Figure S25).

Caution: There were no problems involved during the preparation of rare earth halide salts and hydrazine hydrate, but suitable care should be taken when handling such potentially hazardous compounds.

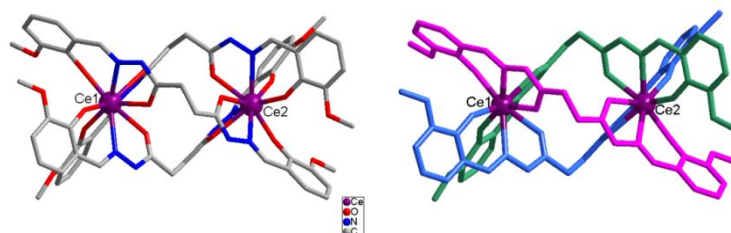


Figure S3. Frame-and-sphere representations of the crystal structure of **3**. For clarity, each ligand is represented in a different color, with cerium ions represented by purple spheres. Hydrogen atoms, external counteranions, and solvent molecules are omitted for clarity.

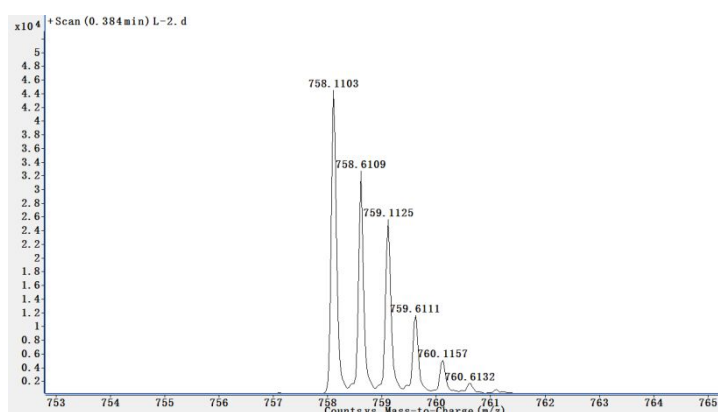


Figure S4. HRESI-MS spectrum of **3**.

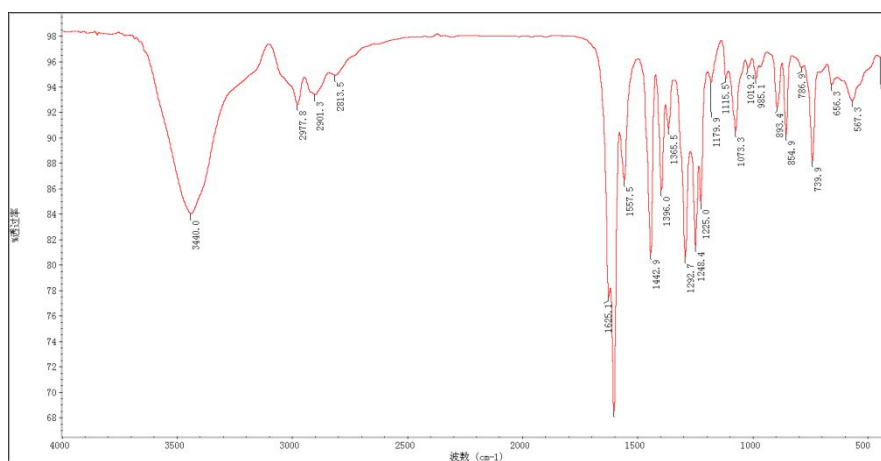


Figure S5. IR spectra of complex **3** in the solid state (KBr disk) at room temperature.

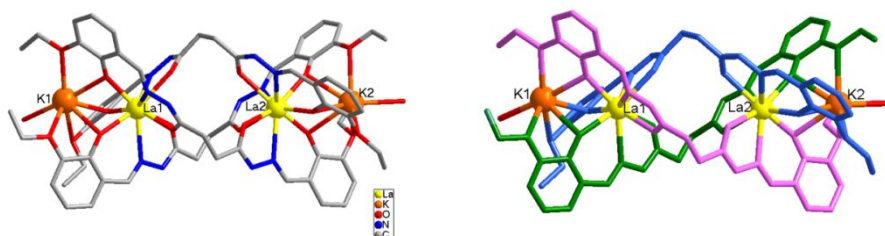


Figure S6. Frame-and-sphere representations of the crystal structure of **4a**. For clarity, each ligand is represented in a different color, with lanthanum ions represented by yellow spheres, potassium ions represented by orange spheres, coordinated H₂O red. Hydrogen atoms, external counteranions, and solvent molecules are omitted for clarity.

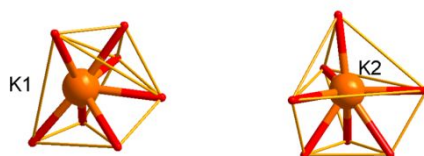


Figure S7. Coordination polyhedrons of the potassium ions in **4a**.

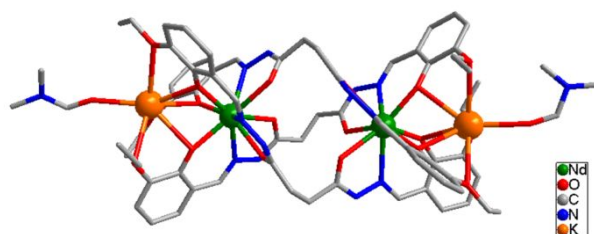


Figure S8. Frame-and-sphere representations of the crystal structure of **4b**. Hydrogen atoms, external counteranions, and solvent molecules are omitted for clarity.

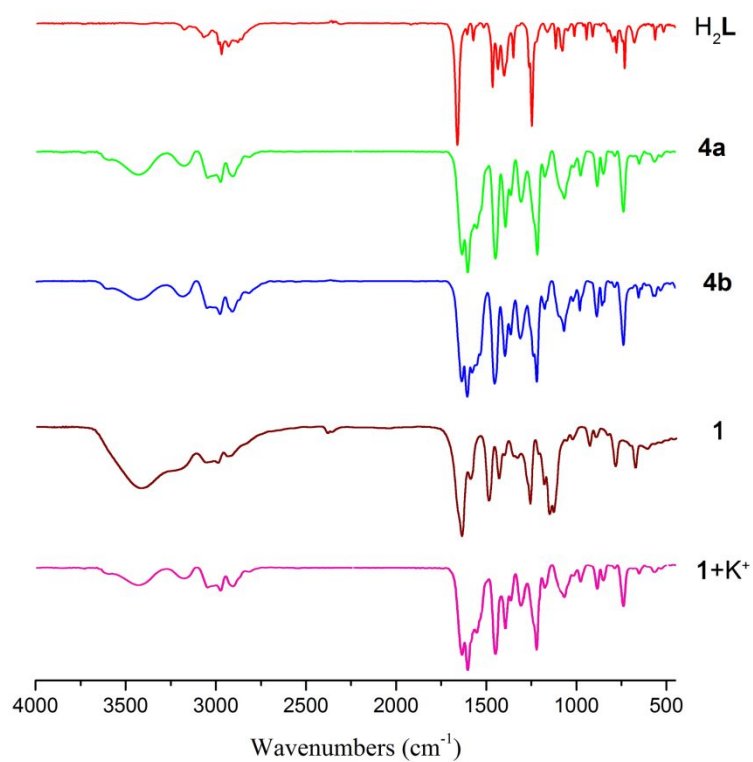


Figure S9. IR spectra of ligand H_2L and complexes (**4a**, **4b**, **1**, $1+\text{K}^+$) in the solid state (KBr disk) at room temperature.

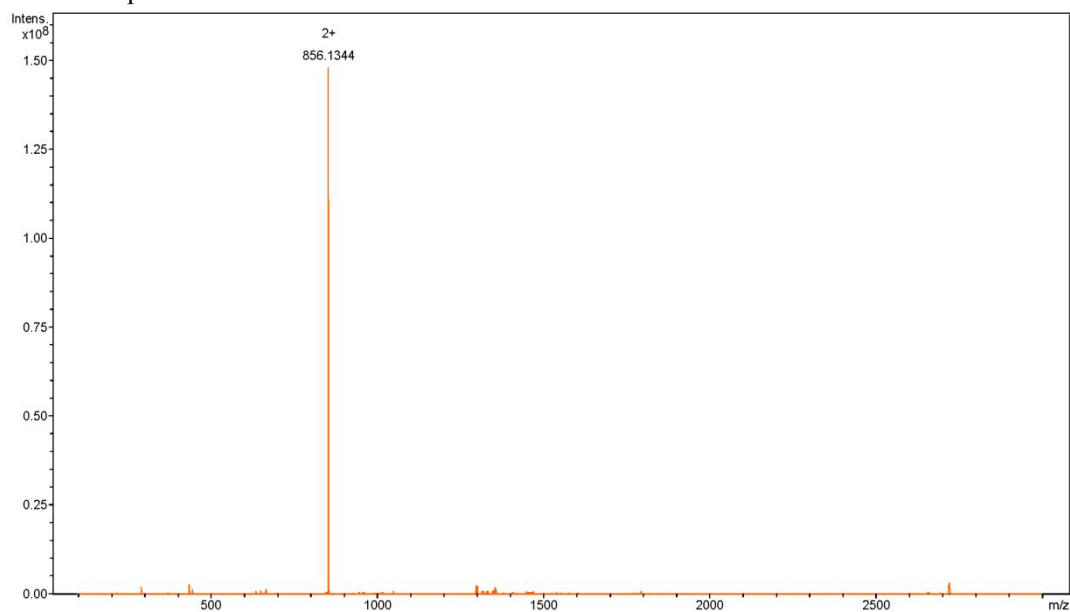


Figure S10. HRESI-MS spectrum of **4a**.

Mass Spectrum List Report

Analysis Info

Analysis Name D:\Data\HYY\method_000552.d
 Method 4_19_MassAccuNeg
 Sample Name 1
 Comment

Acquisition Date 11/3/2015 2:46:03 PM

Operator
 Instrument solariX

Acquisition Parameter

Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	53.8 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	3000.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a	Calibration Date	Fri Feb 21 02:36:54 2014
Pulse Program	basic	n/a	n/a	Data Acquisition Size	1048576
Source Accumulation	0.010 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Ion Accumulation Time	0.200 sec	n/a	n/a	Apodization	Apodization
Flight Time to Acq. Cell	0.001 sec	n/a	n/a		

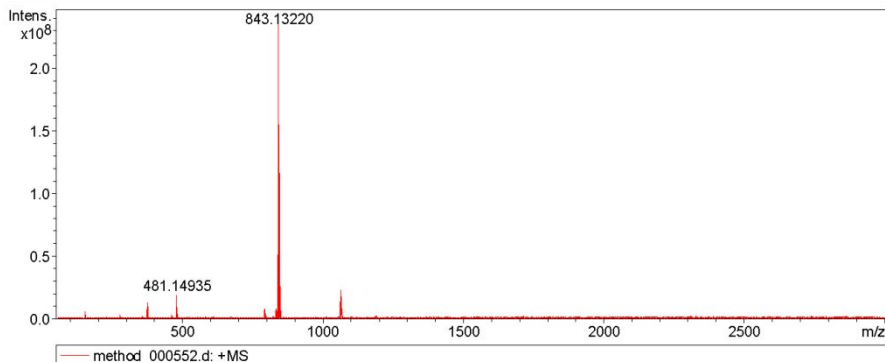


Figure S11. High-resolution electrospray ionization mass spectra (HRESI-MS) of the compound **4b**.

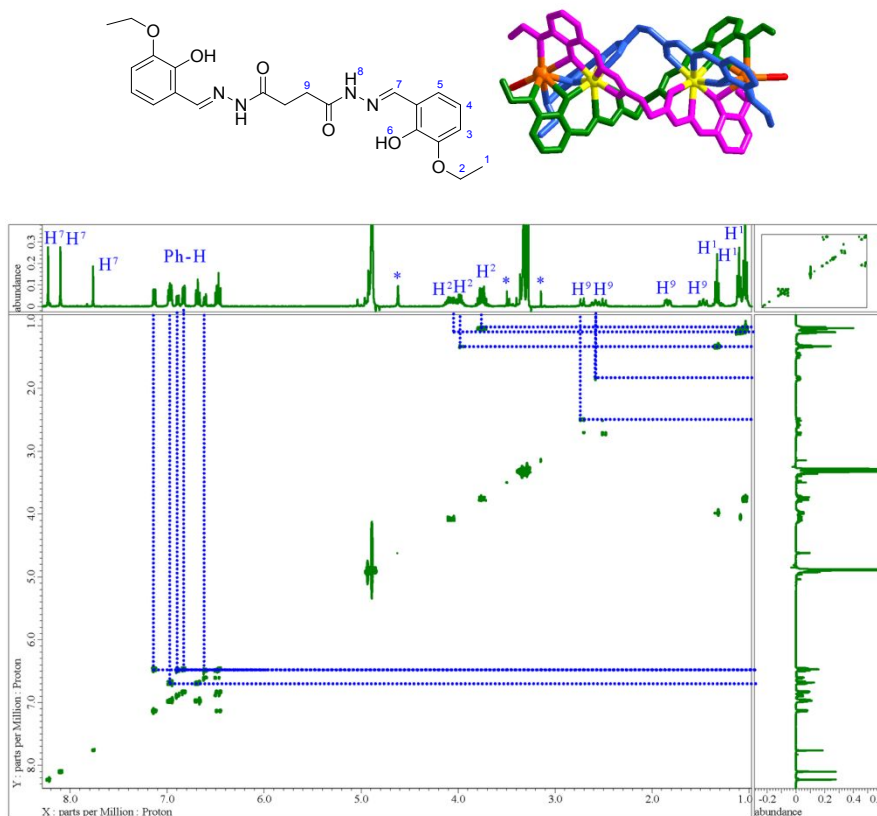


Figure S12. $^1\text{H}/^1\text{H}$ COSY (400 MHz) of **4a** in CD_3OD .

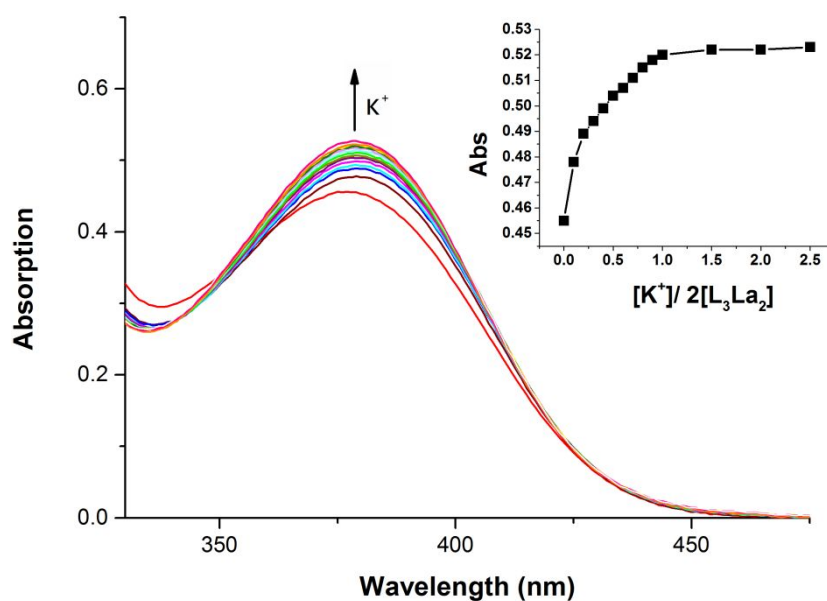


Figure S13. UV-Vis spectral of compound $[L_3La_2]$ upon addition of K^+ in acetonitrile at room temperature. $[L_3La_2] = 1.67 \times 10^{-5}$ M, $[KBr] = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0$ equivalents, $T = 25$ °C. The synthesis of compound $[L_3La_2]$: A mixture of H_2L and $LaBr_3 \cdot 7H_2O$ (H_2L and $LaBr_3$ in a 3:2 ratio) in DMF was rapid stirred under a N_2 atmosphere.

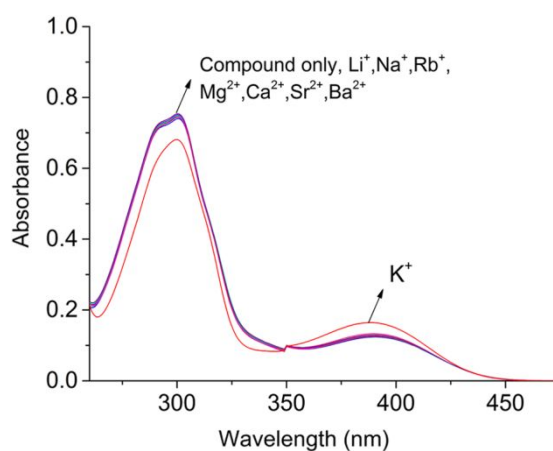


Figure S14. The absorption spectra of the compound $[L_3La_2]$ in the presence of 2 equiv different ions such as Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (all the ions as their Cl^- salts) in methanol. Experimental conditions: $[L_3La_2] = 0.667 \times 10^{-5}$ M, $T = 25$ °C. The synthesis of compound $[L_3La_2]$: A mixture of H_2L and $LaBr_3 \cdot 7H_2O$ (H_2L and $LaBr_3$ in a 3:2 ratio) in DMF was rapid stirred under a N_2 atmosphere.

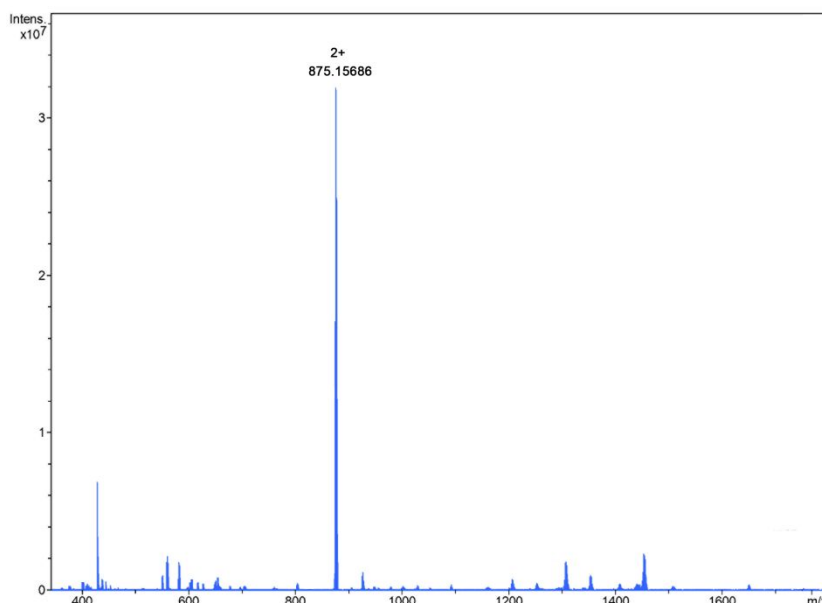


Figure S15. High-resolution electrospray ionization mass spectra (HRESI-MS) of the compound $[L_3Nd_2]$ upon addition of 2 equiv different ions such as Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (all the ions as their Cl^- salts) in DMF- CH_3OH solution. The main peak was observed at $m/z = 875.15686$, which represented the complex $[L_3Nd_2K_2(CH_3OH)_2]^{2+}$. The synthesis of compound $[L_3Nd_2]$: A mixture of H_2L and $NdCl_3 \cdot 7H_2O$ (H_2L and $NdCl_3$ in a 3:2 ratio) in DMF was rapid stirred under a N_2 atmosphere.

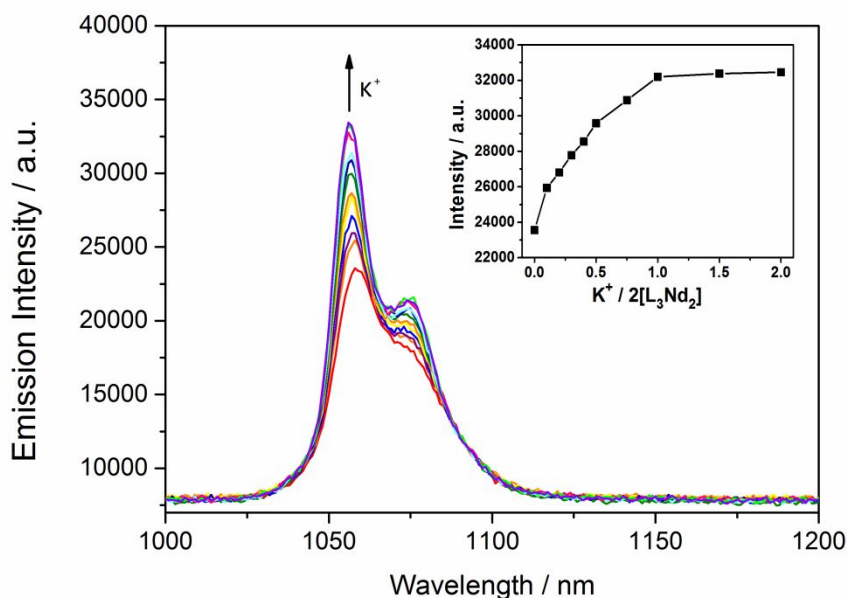


Figure S16. The NIR emission spectra change of $[L_3Nd_2]$ upon addition of K^+ in acetonitrile ($[L_3Nd_2] = 1.67 \times 10^{-5} M$, $[KCl] = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0$ equivalents). Inset: the emission intensity of $[L_3Nd_2]$ at 1058 nm as a function of $K^+/2[L_3Nd_2]$. $\lambda_{ex}=383$ nm. The synthesis of compound $[L_3Nd_2]$: A mixture of H_2L and $NdCl_3 \cdot 7H_2O$ (H_2L and $NdCl_3$ in a 3:2 ratio) in DMF was rapid stirred under a N_2 atmosphere.

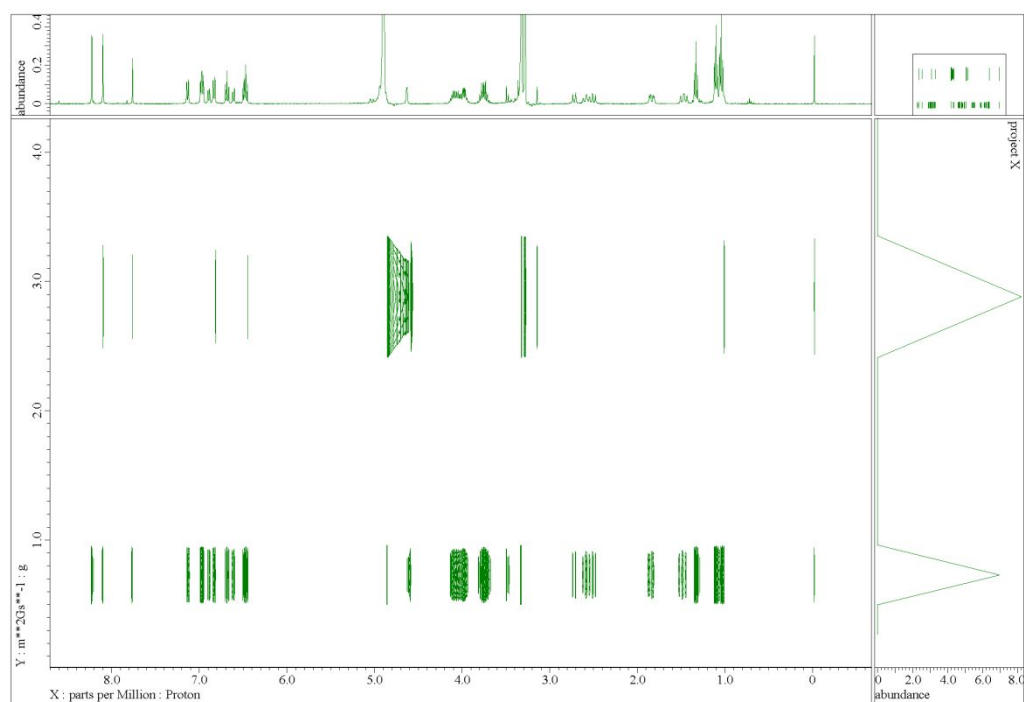
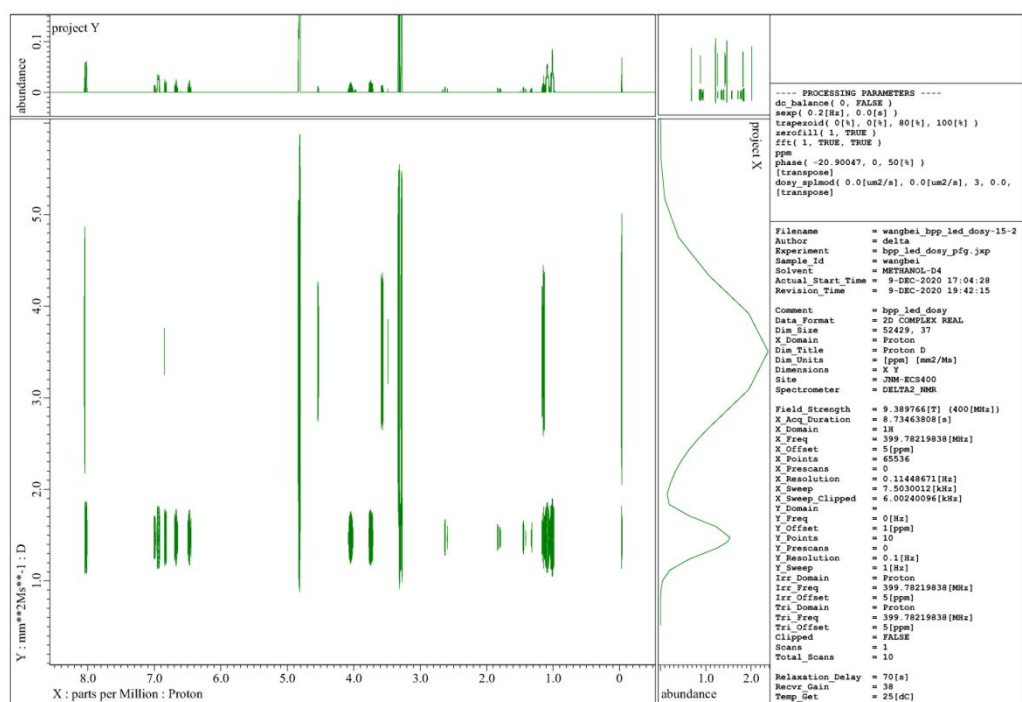


Figure S17. ¹H DOSY spectrum of complex **1** (top) and complex **1** with all kinds of alkali and earth-alkali metal chloride (bottom, logD=-9.106). 400 MHz, CD₃OD, 298K.

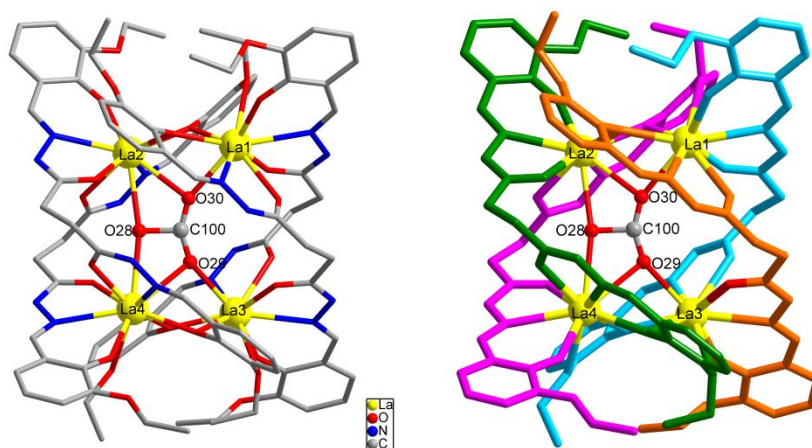


Figure S18. Frame-and-sphere representations of the crystal structure of **5a**. For clarity, each ligand is represented in a different color, with lanthanum ions represented by yellow spheres. Hydrogen atoms, external counteranions, and solvent molecules are omitted for clarity.

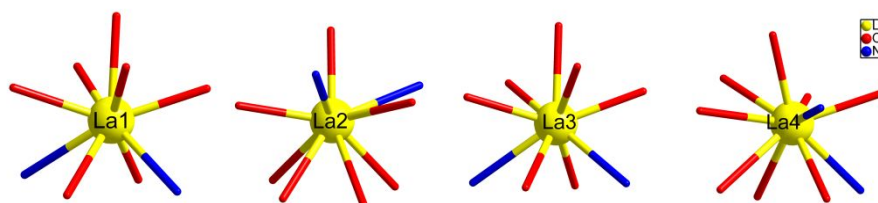


Figure S19. Coordination polyhedrons of the lanthanum ions in **5a**.

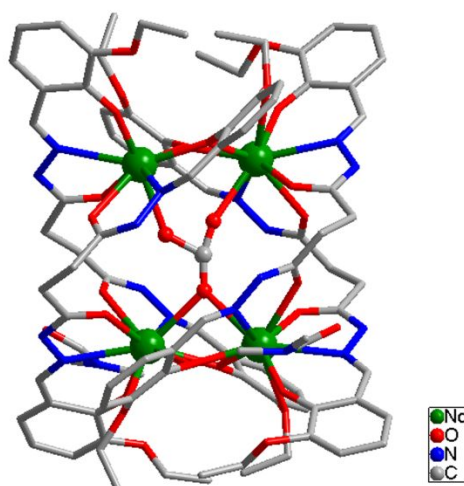


Figure S20. Frame-and-sphere representations of the crystal structure of **5b**. Hydrogen atoms, external counteranions, and solvent molecules are omitted for clarity.

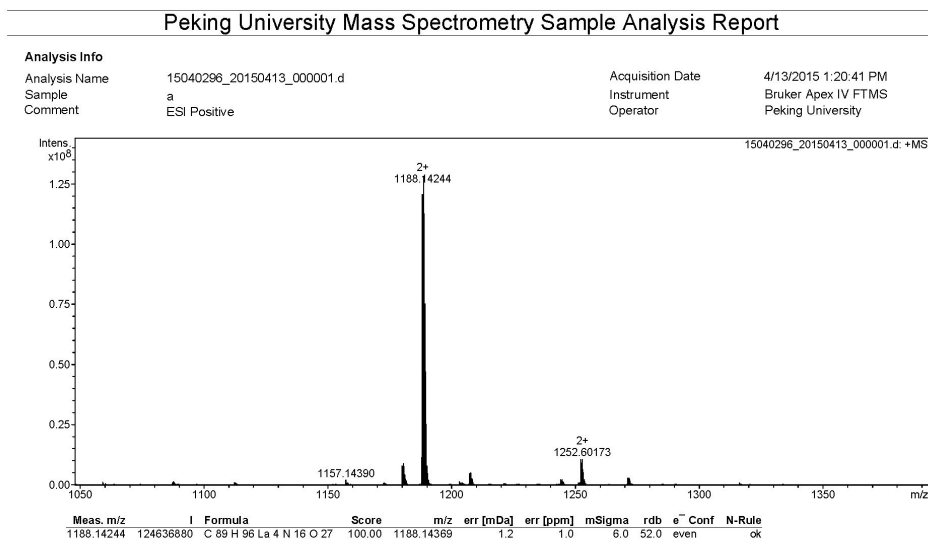


Figure S21. High-resolution electrospray ionization mass spectra (HRESI-MS) of the compound **5a**.

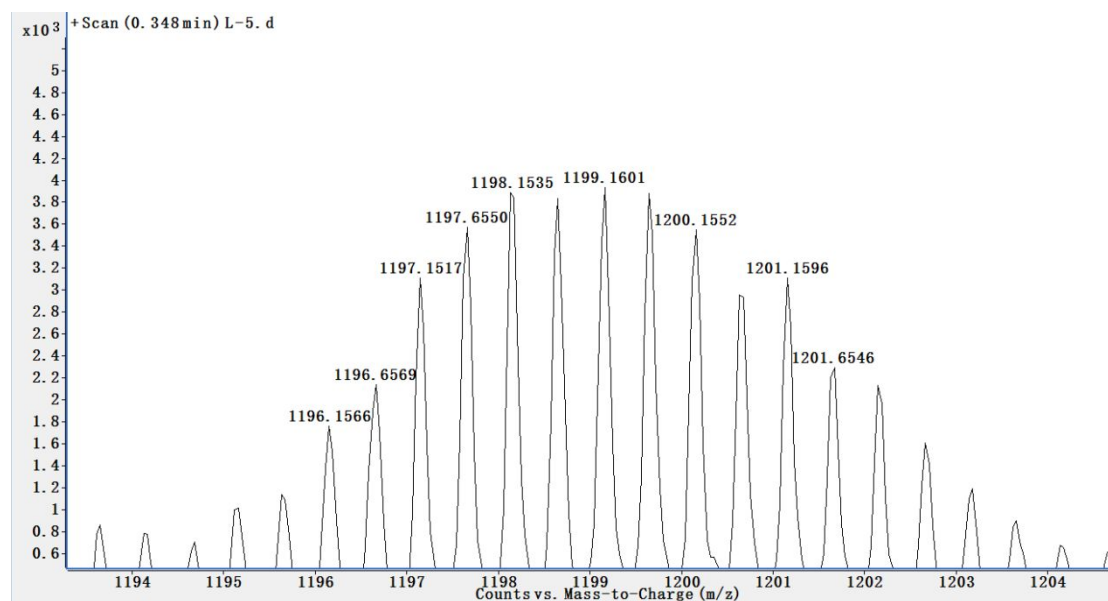


Figure S22. HRESI-MS spectrum of **5b**.

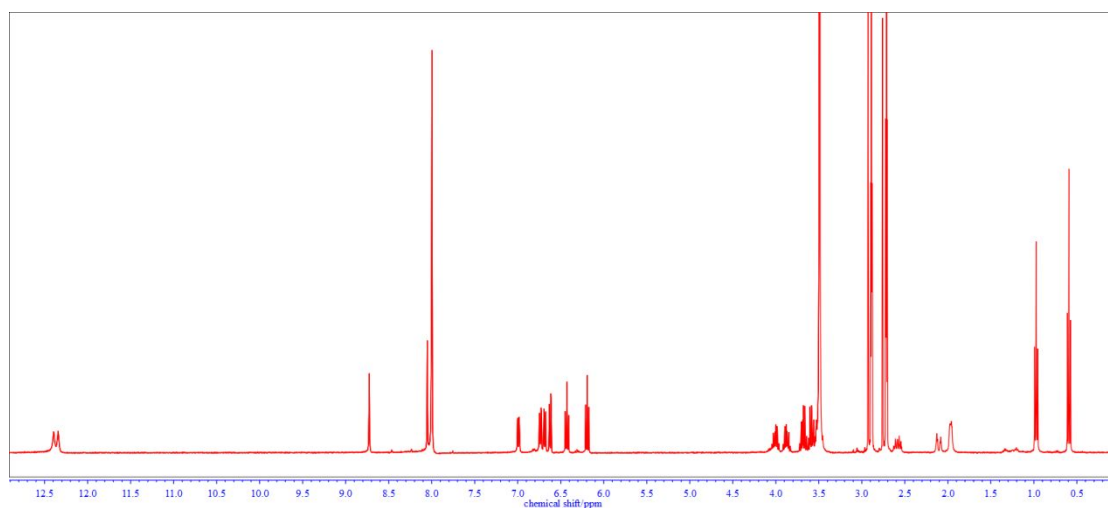


Figure S23. ^1H NMR (400 MHz) of **5a** in DMF-d^7

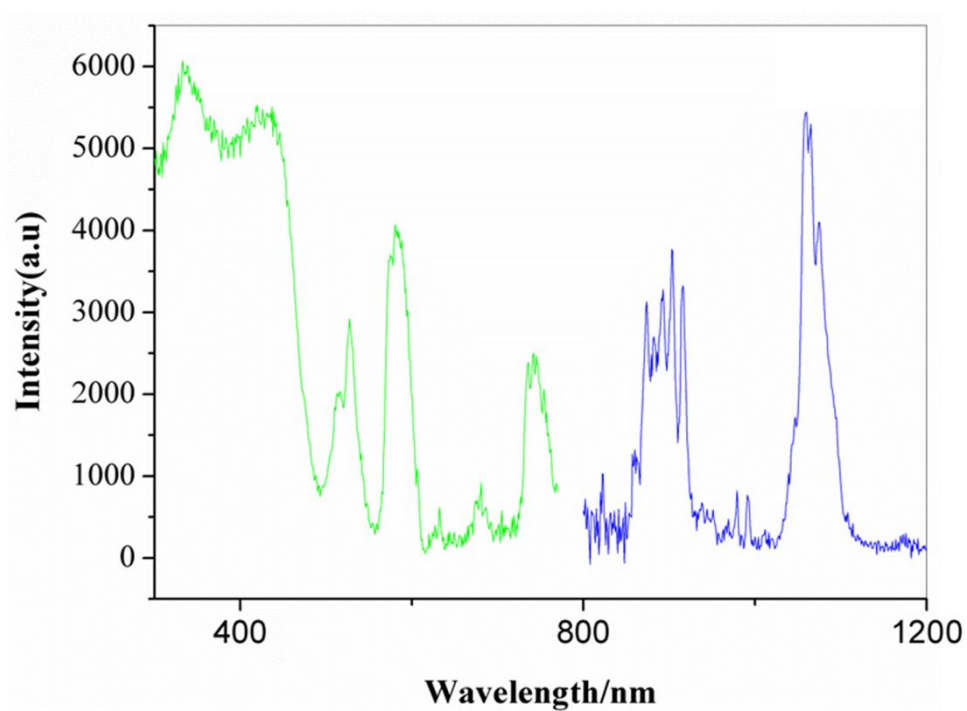


Figure S24. (Left) Excitation and (right) emission spectra of **5b** in solid state ($\lambda_{\text{ex}} = 420 \text{ nm}$, $\lambda_{\text{em}} = 1050 \text{ nm}$, solid traces).

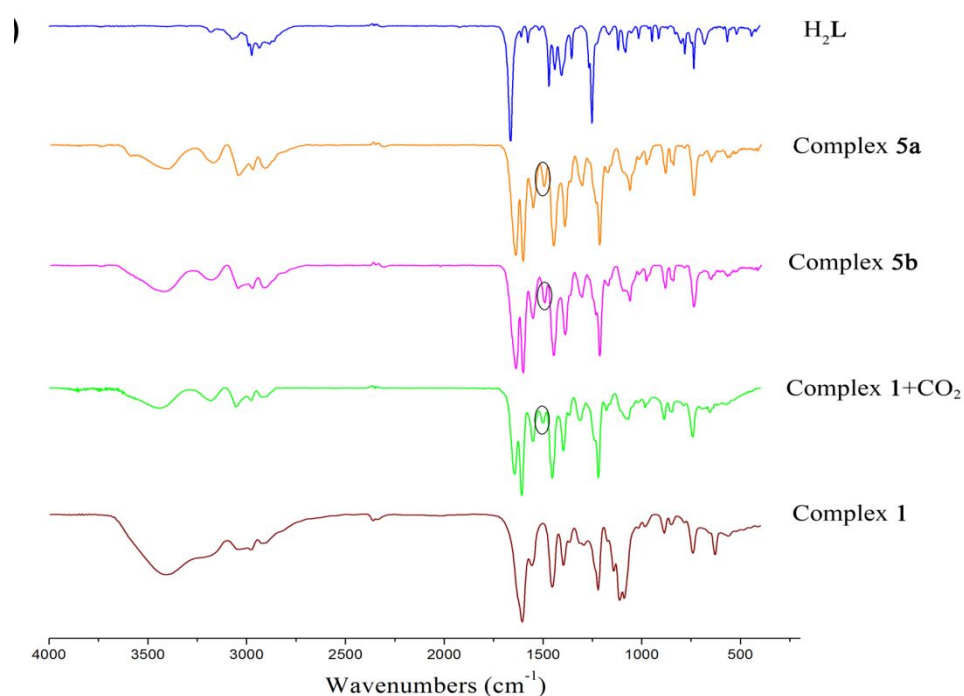


Figure S25. IR spectra of ligand H_2L and complexes (**5a**, **5b**, **1**+ CO_2 , and **1**) in the solid state (KBr disk) at room temperature.

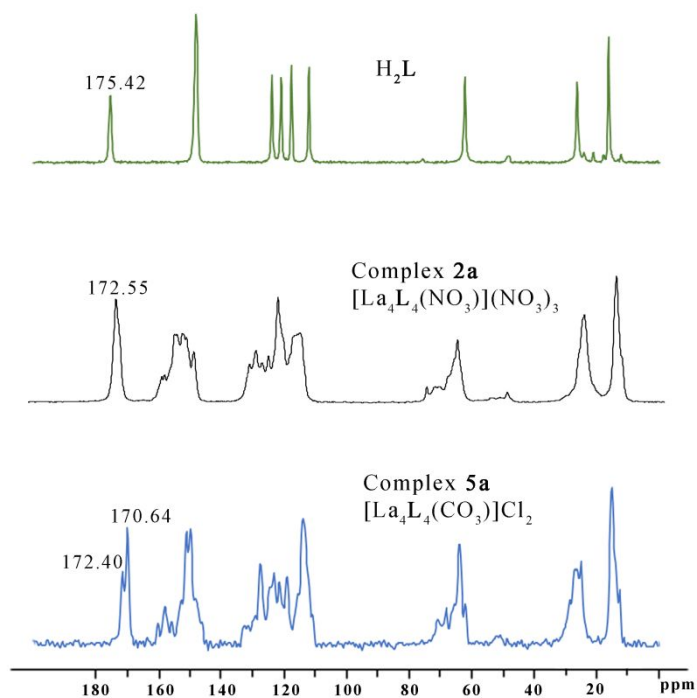


Figure S26. The solid-state ^{13}C NMR spectrum of H_2L , **2a** and **5a**. Complexes **2a** and **5a** are similar structures of tetranuclear quadruple-stranded helicate, but **2a** does not fix carbonate, so we only see one peak at 172.55 ppm. However, **5a** captures carbon dioxide from the air, so we observe a new small peak at 172.40 ppm, it can be assigned to the encapsulated CO_3^{2-} anion. Note that the

chemical shifts of carbonyl groups are slightly altered relative to peaks in complex **5a** due to changes of in coordination environments. (600 MHz)

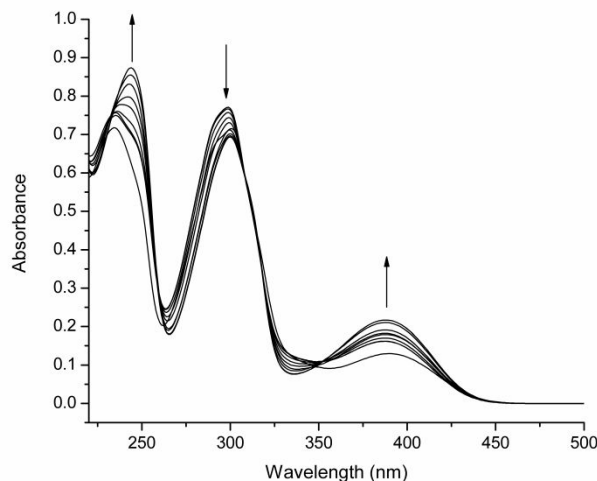


Figure S27. UV-Vis spectral changes for the reaction of the system (L^{2-} and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$) with CO_2 gas in methanol. Experimental conditions: $[\text{L}^{2-}] = [\text{LaCl}_3 \cdot 7\text{H}_2\text{O}] = 2.0 \times 10^{-5} \text{ M}$, $T = 25^\circ\text{C}$.

Experimental method: A mixture of $\text{LiOH} \cdot \text{H}_2\text{O}$ (4.2 mg, 0.1 mmol) and H_2L (22.1 mg, 0.05 mmol) in absolute methanol (3 mL) under a N_2 atmosphere was stirred to obtain a transparent solution. Then a solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (0.05 mmol) in absolute methanol (3 mL) was added and the mixture was rapid stirred under a N_2 atmosphere. The solution system was further diluted to 50 mL with absolute methanol under a N_2 atmosphere. Then 40 μL the solution was inject into 2 mL absolute methanol and CO_2 gas was slowly introduced into the solution, which was continuously recorded by UV-vis spectrophotometry.

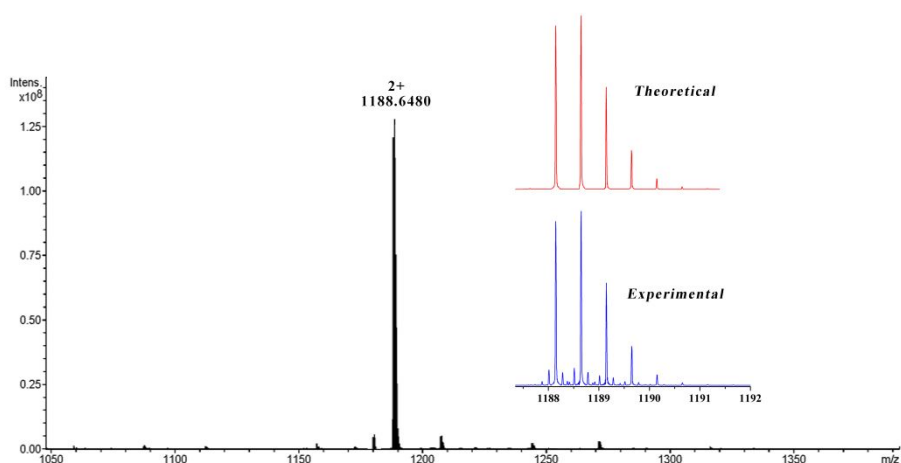


Figure S28. HRESI-MS spectrum of $1 + \text{CO}_2$. The insert exhibits the measured and simulated isotopic patterns at $m/z = 1188.6480$.

Thermogravimetry spectrum of complexes.

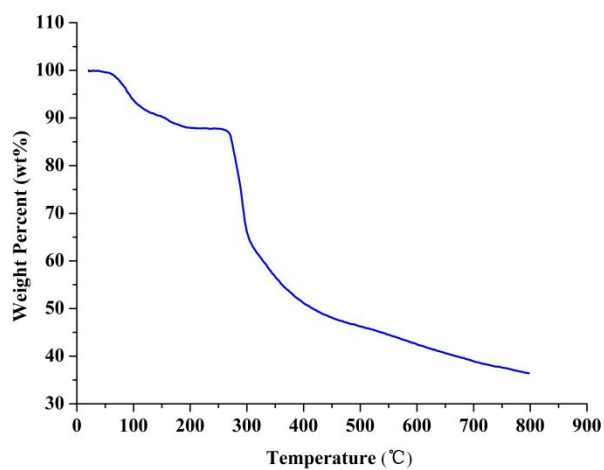


Figure S29. Thermogravimetry spectrum of **3**.

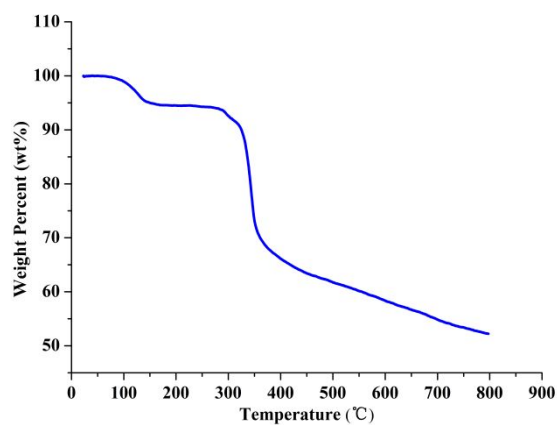


Figure S30. Thermogravimetry spectrum of **4a**.

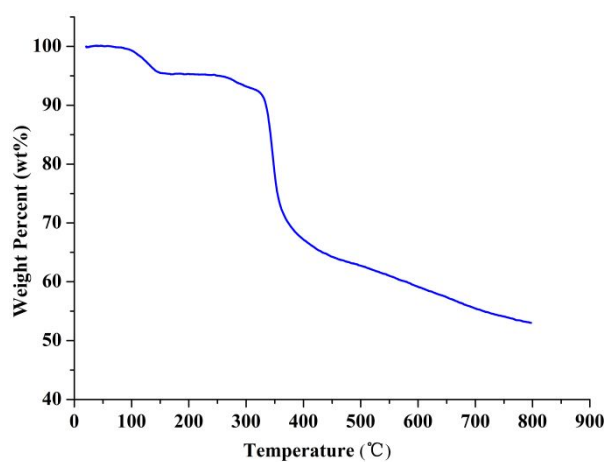


Figure S31. Thermogravimetry spectrum of **4b**.

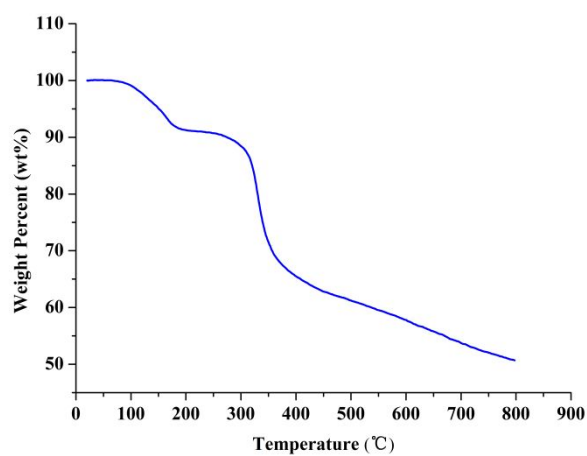


Figure S32. Thermogravimetry spectrum of **5a**.

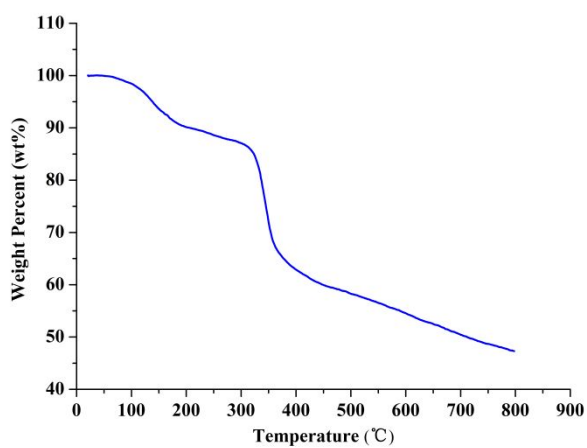


Figure S33. Thermogravimetry spectrum of **5b**.

Table S1: Room Temperature Luminescence lifetime τ_{obs} , absolute quantum yield Φ .

complex	τ_{obs} [μs]	Φ [%]
5b	0.21	1.43

X-ray crystallography of Compounds

Crystallographic data for complexes were collected with a Agilent Technologies SuperNova diffractometer at low temperature, using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F^2 by using the program package SHELXS-97. Hydrogen atoms, except those of the water molecules, were generated geometrically. In the X-ray structure refinements, however, the solvent molecules of complexes could not be located because of their high thermal disorder, and the final structure models were refined without the solvent molecules by using a SQUEEZE routine of PLATON. CCDC 1470814 (**3**), 1817349 (**4a**), 1470815 (**4b**), 1470816 (**5a**), and 1470818 (**5b**) contain the supplementary crystallographic data for this paper.

Table S2. Crystal data and structure refinement for complex 3.

Compound	3
Empirical formula	C ₆₀ H ₆₀ Ce ₂ Cl ₂ N ₁₂ O ₁₈
Formula weight	1588.34
Temperature (K)	296(2)
Crystal system	triclinic
Space group	P-1
a (Å)	16.038(12)
b (Å)	16.987(12)
c (Å)	17.256(12)
α (°)	95.595(12)
β (°)	110.384(12)
γ (°)	115.403(11)
Volume (Å ³)	3808(5)
Z	2
ρ_{calc} (g/cm ³)	1.385
μ (mm ⁻¹)	1.319
F(000)	1596.0
Crystal size (mm)	0.1 × 0.1 × 0.1
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	2.774 to 50.092
Index ranges	-19 ≤ h ≤ 15, -19 ≤ k ≤ 20, -10 ≤ l ≤ 20
Reflections collected	19161
Independent reflections	12997 [R _{int} = 0.0691, R _{sigma} = 0.1565]
Data/restraints/parameters	12997/87/854

Goodness-of-fit on F ²	0.901
Final R indexes [I>=2σ (I)]	R ₁ = 0.0764, wR ₂ = 0.1837
Final R indexes [all data]	R ₁ = 0.1398, wR ₂ = 0.2091
Largest diff. peak/hole / e Å ⁻³	2.40/-2.00

Table S3. Crystal data and structure refinement for complex 4a and 4b.

Compound	4a	4b
Empirical formula	C ₆₆ H ₇₆ Br ₂ K ₂ La ₂ N ₁₂ O ₂₀	C ₁₅₆ H ₂₀₀ Cl ₄ K ₄ N ₃₂ Nd ₄ O ₄₄
Formula weight	1873.22	4102.63
Temperature (K)	173(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a (Å)	17.5279(14)	20.117(5)
b (Å)	20.464(2)	28.903(8)
c (Å)	26.141(2)	17.785(5)
α (°)	90	90.00
β (°)	105.074(9)	105.810(5)
γ (°)	90	90.00
Volume (Å ³)	9053.8(14)	9950(5)
Z	4	2
ρ _{calcd.} (g/cm ³)	1.374	1.369
μ (mm ⁻¹)	1.970	1.240
F(000)	3752.0	4192
Crystal size (mm)	0.2 × 0.16 × 0.12	0.18 × 0.15 × 0.1
Radiation	MoKα (λ = 0.710)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.75 to 50.198	3.84 to 50.02
Index ranges	-19 ≤ h ≤ 20, -24 ≤ k ≤ 24, -31 ≤ l ≤ 31	-23 ≤ h ≤ 20, -34 ≤ k ≤ 34, -21 ≤ l ≤ 20
Reflections collected	41576	50254
Independent reflections	16131 [R _{int} = 0.0659, R _{sigma} = 0.0977]	17441 [R _{int} = 0.0631, R _{sigma} = 0.0780]
Data/restraints/parameters	16131/67/953	17441/131/1122
Goodness-of-fit on F ²	1.030	1.015
Final R indexes [I>=2σ (I)]	R ₁ = 0.0555, wR ₂ = 0.1311	R ₁ = 0.0546, wR ₂ = 0.1403
Final R indexes [all data]	R ₁ = 0.0852, wR ₂ = 0.1510	R ₁ = 0.0825, wR ₂ = 0.1595
Largest diff. peak/hole / e Å ⁻³	2.31/-1.77	2.06/-1.10

Table S4. Selected bond lengths (Å) for complex 4a.

La1–O2	2.382(4)	La2–O4	2.577(4)
La1–O3	2.537(4)	La2–O5	2.386(4)
La1–O8	2.381(4)	La2–O10	2.613(4)
La1–O9	2.590(4)	La2–O11	2.387(4)
La1–O14	2.466(4)	La2–O16	2.597(4)
La1–O15	2.536(4)	La2–O17	2.400(4)
La1–N1	2.729(5)	La2–N4	2.749(5)
La1–N5	2.808(5)	La2–N8	2.787(5)

La1–N9	2.757(5)	La2–N12	2.753(5)
K1–O1	2.787(4)	K2–O5	2.821(4)
K1–O2	2.757(4)	K2–O6	2.836(5)
K1–O7	3.423(5)	K2–O11	2.768(5)
K1–O8	2.696(4)	K2–O12	2.874(6)
K1–O13	2.821(5)	K2–O17	2.771(4)
K1–O14	2.860(4)	K2–O18	2.842(5)
K1–O19	2.735(6)	K2–O20	2.736(6)
La1–K1	3.7345(14)	La2–K2	3.8027(15)

Table S5. Crystal data and structure refinement for complex 5a and 5b.

Compound	5a	5b
Empirical formula	C ₉₂ H ₁₀₃ Cl ₂ La ₄ N ₁₇ O ₂₈	C ₉₅ H ₁₁₀ Cl ₂ N ₁₈ Nd ₄ O ₂₉
Formula weight	2521.45	2615.86
Temperature (K)	173(2)	296(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	16.3322(6)	16.181(9)
b (Å)	19.7882(7)	20.107(12)
c (Å)	21.9567(8)	21.793(12)
α (°)	116.344(4)	115.633(6)
β (°)	93.589(3)	93.383(7)
γ (°)	106.368(3)	106.000(7)
Volume (Å ³)	5954.3(4)	6013(6)
Z	2	2
ρ_{calc} (g/cm ³)	1.406	1.445
μ (mm ⁻¹)	1.522	1.816
F(000)	2520.0	2624.0
Crystal size (mm)	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1
Radiation	MoK α (λ = 0.710)	MoK α (λ = 0.71073)
2 θ range for data collection/°	6.566 to 57.688	3.052 to 55.492
Index ranges	-21 ≤ h ≤ 21, -26 ≤ k ≤ 26, -27 ≤ l ≤ 27	-21 ≤ h ≤ 21, -26 ≤ k ≤ 26, -28 ≤ l ≤ 28
Reflections collected	51497	57536
Independent reflections	27255 [R _{int} = 0.0374, R _{sigma} = 0.0712]	27527 [R _{int} = 0.0727, R _{sigma} = 0.1266]
Data/restraints/parameters	27255/93/1298	27527/385/1353
Goodness-of-fit on F ²	1.019	1.051
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0519, wR ₂ = 0.1222	R ₁ = 0.1263, wR ₂ = 0.3463
Final R indexes [all data]	R ₁ = 0.0773, wR ₂ = 0.1403	R ₁ = 0.1813, wR ₂ = 0.3807
Largest diff. peak/hole / e Å ⁻³	4.35/-2.07	4.62/-2.58

Table S6. Selected bond lengths (Å) and angles (°) for complex 5a.

La1–O8	2.319(3)	La2–O2	2.311(3)
La1–O20	2.425(3)	La2–O14	2.423(3)
La1–O14	2.511(3)	La2–O3	2.515(3)

La1–O9	2.524(3)	La2–O15	2.561(4)
La1–O21	2.534(3)	La2–O20	2.562(3)
La1–O30	2.559(4)	La2–O30	2.663(4)
La1–N5	2.715(4)	La2–N9	2.710(4)
La1–N13	2.761(4)	La2–N1	2.734(4)
La1–O13	2.796(3)	La2–O28	2.772(6)
La3–O23	2.332(3)	La4–O17	2.349(4)
La3–O11	2.418(3)	La4–O5	2.433(3)
La3–O22	2.508(3)	La4–O16	2.506(3)
La3–O10	2.515(3)	La4–O4	2.507(4)
La3–O29	2.552(3)	La4–O11	2.555(3)
La3–O5	2.562(3)	La4–O29	2.675(4)
La3–O6	2.720(3)	La4–N4	2.712(4)
La3–N8	2.736(4)	La4–N12	2.779(4)
La3–N16	2.745(4)	La4–O28	2.804(7)
		La4–O12	2.817(3)
O(28)–C(100)	1.518(10)	O(29)–C(100)	1.144(7)
O(30)–C(100)	1.124(7)		
O(30)–C(100)–O(29)	156.2(11)	O(30)–C(100)–O(28)	100.3(7)
O(29)–C(100)–O(28)	103.4(7)		