Supporting Information

Chiral Auxiliary and Induced Chiroptical Sensing with 5d/4f

Lanthanide-Organic Macrocycles

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1. General

Unless otherwise stated, all chemicals and solvents were purchased from commercial companies and used without further purification. Anhydrous solvents were distilled according to standard procedures. Deuterated solvents were purchased from Admas, J&K scientific and Sigma-Aldrich. 1D and 2D-NMR spectra were measured on a Bruker Biospin Avance III (400 MHz) spectrometer. ¹H-NMR chemical shifts were determined with respect to residual signals of the deuterated solvents used. Electro-spray-ionization time-of-flight mass-spectroscopy (ESI-TOF-MS) were recorded on an Impact II UHR-TOF mass spectrometry from Bruker, with tuning mix as the internal standard. Data analysis was conducted with the Bruker Data Analysis software (Version 4.3) and simulations were performed with the Bruker Isotope Pattern software. UV-Vis spectra are recorded on UV-2700 UV-Visible spectrophotometer from SHIMADZU. Excitation and emission spectra were recorded on the FS5 spectrofluorometer from Edinburg Photonics. Spectra were corrected for the experimental functions.

2. Synthesis and characterization



2.1 Synthetic procedures



The preparation of compound **1** and **2** were followed the literature procedure.¹ Auxiliary chiral ligand 2,6-Bis(4-phenyl-2-oxazolinyl)pyridine (L^R and L^S) was purchased from Bide Pharmatech Ltd.

Synthesis of Pt-L:

Under a nitrogen atmosphere, **1** (126.7 mg, 0.3 mmol, 1.0 equiv), **2** (266 mg, 0.75 mmol, 2.5 equiv), CuI (3.4 mg, 0.03 mmol, 0.1 equiv) and a mixture solvent of DCM/TEA (60 ml, v/v=4:1) were added into a 100 mL Schlenk flask. The mixture were stirred for 24 h at ambient temperature. After the reaction was finished, the solvents were removed in vacuo and the crude material was purified by chromatography on a silica gel column (v/v, CH₂Cl₂/CH₃OH =50:1) to give ligand as dark green powder (218.0 mg, 0.24 mmol, 76.3% yield), m.p.>250°C. ¹H NMR (400 MHz, CDCl₃) δ 9.46 (d, *J* = 5.3 Hz, 2H), 8.19 (d, *J* = 4.1 Hz, 2H), 7.62 (dd, *J* = 9.4, 4.7 Hz, 2H), 7.54 (s, 2H), 3.55 (q, *J* = 7.0 Hz, stirred 8H), 3.35 (q, *J* = 6.9 Hz, 8H), 1.25 (t, *J* = 7.1 Hz, 12H), 1.14 (t, *J* = 7.0 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 168.53, 156.24, 153.56, 151.31, 139.65, 138.02, 127.90, 125.96, 123.13, 99.56, 96.98, 43.35, 40.10, 14.43, 12.98. ESI-TOF-MS: calcd. For C₄₄H₅₂N₈O₄Pt [(Pt-L)+Na]⁺: 974.3654, found 974.3646.

Synthesis of La₂(Pt-L)₂(ClO₄)₆

Ligand Pt-L (28.6 mg, 30.0 µmol, 1.0 equiv) was treated with La(ClO₄)₃·6H₂O (16.4 mg, 30.0 µmol, 1.0 equiv) in 5 mL MeCN, the turbid suspension turned to homogeneous green solution progressively. The mixture was further stirred for 2 h at 40°C. ¹H NMR spectrum showed the quantitative formation of La₂(Pt-L)₂(ClO₄)₆. The solvent was removed under reduced pressure to give the isolated product (35.3 mg, 13.8 µmol, 91.9% yield), m.p.>250°C. ¹H NMR (400 MHz, CD₃CN) δ 9.61 (d, *J* = 5.0 Hz, 2H), 8.45 (d, *J* = 8.1 Hz, 2H), 8.39 (t, *J* = 7.7 Hz, 2H), 7.84 – 7.79 (m, 2H), 7.76 (s, 4H), 3.71 (d, *J* = 7.0 Hz, 8H), 3.42 (d, *J* = 6.9 Hz, 8H), 1.41 (t, *J* = 6.9 Hz, 12H), 1.17 (t, *J* = 6.7 Hz, 12H). ¹³C NMR (100 MHz, CD₃CN) δ 170.47, 157.58, 151.59, 150.76, 141.86, 140.45, 129.05, 128.61, 124.83, 122.95, 119.77, 116.60, 106.39, 100.31, 45.35, 42.98, 13.96, 12.03. ESI-TOF-MS for La₂(Pt-L)₂(ClO₄)₄]²⁺ 1289.6785, found 1289.6802; Calcd for [La₂(Pt-L)₂(ClO₄)₃]³⁺ 826.4694, found 826.4706; Calcd for [La₂(Pt-L)₂(ClO₄)₂]⁴⁺ 595.1150, found 595.1157; Calcd for [La₂(Pt-L)₂(ClO₄)]⁵⁺ 456.1022, found 456.1040.

Synthesis of Eu₂(Pt-L)₂(OTf)₆

The complexe of Eu₂(Pt-L)₂(OTf)₆ was prepared by the same procedure. ligand Pt-L (28.6 mg, 30.0 µmol, 1.0 equiv) was treated with Eu(OTf)₃ (18.0 mg, 30.0 µmol, 1.0 equiv) in 5 mL MeCN, the turbid suspension changed to clear light orange solution within minutes. The mixture was further stirred for 2 h at 40°C. ¹H NMR spectrum showed the quantitative formation of Eu₂(Pt-L)₂(OTf)₆. The solvent was removed under reduced pressure to give the isolated product (42.9 mg, 13.8 µmol, 92.1% yield), m.p.>250°C. ¹H NMR (400 MHz, CD₃CN) δ 8.42 (d, *J* = 5.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 8.0 Hz, 2H), 6.89 (m, 2H). ¹³C NMR (100 MHz, CD₃CN) δ 157.07, 150.92, 141.44, 128.39, 124.40, 114.77, 111.59, 107.97, 94.93. (The signals of pcam are not detectable, probably due to the paramagnetic property of Eu^{III}). ESI-TOF-MS for Eu₂(Pt-L)₂(OTf)₄]²⁺ 1402.2009, found 1402.2009; Calcd for [Eu₂(Pt-L)₂(OTf)₃]³⁺ 884.8162, found 884.8158; Calcd for [Eu₂(Pt-L)₂(OTf)₂]⁴⁺ 626.3740, found 626.3742; Calcd for [Eu₂(Pt-L)₂(OTf)]⁵⁺ 471.3087, found 471.3101.

Synthesis of La₂(Pt-L)₂L^RL^S(ClO₄)₆

ligand Pt-L (28.6 mg, 30.0 µmol, 1.0 equiv) was treated with La(ClO₄)₃·6H₂O (16.4 mg, 30.0 µmol, 1.0 equiv) and auxiliary ligand L^{*R*} (5.5 mg, 15.0 µmol, 0.5 equiv) and L^{*S*} (5.5 mg, 15.0 µmol, 0.5 equiv) in 5 mL MeCN, the turbid suspension turned into clear light green solution gradually. The mixture was further stirred for 1 h at 40°C. ¹H NMR spectrum showed the quantitative formation of La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₆. The solvent was removed under reduced pressure to give the isolated product (45.9 mg, 13.9 µmol, 92.9% yield), m.p.>250°C. ESI-TOF-MS for La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₄]²⁺ 1658.8269, found 1658.8279; Calcd for [La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₃]³⁺ 1072.9019, found 1072.9013; Calcd for [La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₂]⁴⁺ 719.6891, found 719.6883; Calcd for [La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)]⁵⁺ 603.9617, found 603.9613. Calcd for [La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)]⁵⁺ 486.6431, found 486.6443.

Synthesis of La₂(Pt-L)₂(L^R)₂(ClO₄)₆

ligand Pt-L (28.6 mg, 30.0 µmol, 1.0 equiv) was treated with La(ClO₄)₃·6H₂O (16.4 mg, 30.0 µmol, 1.0 equiv) and auxiliary ligand L^{*R*} (11.1 mg, 30.0 µmol, 1.0 equiv) in 5 mL MeCN, the turbid suspension turned into clear light green solution gradually. The mixture was further stirred for 2 h at 40°C. ¹H NMR spectrum showed the quantitative formation of La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₆. The solvent was removed under reduced pressure to give the isolated product (44.8 mg, 13.6 µmol, 90.7% yield), m.p.>250°C. ESI-TOF-MS for La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₆: The following picked signals are those at the highest intensities. *m/z* Calcd for [La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₄]²⁺ 1658.8269, found 1658.8272; Calcd for [La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₃]³⁺ 1072.9019, found 1072.9018; Calcd for [La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₂]⁴⁺ 719.6891, found 719.6888; Calcd for [La₂(Pt-L)₂(L^{*R*})₂(ClO₄)]⁵⁺ 603.9617, found 603.9616. Calcd for [La₂(Pt-L)₂(L^{*R*})₂]⁶⁺ 486.6431, found 486.6441.

La₂(Pt-L)₂(L^S)₂(ClO₄)₆ was synthesized by the same procedure.



Figure S2. ¹³C NMR spectrum of Pt-L (101 MHz, CDCl₃, 298 K).



Figure S4. ¹H NMR spectrum of La₂(Pt-L)₂(ClO₄)₆ (400 MHz, CD₃CN, 298 K).



Figure S6. ¹H-¹H COSY spectrum of La₂(Pt-L)₂(ClO₄)₆ (400 MHz, CD₃CN, 298 K).





Figure S7. ¹H NMR spectrum of $Eu_2(Pt-L)_2(OTf)_6$ (400 MHz, CD₃CN, 298 K) (The signals of *pcam* are not detectable, probably due to the paramagnetic property of Eu^{III}).



Figure S8. ¹³C NMR spectrum of $Eu_2(Pt-L)_2(OTf)_6$ (101 MHz, CD₃CN, 298 K) (The signals of *pcam* are not detectable, probably due to the paramagnetic property of Eu^{III}).



Figure S9. ¹H-¹H COSY spectrum of Eu₂(Pt-L)₂(OTf)₆ (400 MHz, CD₃CN, 298 K).



Figure S10. ¹H NMR spectrum of La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₆ (400 MHz, CD₃CN, 298 K).



Figure S11. ¹H NMR spectra of La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₆ (400 MHz, CD₃CN, 298 K).



Figure S12. ¹H NMR spectrum of La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₆ (400 MHz, CD₃CN, 298 K).



Figure S13. ¹H-¹H COSY spectrum of La₂(Pt-L)₂(L^{*R*})₂(ClO₄)₆ (400 MHz, CD₃CN, 298 K).

2.3 ¹H DOSY spectra

Stokes-Einstein equation:

$$D = \frac{K_B T}{6\pi\eta r} \tag{1}$$

)

was applied to estimate the dynamic radius for macrocycles in solution. D is diffusion coefficient obtained from DOSY spectrum, K_B is Boltzmann constant, T is the absolute temperature, viscosity η was tested to be 0.343 mPa•s, and r is the estimated dynamic radius.



Figure S14. ¹H DOSY spectrum of La₂(Pt-L)₂(ClO₄)₆ (400 MHz, CD₃CN, 298 K, D=9.51×10⁻¹⁰ $m^2 \cdot s^{-1}$, r=0.67 nm).



Fig

ure S15. ¹H DOSY spectrum of Eu₂(Pt-L)₂(OTf)₆ (400 MHz, CD₃CN, 298 K, D=9.11×10⁻¹⁰ $m^2 \cdot s^{-1}$, r=0.69 nm).



Figure S16. ¹H DOSY spectrum of La₂(Pt-L)₂L^{*R*}L^{*S*}(ClO₄)₆ (400 MHz, CD₃CN, 298 K, D=6.16×10⁻¹⁰ m²·s⁻¹, r=1.03 nm).



Figure S17. ¹H DOSY spectrum of La₂(Pt-L)₂(L^{R})₂(ClO₄)₆ (400 MHz, CD₃CN, 298 K, D=6.47×10⁻¹⁰ m²·s⁻¹, r=0.98 nm).

3. Photophysical properties

3.1 UV-Vis absorption and Luminescence Spectra



Figure S18. UV/Vis absorption spectra of Pt-L, $Eu_2(Pt-L)_2$, $Eu_2(Pt-L)_2(L^R)_2$ and $Eu_2(Pt-L)_2L^RL^S$ in CH₃CN.



Figure S19. Excitation spectrum and emission spectra of Pt-L in CH₃CN ([Pt-L]= 1×10^{-5} M, slits =6.0-6.0).



Figure S20. Excitation spectrum and emission spectrum of $Eu_2(Pt-L)_2$ in CH₃CN ([Eu₂(Pt-L)₂]= 1×10^{-5} M, slits =0.8-0.8).



Figure S21. Excitation spectrum and emission spectrum of $Eu_2(Pt-L)_2L^RL^S$ in CH₃CN ([Eu₂(Pt-L)₂L^{*R*}L^{*S*}]=1×10⁻⁵ M, slits =0.7-0.7).



Figure S22. Excitation spectrum and emission spectrum of $Eu_2(Pt-L)_2(L^R)_2$ in CH₃CN ([Eu₂(Pt-L)₂(L^R)₂]=1×10⁻⁵ M, slits =0.7-0.7).

3.2 Chiral optical measurements



Figure S23. Circular dichroism spectra of $La_2(Pt-L)_2(L^R)_2$ and $La_2(Pt-L)_2(L^S)_2$ in CH₃CN ([La₂(Pt-L)₂(L^{*S*})₂]=2×10⁻⁵ M, [La₂(Pt-L)₂(L^{*S*})₂]=2×10⁻⁵ M).



Figure S24. Circular dichroism spectra of $Eu_2(Pt-L)_2(L^R)_2$ and $Eu_2(Pt-L)_2(L^S)_2$ in CH₃CN ([Eu₂(Pt-L)₂(L^S)₂]=2×10⁻⁵ M, [Eu₂(Pt-L)₂(L^S)₂]=2×10⁻⁵ M).



Figure S25. Circular dichroism titration spectra of $La_2(Pt-L)_2$ in CH₃CN ([La₂(Pt-L)₂]=2×10⁻⁵ M) upon addition of different equiv of chiral auxiliary ligand L^{*R*}.



Figure S26. Changes of the molar circular dichroism at 292 nm of $La_2(Pt-L)_2$ containing different equiv of L^R .



Figure S27. (a) Circular dichroism spectra of $Eu_2(Pt-L)_2$ ($[Eu_2(Pt-L)_2]=2\times10^{-5}$ M, CH₃CN) containing 2 equiv. of L^{*R/S*} with various *ee* values, and (b) the corresponding *ee* calibration plots at 254 and 292 nm.



Figure S28. Circular polarized luminescence spectra of $Eu_2(Pt-L)_2(L^R)_2$ and $Eu_2(Pt-L)_2(L^S)_2$ in CH₃CN ($[Eu_2(Pt-L)_2(L^R)_2]=2\times10^{-5}$ M, $[Eu_2(Pt-L)_2(L^S)_2]=2\times10^{-5}$ M).



Figure S29. Circular polarized luminescence spectra of $Eu_2(Pt-L)_2(L^R)_2$ and $Eu_2(Pt-L)_2(L^S)_2$ in CH₃CN ($[Eu_2(Pt-L)_2(L^R)_2]=2\times10^{-5}$ M, $[Eu_2(Pt-L)_2(L^R)_2]=2\times10^{-5}$ M).

3.3 Quantum yields



Figure S30. Quantum yield of Eu₂(Pt-L)₂ in CH₃CN (298 K, [Eu₂(Pt-L)₂]= 1×10^{-5} M, λ_{ex} =368 nm).



Figure S31. Quantum yield of $Eu_2(Pt-L)_2L^RL^S$ in CH₃CN (298 K, $[Eu_2(Pt-L)_2L^RL^S]=1\times 10^{-5}$ M, $\lambda_{ex}=368$ nm).



Figure S32. Quantum yield of Eu₂(Pt-L)₂(L^{*R*})₂ in CH₃CN (298 K, [Eu₂(Pt-L)₂(L^{*R*})₂]=1×10⁻⁵ M, λ_{ex} =368 nm).

3.4 Lifetime measurements



Figure S33. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂ ([Eu₂(Pt-L)₂]=1×10⁻⁵ M in CH₃CN, λ_{ex} = 368 nm, λ_{em} = 614 nm).



Figure S34. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂L^{*R*}L^{*S*} [Eu₂(Pt-L)₂L^{*R*}L^{*S*}]=1×10⁻⁵ M in CH₃CN, λ_{ex} = 368 nm, λ_{em} = 614 nm).



Figure S35. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂(L^{R})₂ ([Eu₂(Pt-L)₂(L^{R})₂]=1×10⁻⁵ M in CH₃CN, λ_{ex} = 368 nm, λ_{em} = 614 nm).

Complex	λ_{abs}^{max}	$\epsilon/10^4$	λ_{ex}^{max}	λ_{ex}^{max}	$ au_{obs}$	$arPhi_{overall}$
	[nm]	$[M^{-1}cm^{-1}]$	[nm]	[nm]		[%]
Pt-L	371	1.00	369	508	2.11ns	1.3
$Eu_2(Pt-L)_2$	372	4.12	368	614	1.09ms	31.9
$Eu_2(Pt-L)_2(L^R)_2$	372	4.34	368	614	1.74ms	52.1
$Eu_2(Pt-L)_2L^RL^S$	373	4.47	368	614	1.77ms	53.3

Table S1. Photophysical data of the ligand and macrocycles in acetonitrile solution.

3.5 Number of coordinated solvent molecules

Here, empirical equation is used to determine the number of solvent molecules q coordinated to Eu^{III} centers in compounds.

$$q = A(\tau_{\text{methanol}}^{-1} - \tau_{\text{deutero-methanol}}^{-1} - B)$$
 (5)

Where, empirically coefficients A = 2.1 and B = 0 were determined in methanol and Methanol-d₄ condition. The calculated q values is 2.66 for Eu₂(Pt-L)₂, 0.52 for Eu₂(Pt-L)₂L^{*R*}L^{*S*}, and 0.56 for Eu₂(Pt-L)₂(L^{*R*})₂.



Figure S36. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂ ([Eu₂(Pt-L)₂]= 2×10^{-5} M in CD₃OD, $\lambda_{ex} = 368$ nm, $\lambda_{em} = 614$ nm).



Figure S37. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂ ([Eu₂(Pt-L)₂]= 2×10^{-5} M in CD₃OH, $\lambda_{ex} = 368$ nm, $\lambda_{em} = 614$ nm).



Figure S38. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂L^{*R*}L^{*S*} [=2×10⁻⁵ M in CD₃OD, $\lambda_{ex} = 368$ nm, $\lambda_{em} = 614$ nm).



Figure S39. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂L^{*R*}L^{*S*}]=2×10⁻⁵ M in CH₃OH, λ_{ex} = 368 nm, λ_{em} = 614 nm).



Figure S40. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂(L^{*R*})₂ ([Eu₂(Pt-L)₂(L^{*R*})₂]= 2×10^{-5} M in CD₃OD, $\lambda_{ex} = 368$ nm, $\lambda_{em} = 614$ nm).



Figure S41. Excitated state decay curve (black line) with mono exponential fit (red line) of Eu₂(Pt-L)₂(L^{*R*})₂ (2×10⁻⁵ M in CD₃OH, λ_{ex} = 368 nm, λ_{em} = 614 nm).

4. Mass spectra



Figure S42. ESI-TOF-MS spectrum for Pt-L.





Figure S43. ESI-TOF-MS spectrum for La₂(Pt-L)₂(ClO₄)₆.



Figure S44. ESI-TOF-MS spectrum for Eu₂(Pt-L)₂(OTf)₆.



Figure S45. ESI-TOF-MS spectrum for La₂(Pt-L)₂L^RL^S(ClO₄)₆.



Figure S46. ESI-TOF-MS spectrum for Eu₂(Pt-L)₂L^{*R*}L^{*S*}(OTf)₆.





Figure S47. ESI-TOF-MS spectrum for La₂(Pt-L)₂(L^R)₂(ClO₄)₆.



Figure S48. ESI-TOF-MS spectrum for Eu₂(Pt-L)₂(DTf)₆.

5. Single crystal X-ray diffraction studies

The X-ray diffraction studies for macrocycles were carried out on Bruker D8 VENTURE photon II diffractometer with Iµs 3.0 microfocus X-ray source using APEX III program.^[2] Data reduction was performed with the SAINT and SADABS package. Both structures were solved by direct methods and refined by full-matrix least-squares on F2 with anisotropic displacement using the SHELX software package.^[3] Solvent molecules were highly disordered and could not be reasonably located. These residual intensities were removed by PLATON/SQUEEZE routine.^[4] CCDC-1972065, 1972066 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).

Identification code	mo_4907_0m_a_sq		
Empirical formula	Eu2 Pt2 C120 H175 F18 N21 O36 S6		
Formula weight	3716.26		
Temperature	275(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	C2/c		
Unit cell dimensions	a = 20.9232(10) Å	α=90°.	
	b = 22.2447(10) Å	β=104.290(2)°.	
	c = 36.0709(18) Å	$\gamma = 90^{\circ}$.	
Volume	16269.0(13) Å ³		
Ζ	4		
Density (calculated)	1.517 Mg/m ³		
Absorption coefficient	2.645 mm ⁻¹		
F(000)	7480		
Crystal size	0.120 x 0.100 x 0.080 mm ³		
Theta range for data collection	2.331 to 26.962°.		
Index ranges	-26<=h<=26, -28<=k<=28, -45<=l<=45		
Reflections collected	268204		
Independent reflections	17640 [R(int) = 0.0703]		
Completeness to theta = 25.242°	99.8 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7455 and 0.4535		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	17640 / 866 / 741		
Goodness-of-fit on F ²	1.083		
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1189		
R indices (all data)	R1 = 0.0601, wR2 = 0.1341		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.741 and -0.575 e.Å ⁻³		

Table S2. Crystal data and structure refinement for $Eu_2(Pt-L)_2$.

Identification code	mo_394_8_0m_a_sq		
Empirical formula	Eu2 Pt2 C174 H213 F18 N29 O35 S6		
Formula weight	4499.18		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 13.8397(9) Å	α= 68.595(2)°.	
	b = 16.9264(9) Å	β= 81.719(2)°.	
	c = 21.3207(12) Å	γ = 77.817(2)°.	
Volume	4532.9(5) Å ³		
Ζ	1		
Density (calculated)	1.648 Mg/m ³		
Absorption coefficient	2.390 mm ⁻¹		
F(000)	2280		
Crystal size	0.200 x 0.180 x 0.170 mm ³		
Theta range for data collection	2.244 to 26.372°.		
Index ranges	-17<=h<=17, -21<=k<=21, -26<=l<=26		
Reflections collected	131836		
Independent reflections	18543 [R(int) = 0.1292]		
Completeness to theta = 25.242°	99.9 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7456 and 0.6164		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	18543 / 1022 / 1014		
Goodness-of-fit on F ²	1.022		
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1534		
R indices (all data)	R1 = 0.1076, wR2 = 0.1806		
Extinction coefficient	n/a		
Largest diff. peak and hole	1.540 and -1.446 e.Å ⁻³		

Table S3. Crystal data and structure refinement for $Eu_2(Pt-L)_2L^RL^S$.



Figure S49. Ortep drawing of the asymmetric unit in the crystal structure of $Eu_2(Pt-L)_2(OTf)_6$ at 30% probability level.



Figure S50. Ortep drawing of the asymmetric unit in the crystal structure of $Eu_2(Pt-L)_2L^RL^S(OTf)_6$ at 30% probability level.

6. Energy minimized structure



Figure S51. Simulated molecular models of two helicates (A) M-($\Lambda\Lambda$)- Eu₂(Pt-L)₂(L^{*R*})₂ and (B) P-($\Delta\Delta$)-Eu₂(Pt-L)₂(L^{*S*})₂. Molecular mechanic modeling was performed by Materials Studio program. First of all, Λ - or Δ - Eu stereogenic centers with the same chiral-inducing group were imported from the crystal structure of Eu₂(Pt-L)₂L^{*R*}L^{*S*}. Then, different configuration of the central bpyPt(C=C)₂ linkers were introduced to produce P and M isomers. We kept the periphery metal stereogenic center as rigid "Motion Groups", and only the central liker units were geometrically optimized. M- $\Lambda\Lambda$ -RR and P- $\Delta\Delta$ -SS helicates were obtained as the final optimized structures as shown above.

7. References

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