

Supporting Information

Unlocking efficient near-infrared circularly polarized phosphorescence reaching 800 nm via rational molecular engineering of cyclometalated Pt(II) complexes

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Materials and Methods

The information of the purchased chemicals used in this work.

| Chemical | CAS No. | Purity | Supplier |
|--|-------------|--------|-------------------------------------|
| 1-chloroisoquinoline | 19493-44-8 | 98% | Aladdin |
| 4-fluorophenylboronic acid | 214360-58-4 | 98% | Aladdin |
| 1-chloroisoquinoline-4-carbonitrile | 53491-80-8 | 98% | Aladdin |
| 1-benzothiophen-2-ylboronic acid | 98437-23-1 | 98% | Aladdin |
| Pd(PPh ₃) ₄ | 14221-01-3 | 99% | Aladdin |
| K ₂ PtCl ₄ | 10025-99-7 | 98+% | Aladdin |
| (<i>R</i>)-4-phenyl-1,3-thiazolidine-2-thione | 110199-18-3 | 98% | Aladdin |
| (<i>S</i>)-4-phenyl-1,3-thiazolidine-2-thione | 185137-29-5 | 98% | Aladdin |
| ferrocene | 102-54-5 | 98% | Aladdin |
| tetra- <i>n</i> -butylammonium hexafluorophosphate | 3109-63-5 | 98% | Aladdin |
| CH ₃ CN | 75-05-8 | 98% | Aladdin |
| ethyl acetate | 141-78-6 | 98% | Shanghai Titan Scientific Co., Ltd. |
| <i>n</i> -hexane | 110-54-3 | 98% | Shanghai Titan Scientific Co., Ltd. |
| K ₂ CO ₃ | 584-08-7 | 99.5% | Shanghai Titan Scientific Co., Ltd. |
| Na ₂ SO ₄ | 7757-82-6 | 99% | Shanghai Titan Scientific Co., Ltd. |
| 2-ethoxyethanol | 110-80-5 | 99% | Shanghai Titan Scientific Co., Ltd. |
| isopropanol | 67-63-0 | 98% | Aladdin |
| diethyl ether | 60-29-7 | 99.9+% | Aladdin |
| methanol | 67-56-1 | 99.8+% | Bide Pharmatech Co., Ltd. |
| ethanol | 64-17-5 | 99.5% | Aladdin |
| toluene | 108-88-3 | 99.5% | Aladdin |

The instrumental information used for characterizations in this work.

| Characterization items | Type | Manufacturer |
|--|-----------------------------------|-----------------------|
| ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR | AVANCE III HD, 400/600 MHz | Bruker, Germany |
| HRMS (ESI) | Agilent 6540 Quadrupole-TOF LC/MS | Agilent Technologies |
| Elemental analysis | VARIO EL cube | Elementar, Germany |
| UV-Vis absorption spectra | LAMBDA 950 | Perkin Elmer USA |
| Photoluminescence spectra | FLS-1000 | Edinburgh, USA |
| Photoluminescence quantum yield | FLS-1000 | Edinburgh, USA |
| Lifetime | FLS-1000 | Edinburgh, USA |
| CD spectra | CD <i>J</i> -1500 | Jasco, Japan |
| Circularly polarized luminescence spectra | CPL-300 | Jasco, Japan |
| CCD X-ray single crystal diffractometer | Bruker D8 VENTURE | Bruker, Germany |
| Electrochemical workstation | CHI600E | CH Instruments, China |

General Experimental Details

Photophysical Measurements. The UV-Vis absorption spectra were recorded on a Perkin Elmer LAMBDA 950 UV-Vis spectrophotometer (Perkin Elmer, Waltham, MA, USA), and the optical HOMO–LUMO energy gaps of binuclear Pt(II) complexes **(R,S,R)/(S,R,S)-Pt1/Pt1** were calculated by the UV-Vis edge absorption ($\lambda_{\text{edge}} = 629\text{-}774$ nm). Steady-state emission experiments at room temperature were measured on an Edinburgh FLS-1000 spectrometer. Excited-state lifetime studies were performed with an Edinburgh FLS-1000 spectrometer with a hydrogen-filled excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using a software package provided by Edinburgh Instruments. Photoluminescence quantum yields (PLQY) of the complexes were determined through an absolute method by employing an integrating sphere. The solution was degassed by three freeze-pump-thaw cycles. Circular dichroism (CD) spectra were measured on a Jasco *J*-1500 circular dichroism spectrometer with a scan speed of 100 nm/min. The circularly polarized luminescence (CPL) spectra were measured on a Jasco CPL-300 spectrophotometer based on ‘Continuous’ scanning mode at 100 nm/min scan speed. The test mode adopts “Slit” mode with the Ex and Em slit width 2500 μm and the digital integration time (D.I.T.) is 2.0 s with multiple accumulations (10 times) and their $|g_{\text{lum}}|$ values were read from the curves recorded with the software bundled on the equipment.

X-ray Crystallographic Analysis. The single crystals of **(R,S,R)/(S,R,S)-Pt1/Pt2** were obtained from the solution mixture of dichloromethane and *n*-hexane. The X-ray diffraction data were collected on a Bruker Smart CCD Apex DUO diffractometer with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å) using the ω - 2θ scan mode. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-2000.¹⁻³ All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Mercury. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference numbers for **(R,S,R)/(S,R,S)-Pt1/Pt2** are 2526096, 2526097, 2526098, and 2526099, respectively. Copies

of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +441223336033; E-mail: deposit@ccdc.cam.ac.uk, or www: <http://www.ccdc.cam.ac.uk>).

Electrochemical measurement. Cyclic voltammetry measurements were carried out in CH₃CN (5×10⁻⁴ M) with a three-electrode cell configuration consisting of platinum working and counter electrodes and a Ag/AgCl (0.01 M in CH₃CN) reference electrode at room temperature. Tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M in CH₃CN) was used as the supporting electrolyte. The redox potentials were recorded at a scan rate of 100 mV/s and are reported with reference to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The energy levels were calculated using the following equations: $E_{\text{HOMO}} = -(E_{\text{ox}}^{1/2} - E_{\text{Fc}/\text{Fc}^+} + 4.8)$ eV,⁴ $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$, optical energy gap $E_{\text{g}}^{\text{opt}}$ was estimated from the absorption onset using the equation ($E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{edge}}$).⁵

Theoretical Calculations. To further interpret the UV-Vis spectral behavior of binuclear Pt(II) complexes (***R,S,R***)/(***S,R,S***)-Pt1/Pt2, the initial computational models of (***R,S,R***)/(***S,R,S***)-Pt1/Pt2 were built according to their crystal structure. Their minimum energy structures based on the ground-state (S₀) were obtained from density functional theory (DFT) calculations which were carried out employing the popular B3LYP functional theory using ORCA software at the def2-TZVP⁶ basis set with def2/J⁷ and def2/JK⁸ as auxiliary basis set. After that, their time-dependent DFT (TD-DFT) calculations were performed to explore energy transitions. The optimized structure of the ground-state (S₀) was used to calculate the UV-Vis absorption, PL, CD and CPL spectra by TD-DFT (dichloromethane as the solvent, pcm method, 100 singlet-singlet transitions and 100 singlet-triplet transitions). The luminescence dissymmetry factor $g_{\text{abs}}/g_{\text{lum}}$ of a given transition (e.g., S_n (n = 1~4)/T₁ to S₀ (S_n (n = 1~4)/T₁ → S₀)) is given by the equation $g_{\text{abs}}/g_{\text{lum}} = 4R/(D + G)$,⁹ where $R = |\mu_{\text{e}}||\mu_{\text{m}}|\cos\theta$ is the transition rotatory strength, $D = |\mu_{\text{e}}|^2$ is the transition electric dipole strength, $G = |\mu_{\text{m}}|^2$ is the transition magnetic electric dipole strength, μ_{e} and μ_{m} are the electric and magnetic transition dipole moments, respectively, and θ the angle between the two. To compute $g_{\text{abs}}/g_{\text{lum}}$, the rotatory and dipole strength for the S₀→S_n (n = 1~4)/T₁→S₀ transition from the S_n (n = 1~4)/T₁ state of binuclear Pt(II) complexes were

extracted from the ORCA output. The dipole strength is the square of the electric dipole moment as the length gauge, in au ($1 \text{ au} = 2.541746 \text{ D} = 10^{-18} \text{ esu cm}$). From there, the g_{abs} and g_{lum} value can be computed at the wavelength of the transition.

Synthesis and Characterizations

Synthesis of HC^N ligand 1-(4-fluorophenyl)isoquinoline (F-Hpiq). The ligand **F-Hpiq** was synthesized from the improved Suzuki coupling reaction¹⁰ of 1-chloroisoquinoline with 4-fluorophenylboronic acid. Tetrakis(triphenylphosphine)palladium (0) ($\text{Pd}(\text{PPh}_3)_4$, 0.347 g, 0.3 mmol) was added to a mixture of 1-chloroisoquinoline (1.080 g, 6.6 mmol), 4-fluorophenylboronic acid (0.840 g, 6 mmol), toluene (21 mL), ethanol (3 mL) and an aqueous potassium carbonate solution (2 M, 0.842 g in 6 mL water) under vigorous stirring. The mixture was stirred at 80 °C for 48 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine several times, and the solvent was then evaporated. Addition of CH_2Cl_2 followed by pentane precipitated a white solid which was filtered off. The residue was purified by column chromatography (SiO_2 , *n*-Hexane/AcOEt, V/V = 8:1; $R_f = 0.5$) and isolated as a white solid. Yield: 1.044 g (78%). Anal calcd for $\text{C}_{15}\text{H}_{10}\text{FN}$: C, 80.70; H, 4.52; N, 6.27%. Found: C, 80.72; H, 4.48; N, 6.29%. ^1H NMR (600 MHz, CDCl_3 , δ) 8.60 (d, $J = 5.7 \text{ Hz}$, 1H), 8.07 (d, $J = 8.5 \text{ Hz}$, 1H), 7.89 (d, $J = 8.2 \text{ Hz}$, 1H), 7.75-7.63 (m, 4H), 7.56 (t, $J = 7.7 \text{ Hz}$, 1H), 7.31-7.18 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , δ) 163.24 (d, $^1J_{\text{C-F}} = 248.11 \text{ Hz}$), 159.77, 142.32, 137.04, 135.76 (d, $^4J_{\text{C-F}} = 3.29 \text{ Hz}$), 131.86 (d, $^3J_{\text{C-F}} = 8.24 \text{ Hz}$), 130.25, 130.25, 127.49, 127.32 (d, $^2J_{\text{C-F}} = 28.86 \text{ Hz}$), 126.80, 120.21, 115.59, 115.45, 115.43. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.4 MHz, CDCl_3 , δ) -113.15 (s). HRMS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_{10}\text{FN} + \text{H}^+$, 224.0870; found, 224.0595.

Synthesis of HC^N ligand 1-(benzo[*b*]thiophen-2-yl)isoquinoline-4-carbonitrile (CN-Hiqbt). The ligand **CN-Hiqbt** was obtained following a procedure analogous to that used for **F-Hpiq**. A mixture of 1-chloroisoquinoline-4-carbonitrile (0.623 g, 3.3 mmol), 1-benzothiophen-2-ylboronic acid (0.535 g, 3.0 mmol) was dissolved into absolute mixed solvents of toluene and EtOH (30 mL; V/V = 2:1) under an N_2 atmosphere. Then an aqueous solution (5 mL) of K_2CO_3

(2 M) was added, and the mixture was degassed by an N₂ flow. Anhydrous Pd(PPh₃)₄ (174 mg, 0.15 mmol) was added to the reaction mixture and then heated at 80 °C for 48 h. The complete consumption of reagents was monitored by thin-layer chromatography (*n*-Hexane/AcOEt, V:V = 5:1; *R_f* = 0.40). After cooling to room temperature, the organic phase was washed with brine and extracted with absolute CH₂Cl₂ (3×20 mL) three times. The combined organic phase was dried over anhydride Na₂SO₄, and further purified with flash-column chromatography on silica gel (*n*-Hexane/AcOEt, V/V = 5:1), affording to an off-white solid. Yield: 0.645 g (75%). Anal calcd for C₁₈H₁₀N₂S: C, 75.50; H, 3.52; N, 9.78%. Found: C, 75.53; H, 3.49; N, 9.74%. ¹H NMR (600 MHz, CDCl₃, δ) 8.94 (s, 1H), 8.75 (d, *J* = 8.5 Hz, 1H), 8.31 – 8.26 (m, 1H), 7.98 – 7.94 (m, 3H), 7.93 – 7.91 (m, 1H), 7.83 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.50 – 7.40 (m, 2H). ¹³C {¹H} NMR (151 MHz, CDCl₃, δ) 157.55, 147.44, 141.66, 141.45, 140.03, 136.05, 132.85, 129.78, 127.90, 127.78, 126.27, 125.47, 125.06, 124.95, 122.59, 116.44, 104.81. HRMS (ESI) (*m/z*): calcd for C₁₈H₁₀N₂S+H⁺, 287.0637; found, 286.9925.

Synthesis of the Pt(II) intermediates [Pt(F-piq)(F-Hpiq)Cl] and [Pt(CN-iqbt)(CN-Hiqbt)Cl]. K₂PtCl₄ (0.415 g, 1 mmol) and **F-Hpiq** (0.446 g, 2 mmol) in a 3:1 (V/V) mixture of 2-ethoxyethanol (18 mL) and H₂O (6 mL) were heated at 80 °C for 16 h under nitrogen atmosphere. After cooling to room temperature, saturated brine (30 mL) was added to the mixture. The precipitated yellow-green solid was collected by filtration and washed successively with isopropanol, diethyl ether, and hexane. The product was then dried under vacuum at 45 °C. The crude Pt(II) intermediate was directly used in the subsequent step without further purification. The Pt(II) intermediate **[Pt(CN-iqbt)(CN-Hiqbt)Cl]** was obtained by similar procedure.

Synthesis of the chiral binuclear Pt(II) complexes (*R,S,R*)/(*S,R,S*)-Pt1/Pt2. A mixture of the Pt(II) intermediate **[Pt(F-piq)(F-Hpiq)Cl]** or **[Pt(CN-iqbt)(CN-Hiqbt)Cl]**, (*R*)/(*S*)-4-phenyl-1,3-thiazolidine-2-thione (***R/S*-Hptt**), and K₂CO₃ (3 equiv.) in a sealed tube with dichloroethane was stirred at 80 °C for 24 h under an argon atmosphere. Then the solvent was removed under reduced pressure, and the residue of (*R,S,R*)/(*S,R,S*)-Pt1/Pt2 was purified through column chromatography using petroleum ether and dichloromethane as the eluent to give the products

as powders.

(R,S,R)-Pt1. Deep-red solid (Yield: 32%): ^1H NMR (600 MHz, CDCl_3 , δ) 8.13 (d, $J = 8.6$ Hz, 2H), 8.03 (d, $J = 6.4$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.64 (d, $J = 7.7$ Hz, 4H), 7.60 (t, $J = 7.4$ Hz, 2H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.23 (d, $J = 6.4$ Hz, 2H), 7.19 (dd, $J = 8.7, 5.7$ Hz, 2H), 7.09 (t, $J = 7.5$ Hz, 4H), 7.03 (t, $J = 7.3$ Hz, 2H), 6.86 (dd, $J = 10.4, 2.7$ Hz, 2H), 5.90 (t, $J = 8.4$ Hz, 2H), 5.79 (td, $J = 8.5, 2.8$ Hz, 2H), 3.95 (dd, $J = 11.4, 8.4$ Hz, 2H), 3.72 (dd, $J = 11.4, 8.4$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , δ) 179.30, 165.20, 161.15 (d, $^1J_{\text{C-F}} = 254.10$ Hz), 146.64 (d, $^4J_{\text{C-F}} = 6.63$ Hz), 141.35, 140.26, 137.30, 130.69, 129.19 (d, $^3J_{\text{C-F}} = 8.79$ Hz), 128.55, 128.53, 128.25, 127.27 (d, $^3J_{\text{C-F}} = 10.13$ Hz), 126.58, 124.55, 119.87 (d, $^2J_{\text{C-F}} = 18.66$ Hz), 119.07, 107.91 (d, $^2J_{\text{C-F}} = 22.92$ Hz), 80.15, 41.90. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.4 MHz, CDCl_3 , δ) -110.87 (s), -110.87 (d, $^4J_{195\text{Pt}-19\text{F}} = 45.17$ Hz). HRMS (ESI) (m/z): calcd for $\text{C}_{48}\text{H}_{34}\text{F}_2\text{N}_4\text{Pt}_2\text{S}_4 + \text{H}^+$, 1223.0995; found, 1223.0996. Anal. calcd for $\text{C}_{48}\text{H}_{34}\text{F}_2\text{N}_4\text{Pt}_2\text{S}_4$: C, 47.13; H, 2.80; N, 4.58; found: C, 47.21; H, 2.81; N, 4.60.

(S,R,S)-Pt1. Deep-red solid (Yield: 35%): ^1H NMR (600 MHz, CDCl_3 , δ) 8.13 (d, $J = 8.6$ Hz, 2H), 8.03 (d, $J = 6.3$ Hz, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.67 – 7.63 (m, 4H), 7.60 (t, $J = 7.4$ Hz, 2H), 7.48 – 7.42 (m, 2H), 7.23 (d, $J = 6.4$ Hz, 2H), 7.19 (dd, $J = 8.6, 5.7$ Hz, 2H), 7.09 (t, $J = 7.5$ Hz, 4H), 7.03 (t, $J = 7.3$ Hz, 2H), 6.86 (dd, $J = 10.3, 2.7$ Hz, 2H), 5.90 (t, $J = 8.4$ Hz, 2H), 5.79 (td, $J = 8.5, 2.8$ Hz, 2H), 3.95 (dd, $J = 11.4, 8.4$ Hz, 2H), 3.72 (dd, $J = 11.4, 8.4$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , δ) 179.30, 165.20, 161.15 (d, $^1J_{\text{C-F}} = 254.10$ Hz), 146.64 (d, $^4J_{\text{C-F}} = 6.63$ Hz), 141.35, 140.26, 137.30, 130.69, 129.19 (d, $^3J_{\text{C-F}} = 8.79$ Hz), 128.55, 128.53, 128.25, 127.27 (d, $^3J_{\text{C-F}} = 10.13$ Hz), 126.58, 124.55, 119.87 (d, $^2J_{\text{C-F}} = 18.66$ Hz), 119.07, 107.91 (d, $^2J_{\text{C-F}} = 22.92$ Hz), 80.15, 41.90. $^{19}\text{F}\{^1\text{H}\}$ NMR (376.4 MHz, CDCl_3 , δ) -110.88 (s), -110.87 (d, $^4J_{195\text{Pt}-19\text{F}} = 45.17$ Hz). HRMS (ESI) (m/z): calcd for $\text{C}_{48}\text{H}_{34}\text{F}_2\text{N}_4\text{Pt}_2\text{S}_4 + \text{H}^+$, 1223.0995; found, 1223.0994. Anal. calcd for $\text{C}_{48}\text{H}_{34}\text{F}_2\text{N}_4\text{Pt}_2\text{S}_4$: C, 47.13; H, 2.80; N, 4.58; found: C, 47.17; H, 2.84; N, 4.60.

(R,S,R)-Pt2. Dark maroon solid (Yield: 28%): ^1H NMR (600 MHz, CDCl_3 , δ) 8.76 (d, $J = 8.1$ Hz, 2H), 8.44 (d, $J = 8.3$ Hz, 2H), 7.82 (s, 2H), 7.80 – 7.73 (m, 4H), 7.63 – 7.51 (m, 6H), 7.19 (dd, $J = 8.6, 6.8$ Hz, 6H), 7.12 – 7.06 (m, 2H), 6.86 – 6.77 (m, 4H), 6.16 (dd, $J = 9.1, 5.4$ Hz,

2H), 4.23 (dd, $J = 11.5, 9.1$ Hz, 2H), 3.90 (dd, $J = 11.5, 5.5$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , δ) 180.20, 165.00, 154.54, 146.92, 143.92, 143.64, 139.95, 137.71, 134.88, 132.82, 129.79, 129.25, 128.87, 128.37, 128.23, 128.12, 127.04, 124.33, 123.83, 122.51, 120.38, 116.11, 100.95, 79.72, 41.49. HRMS (ESI) (m/z): calcd for $\text{C}_{54}\text{H}_{34}\text{N}_6\text{Pt}_2\text{S}_6+\text{H}^+$, 1350.0539; found, 1350.0536. Anal. calcd for $\text{C}_{54}\text{H}_{34}\text{N}_6\text{Pt}_2\text{S}_6$: C, 48.06; H, 2.54; N, 6.23; found: C, 48.04; H, 2.49; N, 6.19.

(S,R,S)-Pt2. Dark maroon solid (Yield: 30%): ^1H NMR (600 MHz, CDCl_3 , δ) 8.76 (d, $J = 8.2$ Hz, 2H), 8.44 (dd, $J = 8.1, 1.6$ Hz, 2H), 7.82 (s, 2H), 7.80 – 7.74 (m, 4H), 7.58 – 7.53 (m, 6H), 7.22 – 7.14 (m, 6H), 7.13 – 7.06 (m, 2H), 6.87 – 6.78 (m, 4H), 6.16 (dd, $J = 9.1, 5.4$ Hz, 2H), 4.23 (dd, $J = 11.5, 9.1$ Hz, 2H), 3.90 (dd, $J = 11.5, 5.4$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3 , δ) 180.20, 167.89, 165.00, 154.54, 146.92, 143.92, 143.63, 139.94, 137.71, 134.88, 132.82, 132.45, 131.08, 129.79, 129.25, 129.00, 128.87, 128.38, 128.22, 128.12, 127.04, 124.34, 123.83, 122.50, 120.38, 116.11, 100.95, 79.72, 41.49. HRMS (ESI) (m/z): calcd for $\text{C}_{54}\text{H}_{34}\text{N}_6\text{Pt}_2\text{S}_6+\text{H}^+$, 1350.0539; found, 1350.0541. Anal. calcd for $\text{C}_{54}\text{H}_{34}\text{N}_6\text{Pt}_2\text{S}_6$: C, 48.06; H, 2.54; N, 6.23; found: C, 48.07; H, 2.56; N, 6.17.

Scheme S1. Chemical structures and synthetic routes of the chiral binuclear Pt(II) complexes.

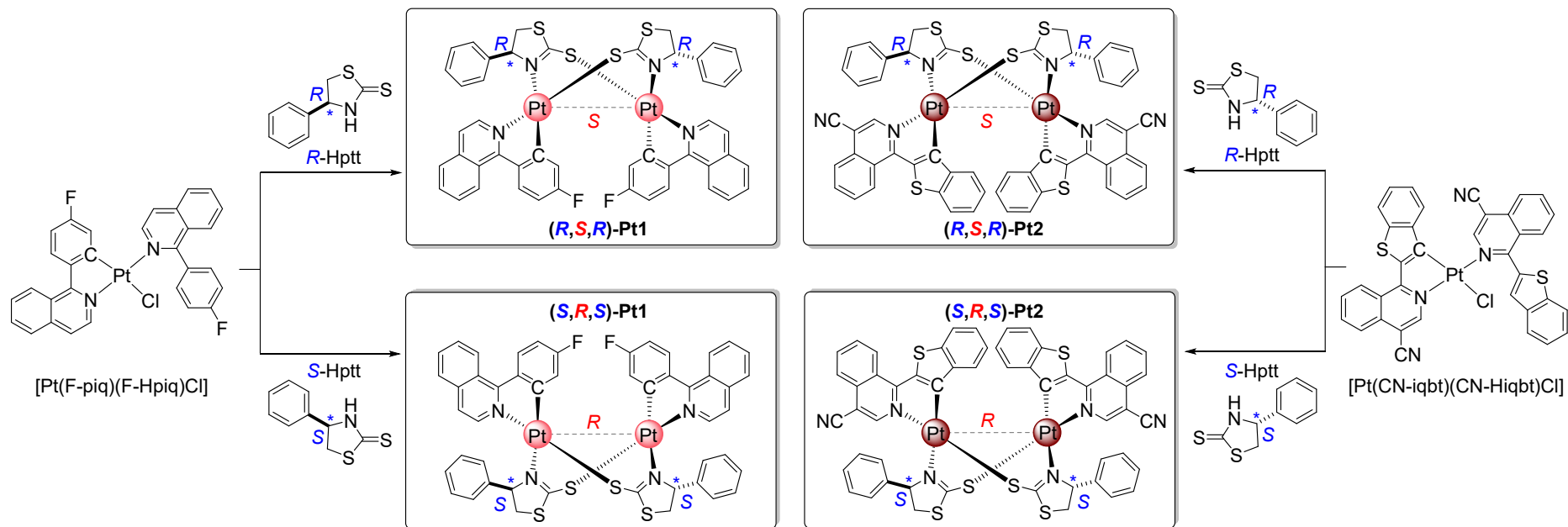
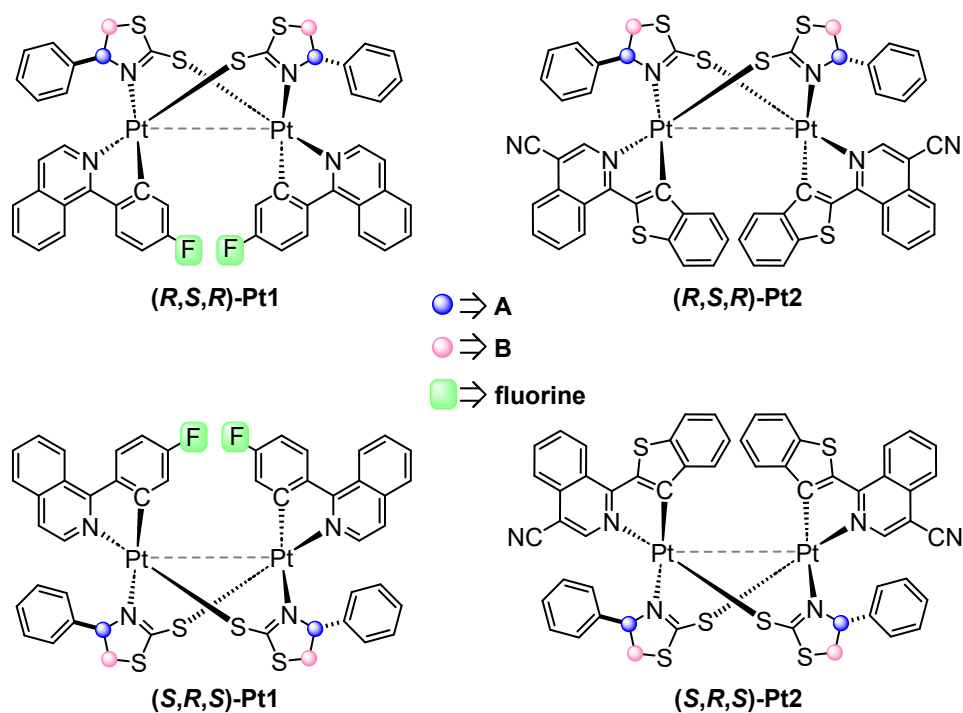


Table S1. The selected ^1H NMR data for the chiral binuclear Pt(II) complexes.



| Complex | Chemical shift (ppm) | | | | | | |
|---------------------------|--------------------------------|---------------------|---------------------|--------------------------------|---------------------|---------------------|-------------------------|
| | The combined proton resonances | H_A | H_B | The combined carbon resonances | C_A | C_B | The fluorine resonances |
| (<i>R,S,R</i>)-Pt1 | 8.13-3.72 | 5.79 | 3.75, 3.72 | 179.30-41.90 | 80.15 | 41.90 | -110.87 |
| (<i>S,R,S</i>)-Pt1 | 8.13-3.72 | 5.79 | 3.75, 3.72 | 179.30-41.90 | 80.15 | 41.90 | -110.88 |
| (<i>R,S,R</i>)-Pt2 | 8.76-3.90 | 6.16 | 4.23, 3.90 | 180.20-41.49 | 79.72 | 41.49 | / |
| (<i>S,R,S</i>)-Pt2 | 8.76-3.90 | 6.16 | 4.23, 3.90 | 180.20-41.49 | 79.72 | 41.49 | / |

^a) All ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 at room temperature.

Table S2. Selected crystallographic data for the chiral binuclear Pt(II) complexes.

| Complex | <i>(R,S,R)</i> -Pt1 | <i>(S,R,S)</i> -Pt1 | <i>(R,S,R)</i> -Pt2 | <i>(S,R,S)</i> -Pt2 |
|---|--|--|---|---|
| Chemical formula | C ₄₈ H ₃₄ F ₂ N ₄ Pt ₂ S ₄ | C ₄₈ H ₃₄ F ₂ N ₄ Pt ₂ S ₄ | C ₅₄ H ₃₄ N ₆ Pt ₂ S ₆ | C ₅₄ H ₃₄ N ₆ Pt ₂ S ₆ |
| CCDC number | 2526096 | 2526097 | 2526098 | 2526099 |
| Crystal size (mm) | 0.20 × 0.20 × 0.18 | 0.21 × 0.20 × 0.17 | 0.20 × 0.18 × 0.20 | 0.20 × 0.20 × 0.18 |
| Temperature/K | 193 | 150 | 150 | 200 |
| Crystal system | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Space group | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| <i>a</i> /Å | 11.3739(10) | 11.2864(5) | 12.5446(9) | 12.6435(11) |
| <i>b</i> /Å | 15.5577(12) | 15.3857(6) | 19.2471(15) | 19.402(2) |
| <i>c</i> /Å | 12.1253(11) | 12.0821(6) | 22.0945(18) | 22.375(3) |
| <i>α</i> /° | 90 | 90 | 90 | 90 |
| <i>β</i> /° | 98.352(3) | 98.285(2) | 90 | 90 |
| <i>γ</i> /° | 90 | 90 | 90 | 90 |
| <i>V</i> /Å ³ | 2122.8(3) | 2076.15(16) | 5334.7(7) | 5489.0(10) |
| <i>Z</i> | 2 | 2 | 4 | 4 |
| ρ_{calc} (g/cm ³) | 1.914 | 1.957 | 1.680 | 1.838 |
| μ /mm ⁻¹ | 6.829 | 6.982 | 5.515 | 5.559 |
| <i>F</i> (000) | 1176.0 | 1176.0 | 2608.0 | 2944.0 |
| Reflections collected | 20000 | 96796 | 189858 | 23637 |
| GOF (<i>F</i> ²) | 1.062 | 1.017 | 0.979 | 1.005 |
| <i>R</i> _{int} | 0.0601 | 0.0532 | 0.0811 | 0.0359 |
| <i>R</i> _{sigma} | 0.0686 | 0.0304 | 0.0314 | 0.0672 |
| <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)] | 0.0444/0.1140 | 0.0146/0.0285 | 0.0242/0.0626 | 0.0362/0.0839 |
| <i>R</i> ₁ / <i>wR</i> ₂ [all data] | 0.0497/0.1188 | 0.0159/0.0288 | 0.0255/0.0632 | 0.0449/0.0877 |
| Flack parameter | 0.074(17) | 0.008(2) | 0.067(5) | 0.090(9) |

Table S3. The selected bond lengths (Å) and bond angles (°) for the chiral binuclear Pt(II) complexes.

| Complex | (<i>R,S,R</i>)-Pt1 | (<i>S,R,S</i>)-Pt1 | Complex | (<i>R,S,R</i>)-Pt2 | (<i>S,R,S</i>)-Pt2 |
|---------------------|----------------------|----------------------|---------------------|----------------------|----------------------|
| Selected bond | Bond length (Å) | | Selected bond | Bond length (Å) | |
| Pt(1)-N(1) | 2.158(14) | 2.151(3) | Pt(1)-N(1) | 2.123(4) | 2.134(7) |
| Pt(1)-N(3) | 2.050(15) | 2.037(3) | Pt(1)-N(3) | 2.072(5) | 2.086(7) |
| Pt(1)-S(2) | 2.299(5) | 2.291(10) | Pt(1)-S(2) | 2.295(14) | 2.303(2) |
| Pt(1)-C(29) | 2.021(8) | 1.982(4) | Pt(1)-C(29) | 1.993(5) | 2.008(8) |
| Pt(2)-N(2) | 2.105(13) | 2.140(3) | Pt(2)-N(2) | 2.127(5) | 2.168(8) |
| Pt(2)-N(4) | 2.053(11) | 2.049(3) | Pt(2)-N(4) | 2.066(5) | 2.055(8) |
| Pt(2)-S(1) | 2.286(4) | 2.2821(8) | Pt(2)-S(1) | 2.290(15) | 2.290(3) |
| Pt(2)-C(44) | 2.013(7) | 1.980(3) | Pt(2)-C(47) | 1.991(6) | 2.015(9) |
| Selected bond angle | Bond angles (°) | | Selected bond angle | Bond angles (°) | |
| C(29)-Pt(1)-N(1) | 176.7(5) | 176.69(15) | C(29)-Pt(1)-N(1) | 174.7(2) | 174.9(4) |
| C(29)-Pt(1)-N(3) | 79.7(5) | 80.17(15) | C(29)-Pt(1)-N(3) | 79.9(2) | 79.9(3) |
| N(1)-Pt(1)-S(2) | 87.1(4) | 87.97(9) | N(1)-Pt(1)-S(2) | 85.65(15) | 85.5(2) |
| N(3)-Pt(1)-S(2) | 175.2(4) | 174.88(9) | N(3)-Pt(1)-S(2) | 79.18(16) | 179.4(2) |
| C(44)-Pt(2)-N(2) | 176.8(5) | 177.85(13) | C(47)-Pt(2)-N(2) | 175.9(2) | 175.1(3) |
| C(44)-Pt(2)-N(4) | 79.8(5) | 80.27(12) | C(47)-Pt(2)-N(4) | 80.1(2) | 79.8(3) |
| N(2)-Pt(2)-S(1) | 86.9(4) | 86.75(8) | N(2)-Pt(2)-S(1) | 86.18(13) | 86.6(2) |
| N(4)-Pt(2)-S(1) | 174.9(4) | 174.76(8) | N(4)-Pt(2)-S(1) | 177.65(16) | 178.0(2) |

Table S4. Intramolecular Pt-Pt distances, intermolecular noncovalent interactions and intermolecular π - π interactions between molecules for the chiral binuclear Pt(II) complexes.

| Complex | Intramolecular Pt-Pt distances (Å) | Intermolecular noncovalent interactions (Å) | Intermolecular π - π interactions between molecules (Å) |
|--------------------|------------------------------------|---|---|
| (R,S,R)-Pt1 | 2.922 | S···H 2.970, 2.931 | 3.395 |
| | | F···H 2.617, 2.647, 2.609 | |
| (S,R,S)-Pt1 | 2.910 | S···H 3.343, 2.872 | 3.370 |
| | | F···H 2.603, 2.527, 2.617 | |
| (R,S,R)-Pt2 | 2.941 | S···H 2.818, 2.999 | 3.422 |
| | | F···H 2.396 | |
| (S,R,S)-Pt2 | 2.948 | S···H 2.919 | 3.417 |
| | | F···H 2.518 | |

Table S5. Photophysical properties of the chiral binuclear Pt(II) complexes at room temperature.

| Complex | Medium | Absorption | | Emission | | | | |
|--------------------|---------------------------------|--|--|--|--------------------------|--|--|---------------------------------------|
| | | λ_{abs} ($\epsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) [$\lambda_{\text{edge}}^{\text{onset}}$] (nm) | $\lambda_{\text{PL}}^{\text{a}}$ (nm) | τ^{a} (μs) | PLQY ^a (%) | $g_{\text{lum}}^{\text{b}}$ (10^{-3}) | $B_{\text{CPL}}^{\text{c}}$ ($\text{M}^{-1} \text{ cm}^{-1}$) | $E_{\text{g}}^{\text{opt d}}$ (eV) |
| (R,S,R)-Pt1 | CH ₂ Cl ₂ | 228 (60.4), 272 (40.1), 350 (11.5), 383 (8.5), 416 (4.8), 523 (2.7), 546 (2.6) [629] ^e | 733 ^e | 0.35 ^e | 20.6 ^e | -2.5 ^f | 0.7 ^f | 1.97 |
| | Doped film | - | 709 ^g | 1.83 ^g | 35.4 ^g | -2.8 ^h | - | - |
| (S,R,S)-Pt1 | CH ₂ Cl ₂ | 225 (56.8), 272 (36.7), 350 (10.5), 382 (7.8), 416 (4.4), 521 (2.4), 546 (2.4) [629] ^e | 731 ^e | 0.40 ^e | 21.0 ^e | +2.5 ^f | 0.6 ^f | 1.97 |
| | Doped film | - | 708 ^g | 1.84 ^g | 34.2 ^g | +2.7 ^h | - | - |
| (R,S,R)-Pt2 | CH ₂ Cl ₂ | 236 (54.3), 319 (22.6), 412 (12.1), 472 (11.2), 542 (8.9), 616 (4.3) [774] ^e | 780, 835(sh) ^e | 0.35 ^e | 18.9 ^e | -2.1 ^f | 0.9 ^f | 1.60 |
| | Doped film | - | 792 ^g | 1.25 ^g | 29.2 ^g | -3.9 ^h | - | - |
| (S,R,S)-Pt2 | CH ₂ Cl ₂ | 236 (56.8), 330 (22.5), 412 (12.6), 473 (11.8), 541 (9.2), 613 (4.4) [774] ^e | 775, 837(sh) ^e | 0.32 ^e | 17.8 ^e | +2.1 ^f | 0.8 ^f | 1.60 |
| | Doped film | - | 794 ^g | 1.29 ^g | 28.5 ^g | +3.8 ^h | - | - |

^aExcitation wavelength 375 nm; ^bat Wavelength of the PL maximum ($\lambda_{\text{PL}}^{\text{Max}}$), ^cCPL brightness (B_{CPL}) were defined as the following equation $B_{\text{CPL}} = \epsilon_{\lambda} \times \text{PLQY} \times |g_{\text{lum}}|/2$, ^d $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{edge}}^{\text{onset}}$; ^eAt 1.0×10^{-5} mol/L in degassed CH₂Cl₂; ^fAt 0.5×10^{-5} mol/L in degassed CH₂Cl₂; ^gThe complex was doped in poly(methyl methacrylate (PMMA) film (5 wt%); ^hThe complex was doped in poly(methyl methacrylate (PMMA) film (2 wt%).

Table S6. Excitation wavelengths (nm), oscillator strengths (f) and the corresponding transition and properties for the chiral binuclear Pt(II) complexes.

| Complex | State | λ (nm) | E (eV) | Oscillator (f) | Orbital contribution ($>5\%$) |
|--------------------|--------------------------------|-------------------|-------------|-----------------------|------------------------------------|
| (R,S,R)-Pt1 | S ₀ →T ₁ | 1056 | 1.17 | 0.0082 | HOMO→LUMO (93.9%) |
| | S ₀ →S ₁ | 895 | 1.39 | 0.0241 | HOMO→LUMO (99.3%) |
| (S,R,S)-Pt1 | S ₀ →T ₁ | 1056 | 1.17 | 0.0083 | HOMO→LUMO (94.0%) |
| | S ₀ →S ₁ | 895 | 1.39 | 0.0242 | HOMO→LUMO (99.3%) |
| (R,S,R)-Pt2 | S ₀ →T ₁ | 1226 | 1.01 | 0.0002 | HOMO→LUMO (94.3%) |
| | S ₀ →S ₁ | 986 | 1.26 | 0.0298 | HOMO → LUMO (99.3%) |
| (S,R,S)-Pt2 | S ₀ →T ₁ | 1216 | 1.02 | 0.0001 | HOMO → LUMO (94.2%) |
| | S ₀ →S ₁ | 978 | 1.27 | 0.0301 | HOMO → LUMO (99.3%) |

Table S7. Frontier orbitals and their corresponding electron cloud density distributions for the chiral binuclear Pt(II) complexes.

| Complex | Orbital | Contribution of metal d_{π} orbitals and π orbitals of ligand to MOs (%) | | |
|--------------------|---------|--|---------|---------|
| | | Pt | F-piq | R/S-ptt |
| (R,S,R)-Pt1 | LUMO | 6.18 | 92.00 | 1.82 |
| | HOMO | 78.97 | 11.70 | 9.33 |
| (S,R,S)-Pt1 | LUMO | 6.00 | 92.25 | 1.75 |
| | HOMO | 79.10 | 11.39 | 9.51 |
| ----- | | | | |
| | Orbital | Pt | CN-iqbt | R/S-ptt |
| (R,S,R)-Pt2 | LUMO | 7.27 | 90.77 | 1.96 |
| | HOMO | 73.77 | 17.05 | 9.18 |
| (S,R,S)-Pt2 | LUMO | 7.02 | 91.17 | 1.82 |
| | HOMO | 75.69 | 14.99 | 9.32 |

Table S8. Voltammetric data for the chiral binuclear Pt(II) complexes.

| Complex | $E_{\text{ox}}^{1/2}$ (V) ^a | E_{HOMO} (eV) ^b | $\lambda_{\text{edge}}^{\text{onset}}$ (nm) | $E_{\text{g}}^{\text{opt}}$ (eV) ^c | E_{LUMO} (eV) ^d |
|--------------------|--|-------------------------------------|---|---|-------------------------------------|
| (R,S,R)-Pt1 | 0.61 | -4.90 | 629 | 1.97 | -2.93 |
| (S,R,S)-Pt1 | 0.60 | -4.89 | 629 | 1.97 | -2.92 |
| (R,S,R)-Pt2 | 0.89 | -5.18 | 774 | 1.60 | -3.58 |
| (S,R,S)-Pt2 | 0.88 | -5.17 | 774 | 1.60 | -3.57 |

^aReversible. The values were derived from the anodic peak potential. ^bHOMO levels are calculated from the equation ($E_{\text{HOMO}} = -(E_{\text{ox}}^{1/2} - E_{\text{Fc}/\text{Fc}^+} + 4.8)$ eV; where $E_{\text{ox}}^{1/2}$ is measured in CH_2Cl_2 and reported *versus* the Ag/AgCl). ^cOptical energy gap $E_{\text{g}}^{\text{opt}}$ was estimated from the absorption onset using the equation ($E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{edge}}^{\text{onset}}$). ^dThe LUMO energy levels of each complex were calculated according to the following equation ($E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}}$). Note: $E_{\text{Fc}/\text{Fc}^+} = 0.51$ V.

Table S9. Calculated transition dipole moments and chiroptical properties for the chiral binuclear Pt(II) complexes based on optimized S₀ geometries.

| Complex | State | E (eV) | $ \mu_e ^a$ ($\times 10^{-20}$ esu·cm) | $ \mu_m ^b$ ($\times 10^{-18}$ erg·G ⁻¹) | $\theta_{e,m}^c$ (°) | g_{abs}^d ($\times 10^{-2}$) |
|--------------------|----------------|----------|---|---|----------------------|---|
| (R,S,R)-Pt1 | S ₁ | 1.39 | 21.5 | 8.7 | 14.9 | -0.3 |
| | S ₂ | 1.73 | 11.3 | 6.5 | 137.2 | 0.3 |
| | S ₃ | 2.40 | 36.9 | 25.6 | 109.1 | 1.8 |
| | S ₄ | 2.43 | 34.2 | 22.3 | 150.1 | 4.5 |
| (S,R,S)-Pt1 | S ₁ | 1.39 | 84.6 | 9.4 | 163.1 | 0.3 |
| | S ₂ | 1.74 | 45.1 | 7.3 | 43.4 | -0.3 |
| | S ₃ | 2.39 | 12.6 | 25.5 | 71.7 | -1.8 |
| | S ₄ | 2.43 | 14.3 | 22.8 | 22.9 | -4.2 |
| (R,S,R)-Pt2 | S ₁ | 1.26 | 97.4 | 9.8 | 9.9 | -0.3 |
| | S ₂ | 1.59 | 49.7 | 1.8 | 21.6 | -0.1 |
| | S ₃ | 1.89 | 25.4 | 43.1 | 177.1 | 4.9 |
| | S ₄ | 2.10 | 51.1 | 45.7 | 68.6 | -0.9 |
| (S,R,S)-Pt2 | S ₁ | 1.27 | 97.6 | 9.5 | 170.1 | 0.3 |
| | S ₂ | 1.59 | 50.1 | 1.4 | 170.6 | 0.1 |
| | S ₃ | 1.89 | 23.8 | 43.2 | 1.4 | -5.3 |
| | S ₄ | 2.10 | 51.3 | 45.4 | 111.9 | 0.9 |

^aTransition electric dipole moment (TEDM). ^bTransition magnetic dipole moment (TMDM). ^c $\theta_{e,m}$ represents the angle of TEDM and TMDM. ^dAbsorption asymmetry g -factors (g_{abs}) is calculated as follows: $g_{\text{abs}} = 4R/(D + G)$, where R , D , and G represent the rotatory, electric dipole, and magnetic dipole strength, respectively ($R = |\mu_e||\mu_m|\cos\theta$, $D = |\mu_e|^2$, $G = |\mu_m|^2$).

Table S10. Calculated transition dipole moments and chiroptical properties for the chiral binuclear Pt(II) complexes based on optimized T₁ geometries.

| Complex | State | <i>E</i> (eV) | $ \mu_e ^a$ ($\times 10^{-20}$ esu·cm) | $ \mu_m ^b$ ($\times 10^{-22}$ erg·G ⁻¹) | $\theta_{e,m}^c$ (°) | g_{lum}^d ($\times 10^{-3}$) |
|--------------------|----------------|---------------|--|--|----------------------|----------------------------------|
| (R,S,R)-Pt1 | T ₁ | 1.24 | 3.9 | 0.6 | 45.4 | 3.3 |
| (S,R,S)-Pt1 | | 1.24 | 3.9 | 0.7 | 44.2 | -3.4 |
| (R,S,R)-Pt2 | | 1.08 | 2.9 | 0.2 | 2.4 | 1.8 |
| (S,R,S)-Pt2 | | 1.09 | 3.0 | 0.2 | 0.4 | -1.6 |

^aTransition electric dipole moment (TEDM). ^bTransition magnetic dipole moment (TMDM).

^c $\theta_{e,m}$ represents the angle of TEDM and TMDM. ^dLuminescence asymmetry *g*-factors (g_{lum}) is calculated as follows: $g_{lum} = 4R/(D + G)$, where *R*, *D*, and *G* represent the rotatory, electric dipole, and magnetic dipole strength, respectively ($R = |\mu_e||\mu_m|\cos\theta$, $D = |\mu_e|^2$, $G = |\mu_m|^2$).

Table S11. Comparison of PLQYs of the designed Pt(II) complexes with the reported Ir(III) and Pt(II) complexes showing PL at NIR region.

| Complex | λ_{PL} (nm) | PLQY | Ref. |
|---|----------------------------|--------|--|
| The reported near-infrared photoluminescent dinuclear Pt(II) complexes | | | |
| 5 | 706 | 0.36 | <i>Angew. Chem. Int. Ed.</i> 2026, 65 , e19762 |
| 7 | 702 | 0.64 | |
| 4b | 794 | 0.3 | <i>J Korean Chem Soc</i> , 2025, 69 , 39 |
| [Pt(tfppy)(μ-PyXZ)] (2) | 705 | 0.46 | <i>Adv. Optical Mater.</i> , 2023, 11 , 2300201 |
| [Pt(piq)(μ-Czl)] (Pt-4) | 740 | 0.29 | <i>Mater. Chem. Front.</i> , 2023, 7 , 873 |
| 1 | 726 | 0.11 | <i>Adv. Funct. Mater.</i> , 2023, 33 , 2211853 |
| 2 | 712 | 0.16 | |
| 3 | 722 | 0.18 | |
| 4 | 701 | 0.17 | |
| 1 | 706 | 0.16 | |
| 2 | 725 | 0.095 | |
| 3 | 736 | 0.083 | |
| 4 | 710 | 0.013 | |
| 5 | 725 | 0.104 | |
| Pt-4 | 802 | 0.05 | |
| Pt-5 | 758 | 0.07 | <i>Inorg. Chem.</i> , 2022, 61 , 5178 |
| Pt₂(bis-dthpym)(dpm)₂ | 725 | 0.17 | <i>J. Mater. Chem. C</i> , 2021, 9 , 127 |
| (DIQB)[Pt(DPM)]₂ | 730 | 0.0077 | <i>Org. Electron.</i> , 2020, 87 , 105902 |
| (BuPh-BDIQ)Pt₂(dpm)₂ | 718 | 0.0364 | <i>J. Mater. Chem. C</i> , 2018, 6 , 5769 |
| 1 | 726 | 0.0397 | <i>Inorg. Chem.</i> , 2018, 57 , 1298 |

| | | | |
|--|-----|--------|--|
| 2 | 738 | 0.0188 | |
| 3 | 766 | 0.0051 | |
| 4 | 777 | 0.033 | |
| 4 | 744 | 0.062 | |
| 7 | 745 | 0.046 | <i>Dyes Pigment.</i> , 2017, 145 , 144 |
| (piq) ₂ Pt ₂ (μ-PhOXT) ₂ | 702 | 0.315 | |
| (piq) ₂ Pt ₂ (μ-C ₈ PhOXT) ₂ | 703 | 0.295 | <i>J. Mater. Chem. C</i> , 2016, 4 , 6007 |
| (piq)Pt(μ-C ₈ OXT) ₂ Pt(piq) | 721 | 0.18 | <i>Org. Electron.</i> , 2012, 13 , 932 |
| 4 | 715 | 0.0005 | <i>Bull. Chem. Soc. Jpn.</i> , 2011, 84 , 219 |
| (<i>R,S,R</i>)-Pt1 | 733 | 0.206 | |
| (<i>S,R,S</i>)-Pt1 | 731 | 0.210 | |
| (<i>R,S,R</i>)-Pt2 | 780 | 0.189 | This work |
| (<i>S,R,S</i>)-Pt2 | 775 | 0.178 | |
| The reported near-infrared photoluminescent Ir(III) complexes | | | |
| IrFTIQ | 738 | 0.085 | <i>Dyes Pigment.</i> , 2025, 232 , 112500 |
| Ir(Bpiq) ₂ acac | 722 | 0.35 | |
| Ir(Bpiq) ₂ dpm | 728 | 0.33 | <i>Chin. Chem. Lett.</i> , 2025, 36, 109596 |
| (Epptt) ₂ Iracac (1) | 756 | 0.124 | |
| (pptt) ₂ Iracac (2) | 796 | 0.078 | <i>Adv. Optical Mater.</i> , 2025, 13 , 2402178 |
| (ppCz) ₂ Irtmd (3) | 862 | 0.006 | |
| [Ir(dpbq) ₂ (pbi)] (1) | 783 | 0.034 | |
| [Ir(dpbq)(iqbt)(pbi)] (2) | 791 | 0.042 | <i>J. Mater. Chem. C</i> , 2025, 13 , 7110 |
| [Ir(iqbt)(pbao)(acac)] (2) | 719 | 0.023 | <i>J. Lumin.</i> , 2025, 288 , 121550 |

| | | | |
|--|-----|-------|---|
| [Ir(dpbq)₂(L¹)] (1) | 787 | 0.022 | <i>J. Lumin.</i> , 2024, 269 , 120487 |
| [Ir(dpbq)₂(L²)] (2) | 784 | 0.036 | |
| TPAIr | 774 | 0.15 | |
| HTIr | 788 | 0.09 | <i>Chem. Eng. J.</i> , 2023, 452 , 138956 |
| DPTAIr | 798 | 0.11 | |
| DTCNIr | 722 | 0.15 | <i>Adv. Optical Mater.</i> , 2022, 10 , 2200111 |
| PTCNIr | 750 | 0.26 | |
| BiqThIr | 731 | 0.68 | <i>Angew. Chem. Int. Ed.</i> , 2023, 62 , e202309739 |
| BiqThIrO | 728 | 0.70 | |
| DBPzIr | 746 | 0.40 | <i>Dalton Trans.</i> , 2023, 52 , 16276 |
| PPzIr | 789 | 0.14 | |
| 1 | 712 | 0.29 | <i>J. Mater. Chem. C</i> , 2022, 10 , 3178 |
| 2 | 714 | 0.36 | |
| Ir(dotbpa)₃ | 839 | 0.015 | <i>J. Mater. Chem. C</i> , 2020, 8 , 8484 |
| Ir1 | 712 | 0.18 | |
| Ir2 | 741 | 0.2 | |
| Ir3 | 716 | 0.25 | <i>Adv. Optical Mater.</i> , 2020, 8 , 2000154 |
| Ir4 | 728 | 0.3 | |
| TCNIr | 708 | 0.06 | <i>Chem. Sci.</i> , 2020, 11 , 2342 |
| Ir-R | 732 | 0.28 | <i>J. Mater. Chem. C</i> , 2020, 8 , 7079 |
| Ir-OR | 775 | 0.08 | |
| (PPz-11,12-DO)₂Iracac | 732 | 0.13 | <i>J. Mater. Chem. C</i> , 2019, 7 , 10961 |
| [(iqbt)₂Ir-(btp)-Ir(iqbt)₂] | 722 | 0.15 | <i>J. Lumin.</i> , 2019, 209 , 427 |

| | | | |
|---|-----|-------|---|
| Ir-3 | 758 | 0.011 | |
| | | | <i>J. Mater. Chem. C</i> , 2018, 6 , 10640 |
| Ir-4 | 722 | 0.106 | |
| <i>fac</i>-Ir(dtbpa)₃ (1) | 824 | 0.029 | |
| | | | <i>Chem. Mater.</i> , 2017, 29 , 4775 |
| <i>fac</i>-Ir(Ftbpa)₃ (2) | 765 | 0.147 | |
| [Ir(iqbt)₂(dpm)] (1) | 710 | 0.16 | |
| [Ir(iqbt)₂(tta)] (2) | 704 | 0.07 | <i>Angew. Chem. Int. Ed.</i> , 2016, 55 , 2714 |
| [Ir(iqbt)₂(dtdk)] (3) | 707 | 0.14 | |
| (thdpqx)₂Ir(acac) | 713 | 0.149 | <i>Chem. Mater.</i> , 2015, 27 , 96 |

Table S12. Summary of photophysical properties for the chiral Pt(II) complexes.

| Complex | λ_{PL} (nm) | PLQY | $g_{\text{lum}}(10^{-3})$ | Ref. |
|---|-------------------------------|-------|---------------------------|---|
| <i>R</i> -PtCl ₂ | 660 | 0.357 | 4.0 | <i>Inorg. Chim. Acta</i> , 2025, 579 , 122589 |
| (<i>D,R,D</i>)/(<i>L,S,L</i>)- [(L1)(L2)Pt ₂ (μ -itt) ₂] | 624 | 0.127 | 0.87/-1.02 | |
| (<i>D,R,D</i>)/(<i>L,S,L</i>)- [(L2)(L3)Pt ₂ (μ -itt) ₂] | 666 | 0.036 | 1.68/-2.23 | |
| (<i>D,R,D</i>)/(<i>L,S,L</i>)- [(L1) ₂ Pt ₂ (μ -itt) ₂] | 622 | 0.198 | 2.58/-2.62 | <i>Org. Lett.</i> , 2025, 27 , 6971 |
| (<i>D,R,D</i>)/(<i>L,S,L</i>)- [(L2) ₂ Pt ₂ (μ -itt) ₂] | 616 | 0.114 | 1.36/-2.12 | |
| (<i>D,R,D</i>)/(<i>L,S,L</i>)- [(L3) ₂ Pt ₂ (μ -itt) ₂] | 694 | 0.024 | 1.68/-1.70 | |
| <i>R,R/S,S</i> | ~615 | 0.003 | ± 2.5 | <i>Chem. Lett.</i> , 2025, 54 , upaf140 |
| <i>L</i> -Pt | 580 | 0.53 | 0.40 | <i>Angew. Chem. Int. Ed.</i> , 2024, 63 , e202403898 |
| (<i>R</i>)/(<i>S</i>)-OMOM-Me | 660 | 0.302 | 1.00/-0.92 | |
| (<i>R</i>)/(<i>S</i>)-OAc-Me | 656 | 0.315 | 1.31/-1.32 | <i>Sci. China Chem.</i> , 2024, 67 , 3757 |
| (<i>R</i>)/(<i>S</i>)-OMe-Me | 665 | 0.295 | 1.30/-1.20 | |
| <i>R</i> -ABA•[Pt(ppy)Cl ₂] | 521 | 0.199 | 1.40 | |
| <i>S</i> -ABA•[Pt(ppy)Cl ₂] | 520 | 0.196 | -1.80 | |
| <i>R</i> -MBA•[Pt(ppy)Cl ₂] | 522 | 0.133 | 4.40 | <i>Mater. Horiz.</i> , 2024, 11 , 6089 |
| <i>S</i> -MBA•[Pt(ppy)Cl ₂] | 523 | 0.132 | -2.80 | |
| 12a | ~515 | | 5.0 | |
| 12b | ~515 | | 2.0 | <i>Acc. Chem. Res.</i> , 2024, 57 , 2941 |
| (<i>S</i>)- 1a | 508 | 0.02 | 3.0 | |
| (<i>S</i>)- 1b | 512 | 0.04 | 2.0 | |
| (<i>S</i>)- 1c | 518 | 0.03 | 3.0 | <i>Inorg. Chem.</i> , 2024, 63 , 23642 |
| (<i>S</i>)- 2a | 555 | <0.01 | - | |

| | | | | |
|--|------|--------|------------|---|
| (S)-2b | 550 | <0.01 | - | |
| (S)-2c | 530 | <0.01 | - | |
| (R,R,R,R_p,M)/(S,S,S,S_p,P)-Me | 635 | 0.062 | -0.67/0.67 | <i>Inorg. Chem.</i> , 2023, 62 , 14152 |
| (R,R,R,R_p,M)/(S,S,S,S_p,P)-iPr | 635 | 0.066 | -1.09/0.89 | |
| R-Pt | 621 | 0.0046 | 3.4 | <i>Chem. Commun.</i> , 2023, 59 , 4004 |
| S-Pt | 621 | 0.0055 | -2.3 | |
| (L,S,L)Pt4a | 622 | 0.198 | -1.21 | <i>Angew. Chem. Int. Ed.</i> , 2023, 62 , e202302011 |
| (L,S,L)Pt4b | 617 | 0.215 | -4.13 | |
| 1 | 520 | 0.05 | 0.67 | <i>ChemPhotoChem</i> , 2023, 7 , e202300010 |
| (RR)(SS)-Py-Pt | ~550 | 0.0672 | -0.77/0.63 | <i>Chin. Chem. Lett.</i> , 2022, 33 , 1459 |
| (RR)(SS)-P/M-QPt | ~634 | 0.0199 | -3.5/3.1 | |
| (R)-Cy-A | 605 | 0.152 | 2.0 | |
| (R,R,R)-BINA-A | 520 | 0.342 | 2.4 | <i>J. Am. Chem. Soc.</i> , 2022, 144 , 2233 |
| (R,R,R)-BINA-B | 718 | 0.081 | 1.0 | |
| trans-[Pt(ppy)(D-tac)] | 521 | - | <0.2 | <i>Inorg. Chem.</i> , 2022, 61 , 17154 |
| cis-[Pt(ppy)(D-tac)] | 521 | - | <0.2 | |
| trans-[Pt(ppy)(D-pbc)] | 518 | - | <0.2 | |
| cis-[Pt(ppy)(D-pbc)] | 550 | - | <0.2 | |
| (S,S)-1 | 533 | 0.10 | 1.0 | <i>Chem. Lett.</i> 2022, 51 , 832 |
| (S,S)-2 | 575 | 0.05 | 0.8 | |
| R-NCN | 523 | 0.200 | 0.10 | |
| S-NCN | 523 | 0.196 | 0.10 | <i>J. Organomet. Chem.</i> , 2022, 973-974 , 122394. |
| Phen-NCN | 530 | 0.224 | 0.10 | |

| | | | | |
|---|-----|-------|-------|--|
| <i>P</i>-Pt | 650 | - | -6.0 | <i>Front. Chem.</i> , 2020, 8 , 501 |
| <i>M</i>-Pt | 650 | - | 6.0 | |
| (<i>R</i>)/(<i>S</i>)-BP1 | 645 | 0.32 | ±1.3 | <i>ACS Appl. Mater. Interfaces</i> , 2020, 12 , 9520 |
| (<i>R</i>)/(<i>S</i>)-BP2 | 639 | 0.12 | ±1.0 | |
| [Pt(iqbt)(<i>S</i>-L¹)] (1) | 731 | 0.13 | -2.14 | <i>J. Mater. Chem. C</i> , 2019, 7 , 13743 |
| [Pt(iqbt)(<i>S</i>-L²)] (2) | 729 | 0.21 | 2.04 | |
| [Pt(iqbt)(<i>S</i>-L²)] (3) | 730 | 0.16 | -1.76 | |
| [Pt(iqbt)(<i>S</i>-L²)] (4) | 731 | 0.14 | -2.75 | |
| (<i>R,S,R</i>)-Pt1 | 709 | 0.354 | -2.8 | This work |
| (<i>S,R,S</i>)-Pt1 | 708 | 0.342 | 2.7 | |
| (<i>R,S,R</i>)-Pt2 | 792 | 0.292 | -3.9 | |
| (<i>S,R,S</i>)-Pt2 | 794 | 0.285 | 3.8 | |

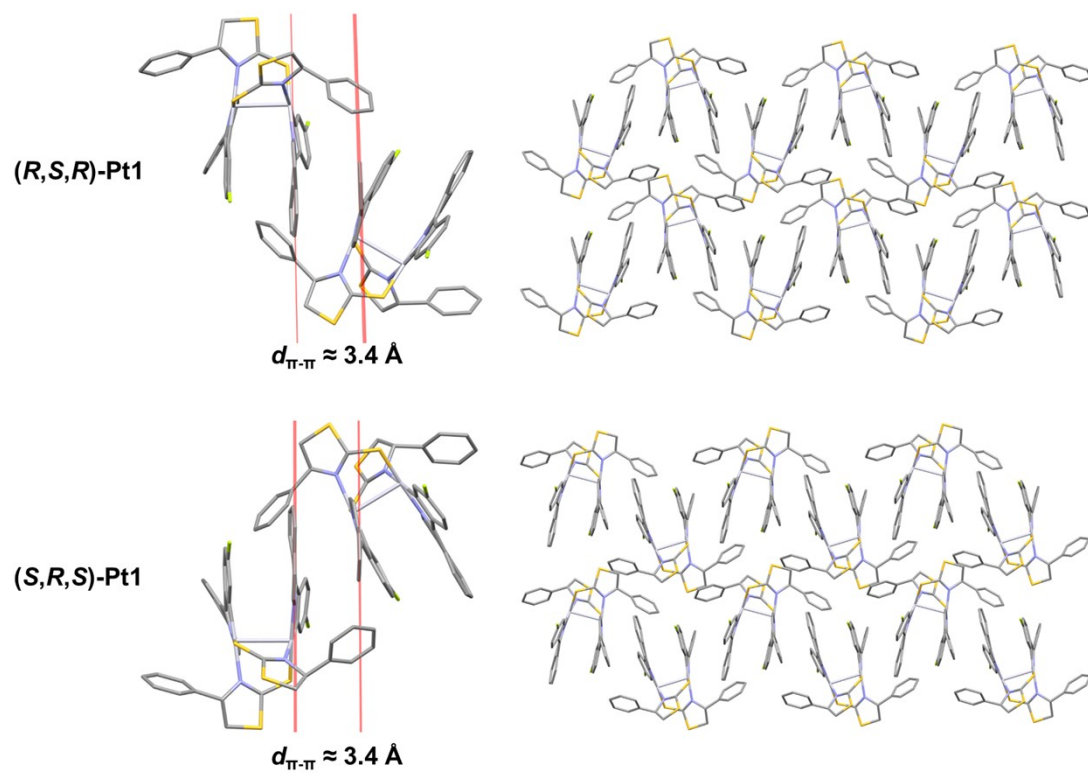


Figure S1. The molecular stacking and intermolecular $\pi \cdots \pi$ interactions between molecules in the crystals of (*R,S,R*)/(*S,R,S*)-Pt1.

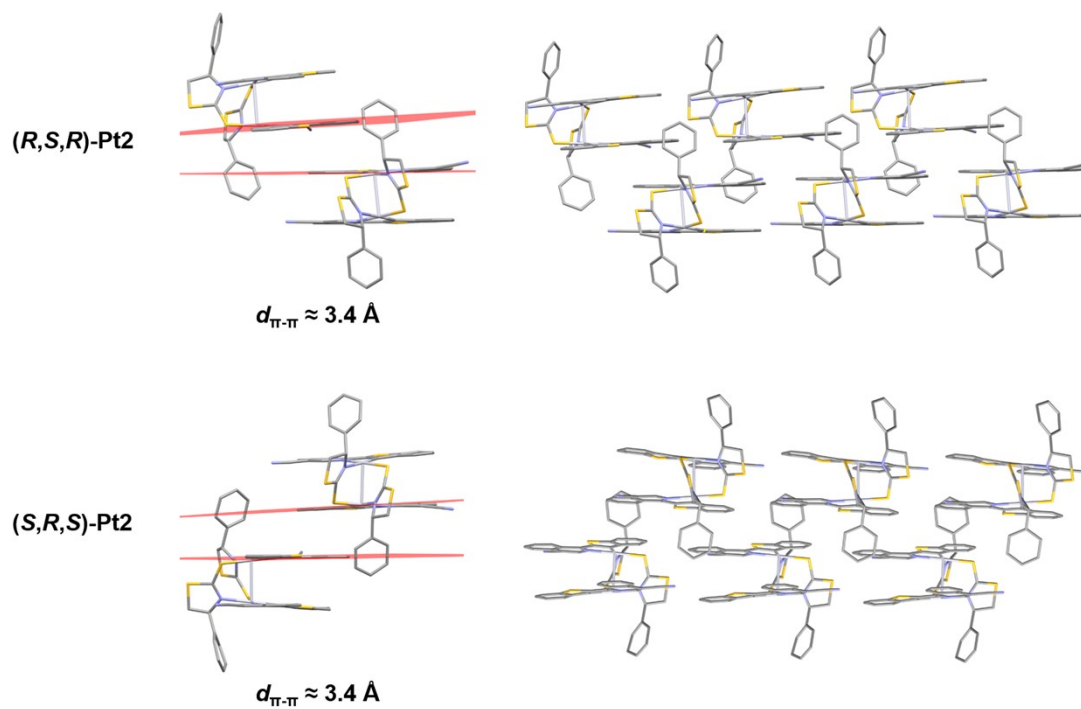


Figure S2. The molecular stacking and intermolecular $\pi \cdots \pi$ interactions between molecules in the crystals of $(R,S,R)/(S,R,S)$ -Pt2.

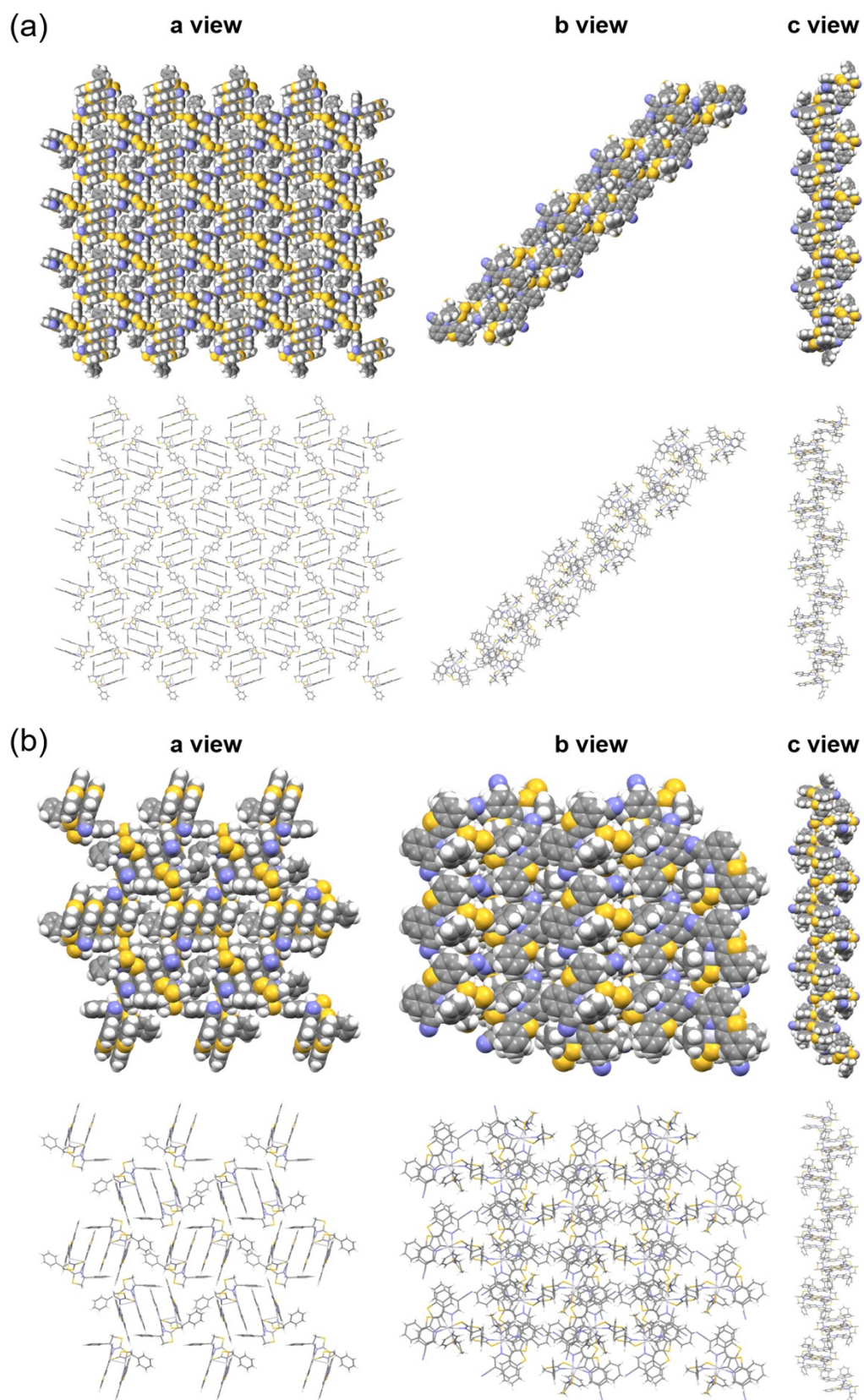


Figure S3. Molecular stacking in crystals of (a) *(R,S,R)*-Pt₂ and (b) *(S,R,S)*-Pt₂ with different view direction.

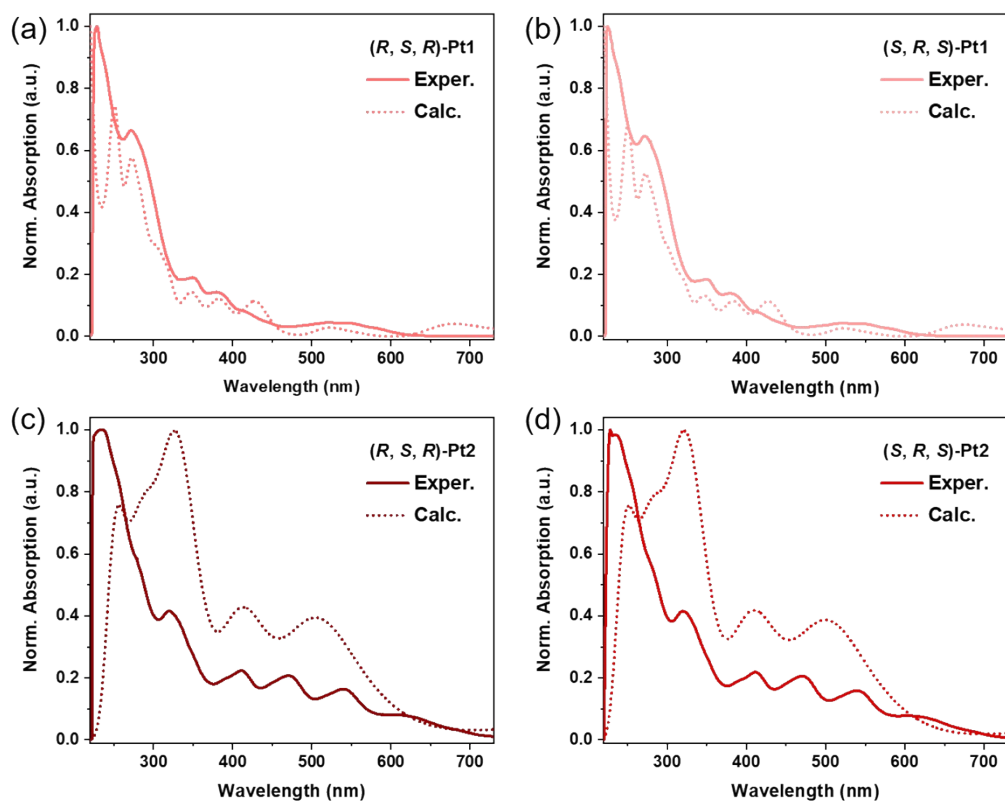


Figure S4. Experimental and calculated absorption spectra of Pt(II) complexes in CH_2Cl_2 .

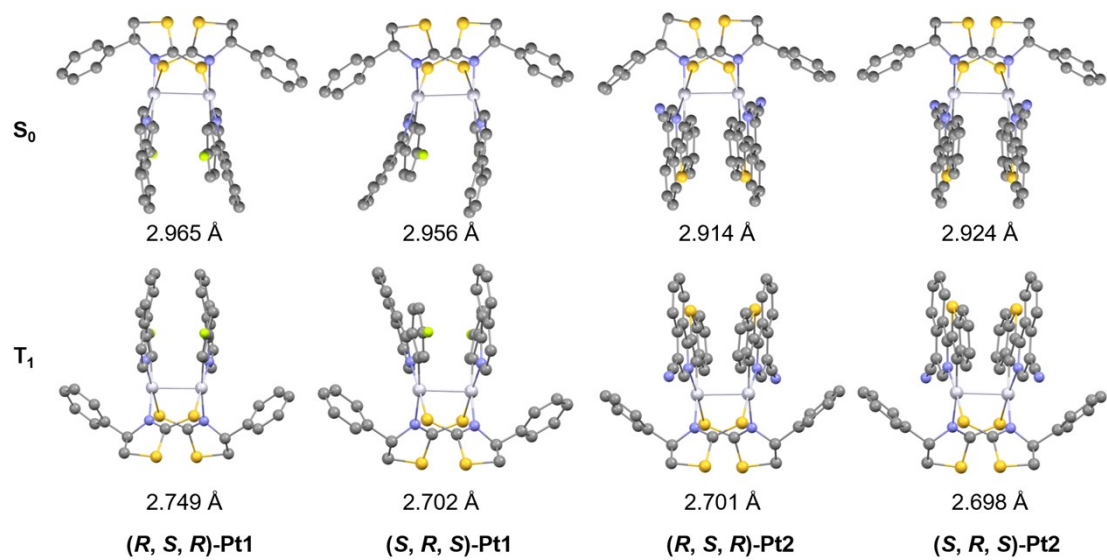


Figure S5. Optimized S_0 and T_1 geometries of Pt(II) complexes and their Pt-Pt distances.

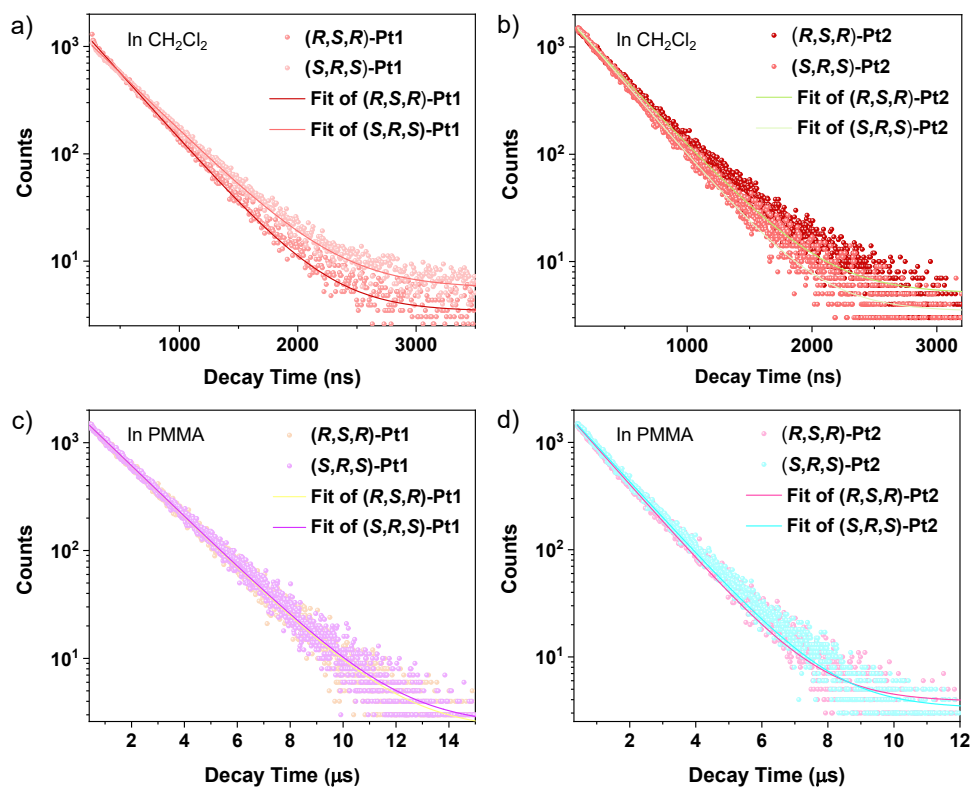


Figure S6. PL decay curves of Pt(II) complexes in degassed CH_2Cl_2 at 1×10^{-5} M (a,b) and 5 wt% PMMA film (c,d) at room temperature under the excitation of a 375 nm-laser.

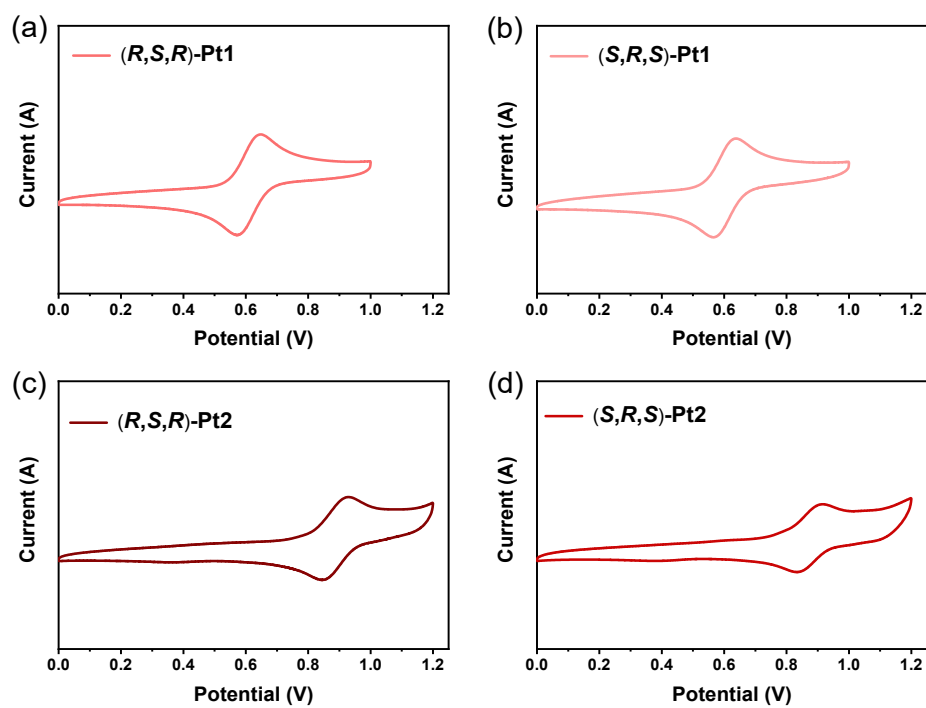


Figure S7. Cyclic voltammety curves of Pt(II) complexes in CH₃CN with ferrocene as the internal standard under a scan rate of 100 mV/s.

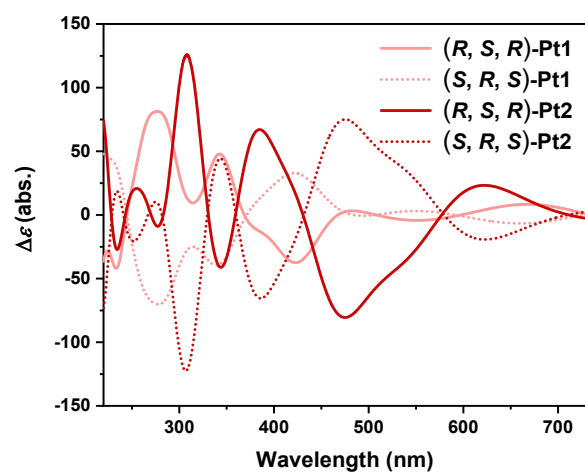


Figure S8. The calculated CD spectra for Pt(II) complexes.

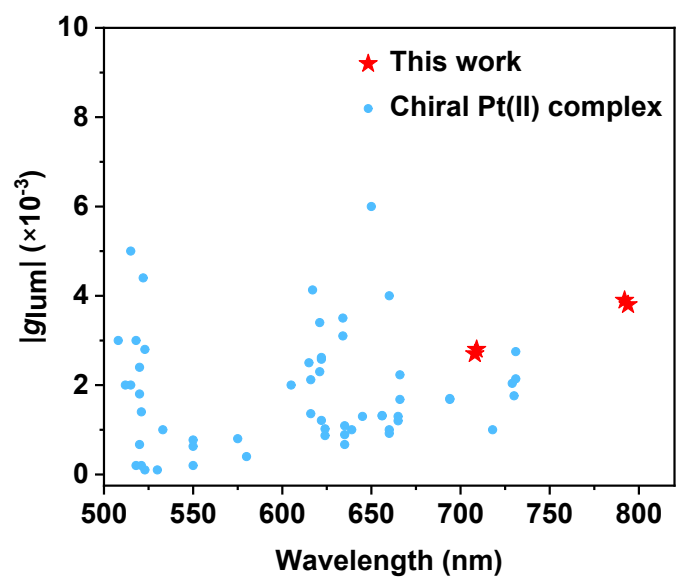


Figure S9. Comparison of g_{lum} of designed Pt(II) complexes with the reported chiral Pt(II) complexes.

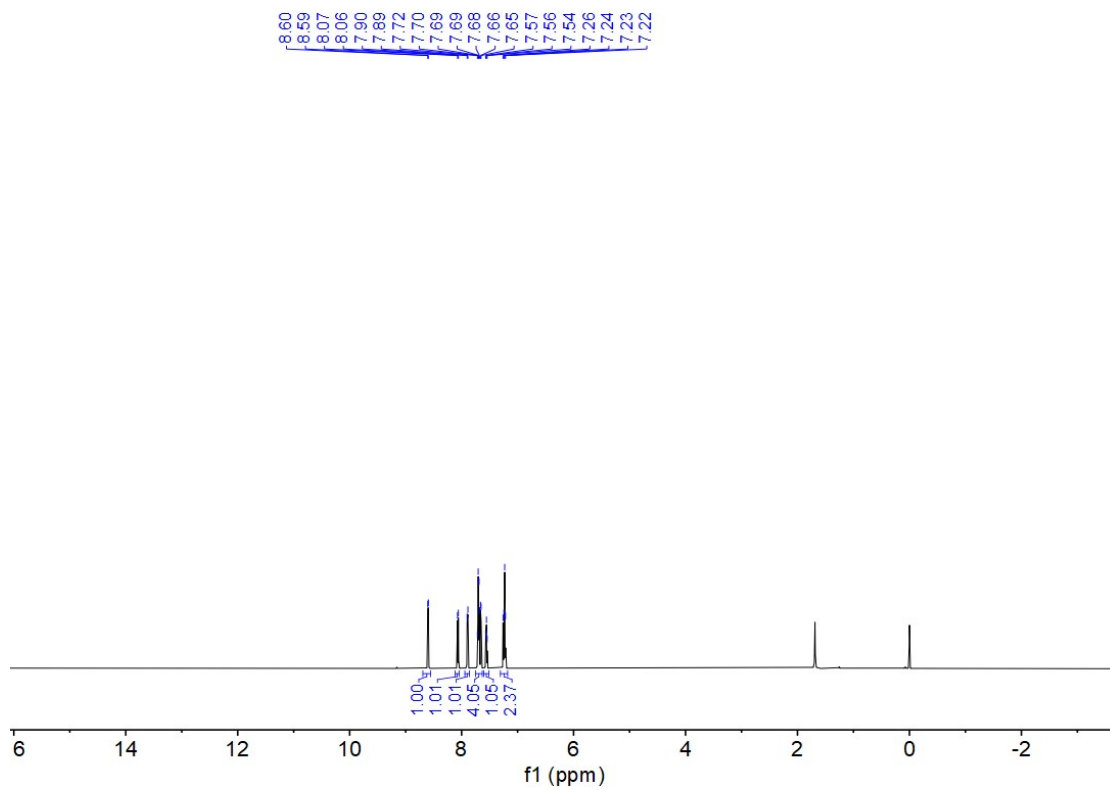


Figure S10. ¹H NMR spectrum for F-Hpiq in CDCl₃ at room temperature.

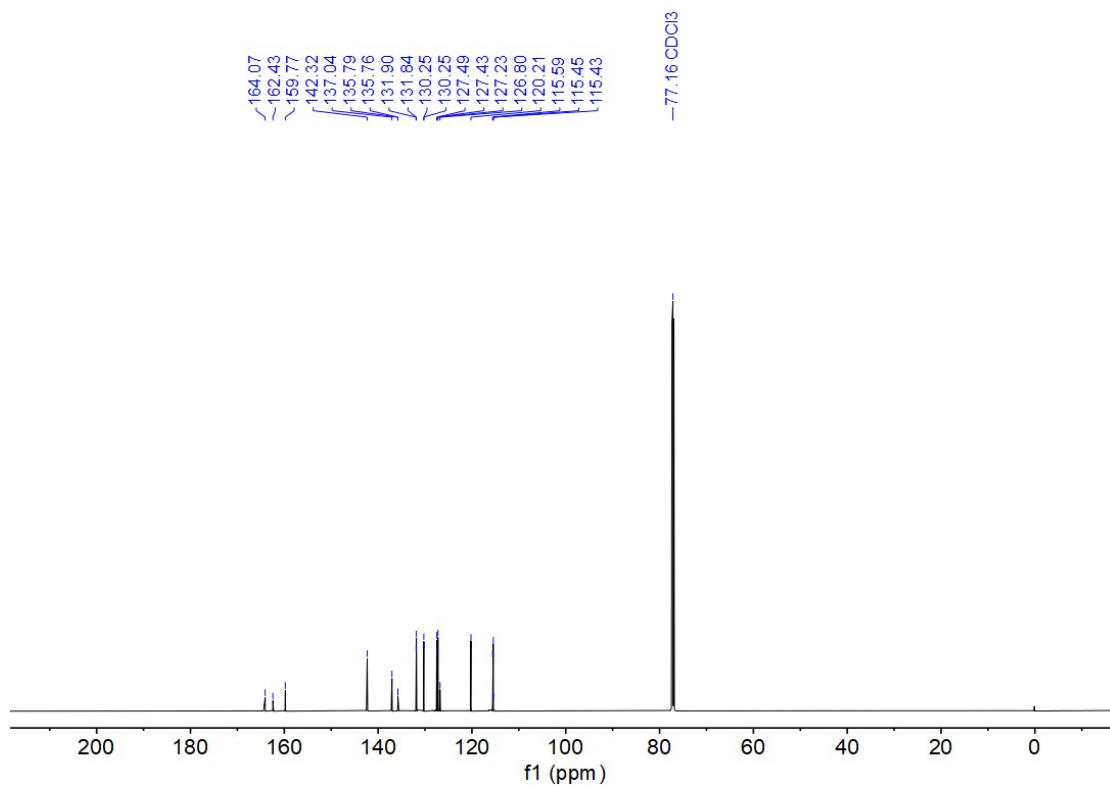


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for F-Hpiq in CDCl_3 at room temperature.

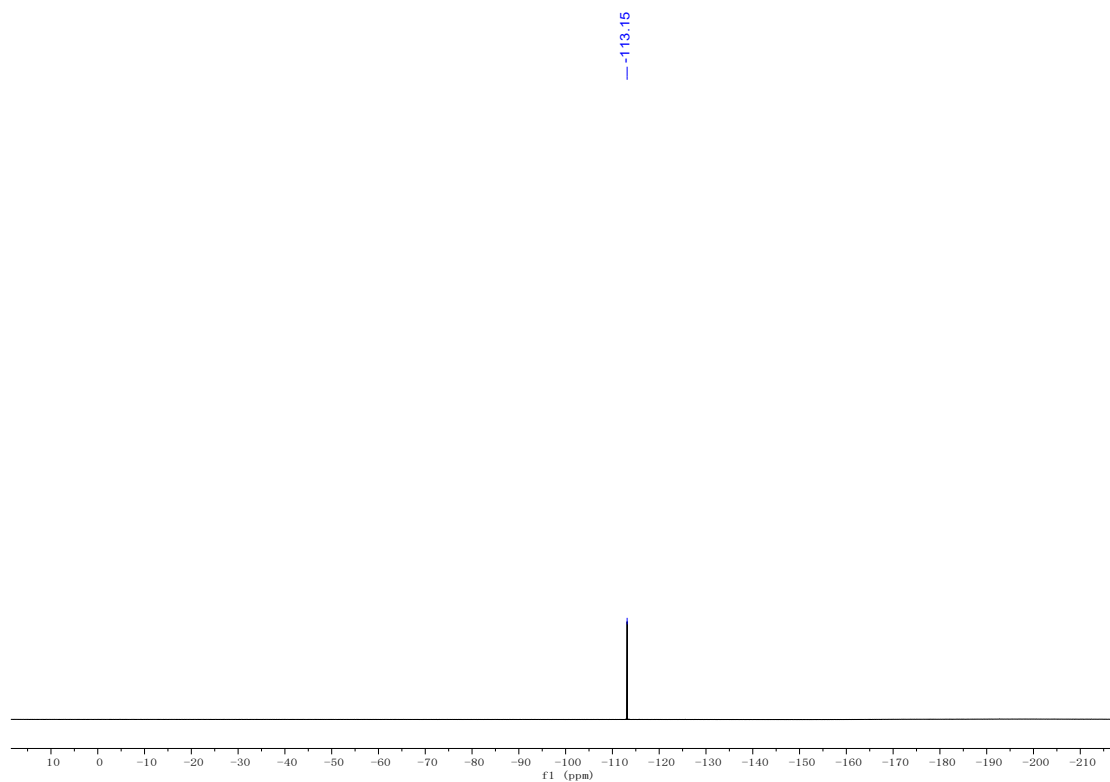


Figure S12. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum for F-Hpiq in CDCl_3 at room temperature.

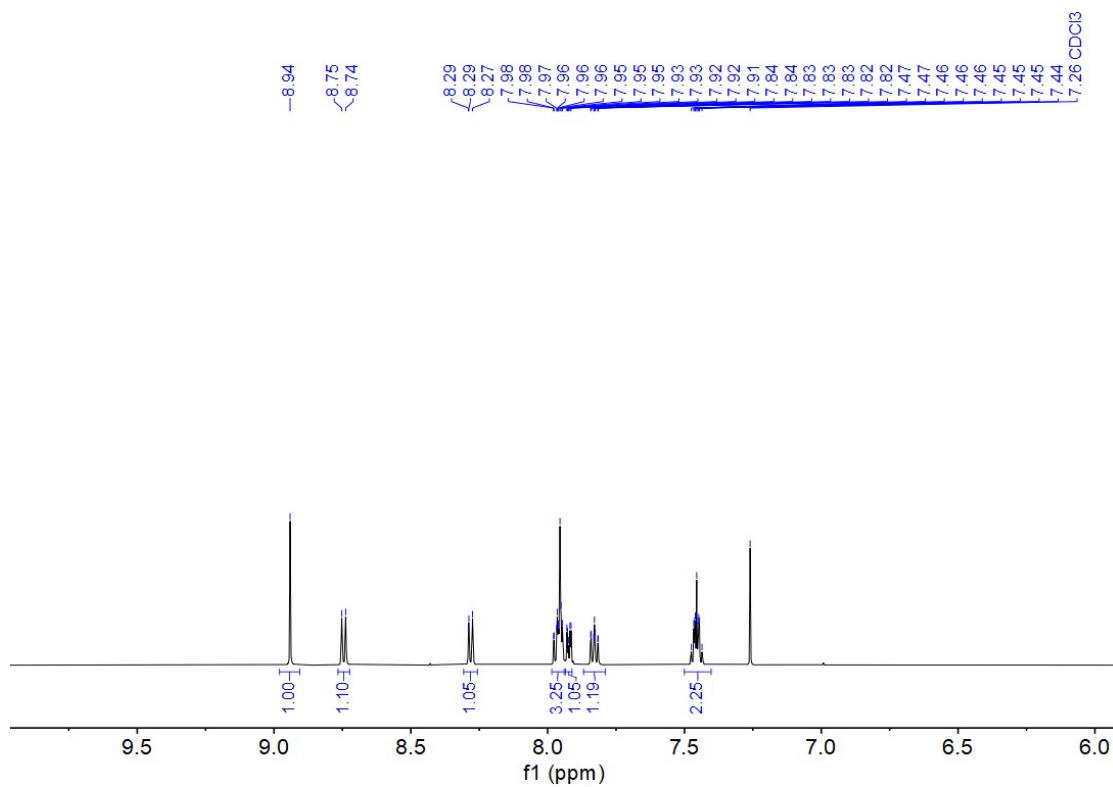


Figure S13. ¹H NMR spectrum for CN-Hiqt in CDCl₃ at room temperature.

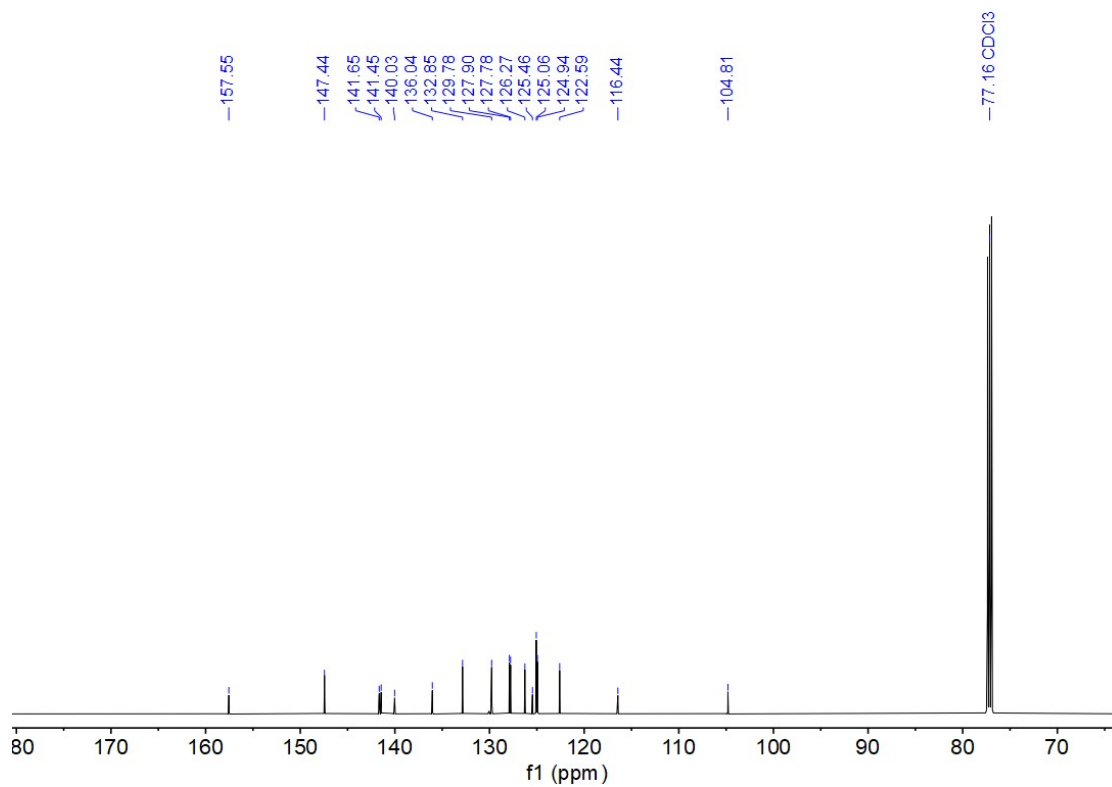


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for CN-Hiqbt in CDCl_3 at room temperature.

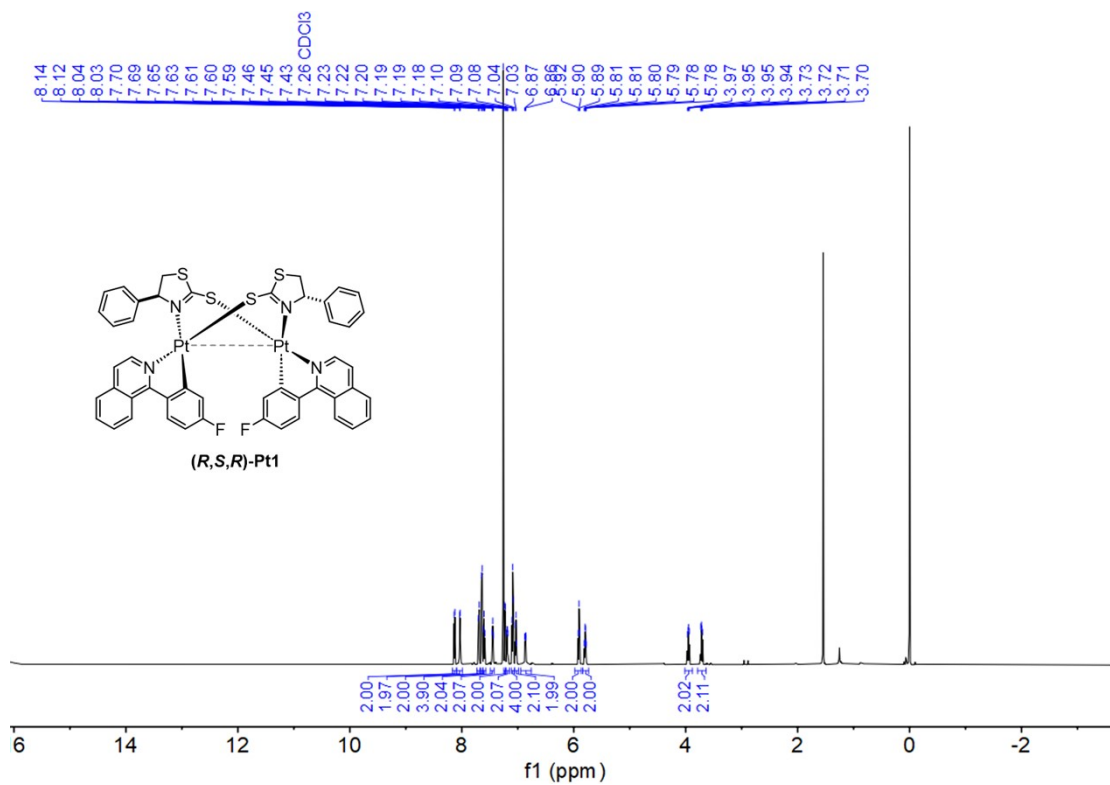


Figure S15. ^1H NMR spectrum for **(R,S,R)-Pt1** in CDCl_3 at room temperature.

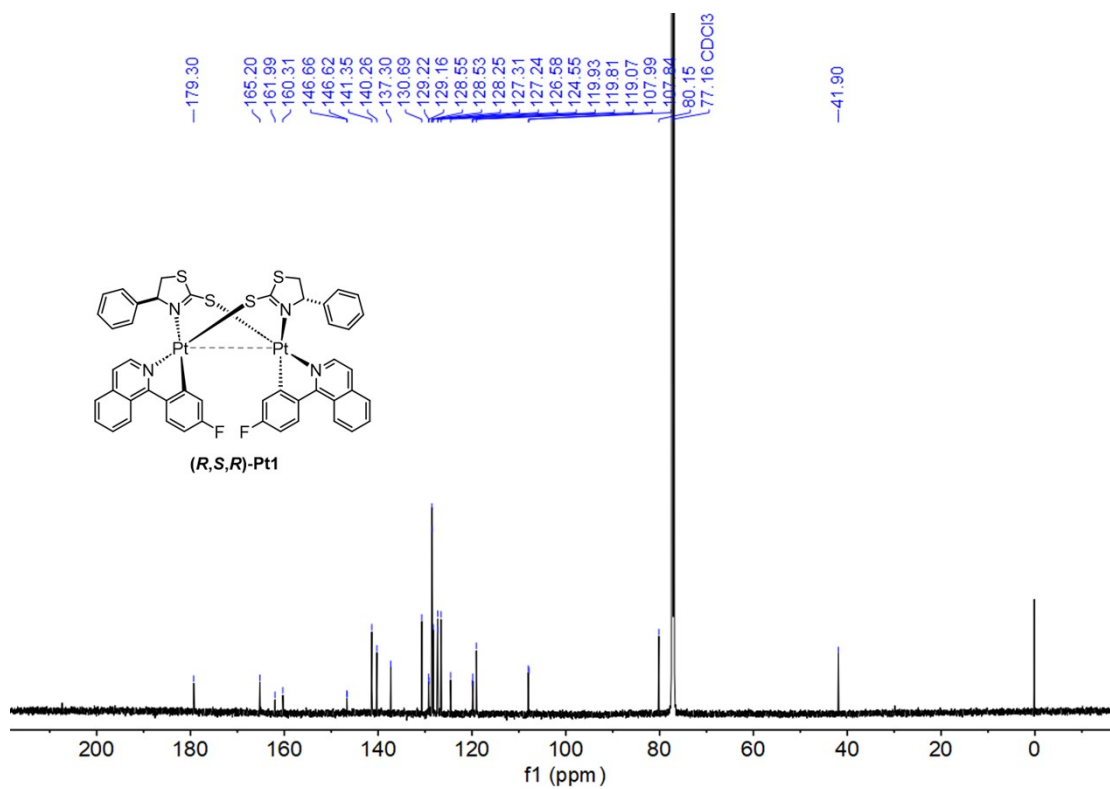


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **(R,S,R)-Pt1** in CDCl_3 at room temperature.



Figure S17. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum for $(R,S,R)\text{-Pt1}$ in CDCl_3 at room temperature.

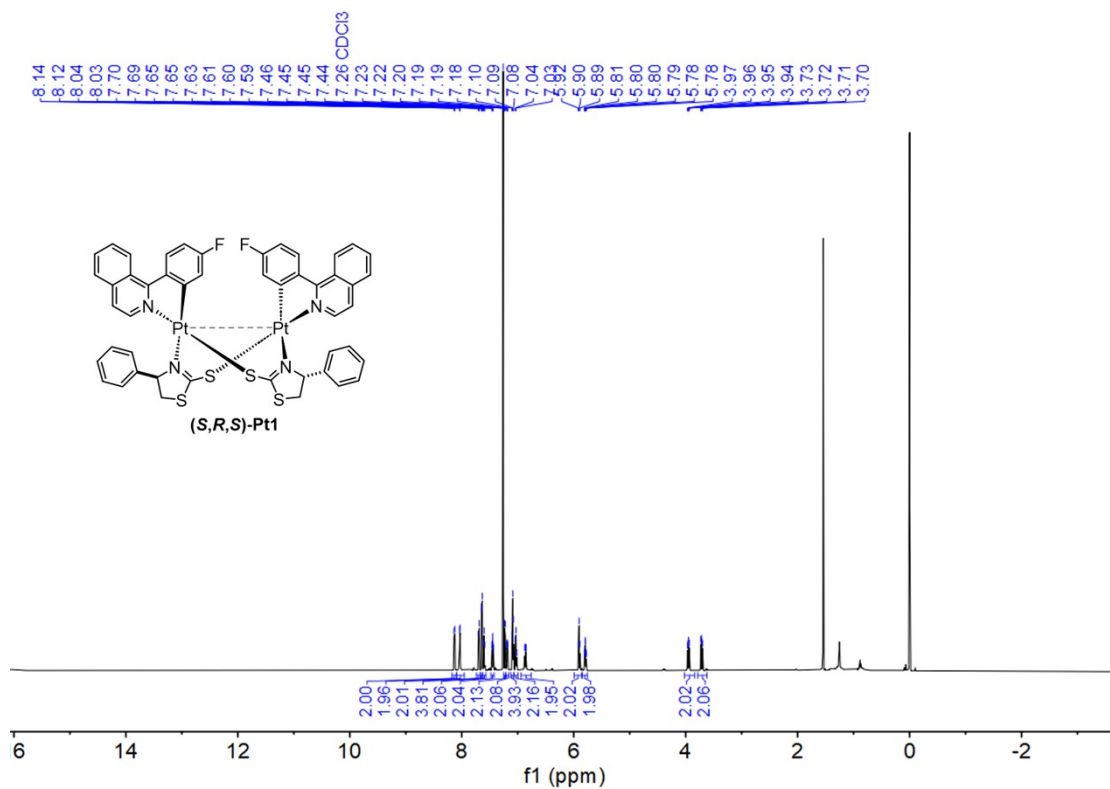


Figure S18. ¹H NMR spectrum for **(S,R,S)-Pt1** in CDCl₃ at room temperature.

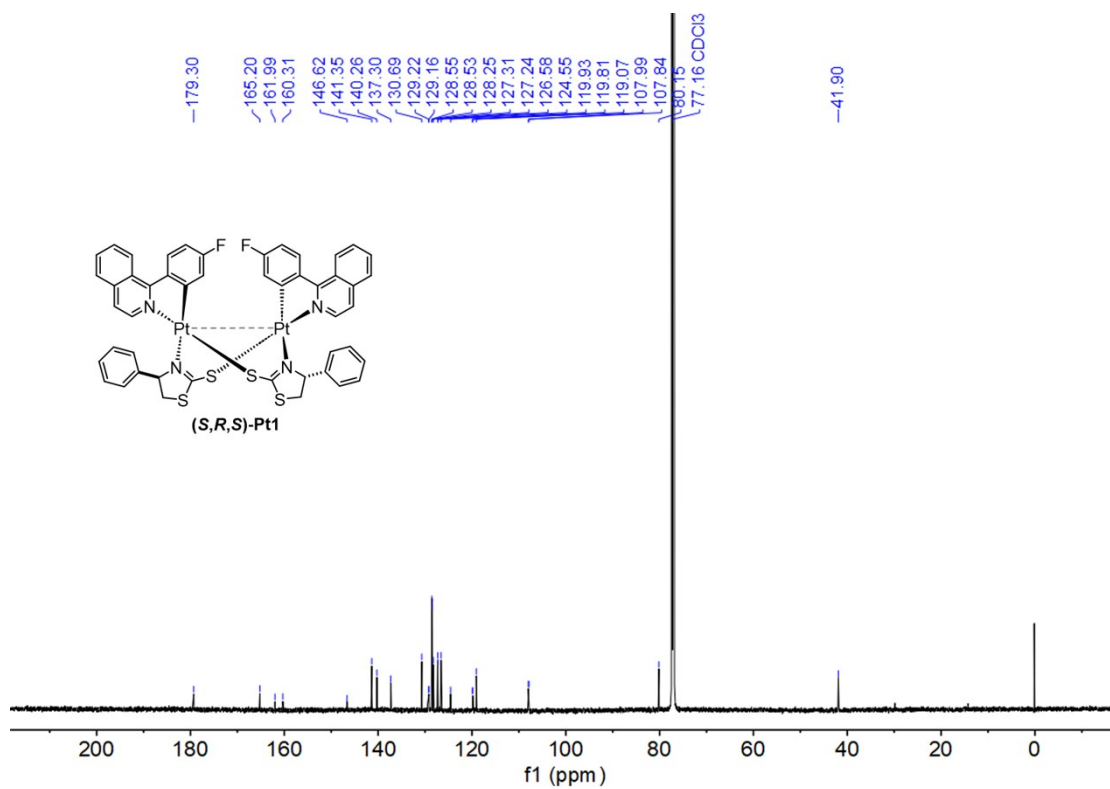


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **(S,R,S)-Pt1** in CDCl_3 at room temperature.

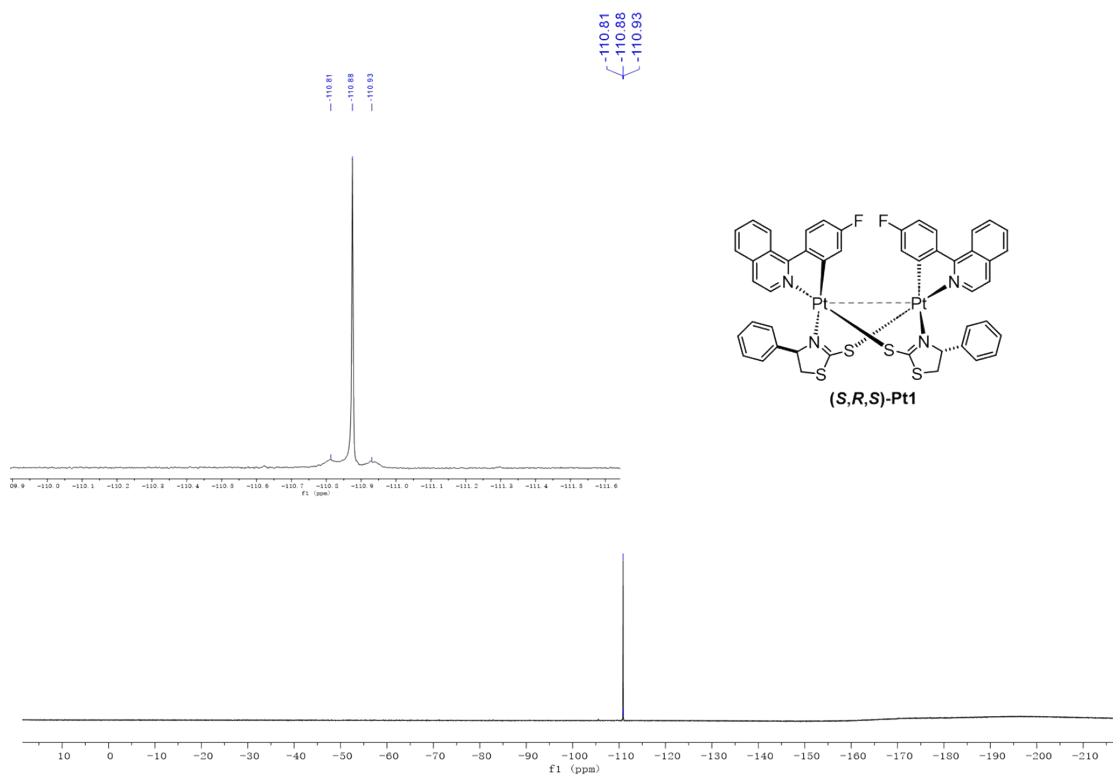


Figure S20. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum for $(S,R,S)\text{-Pt1}$ in CDCl_3 at room temperature.

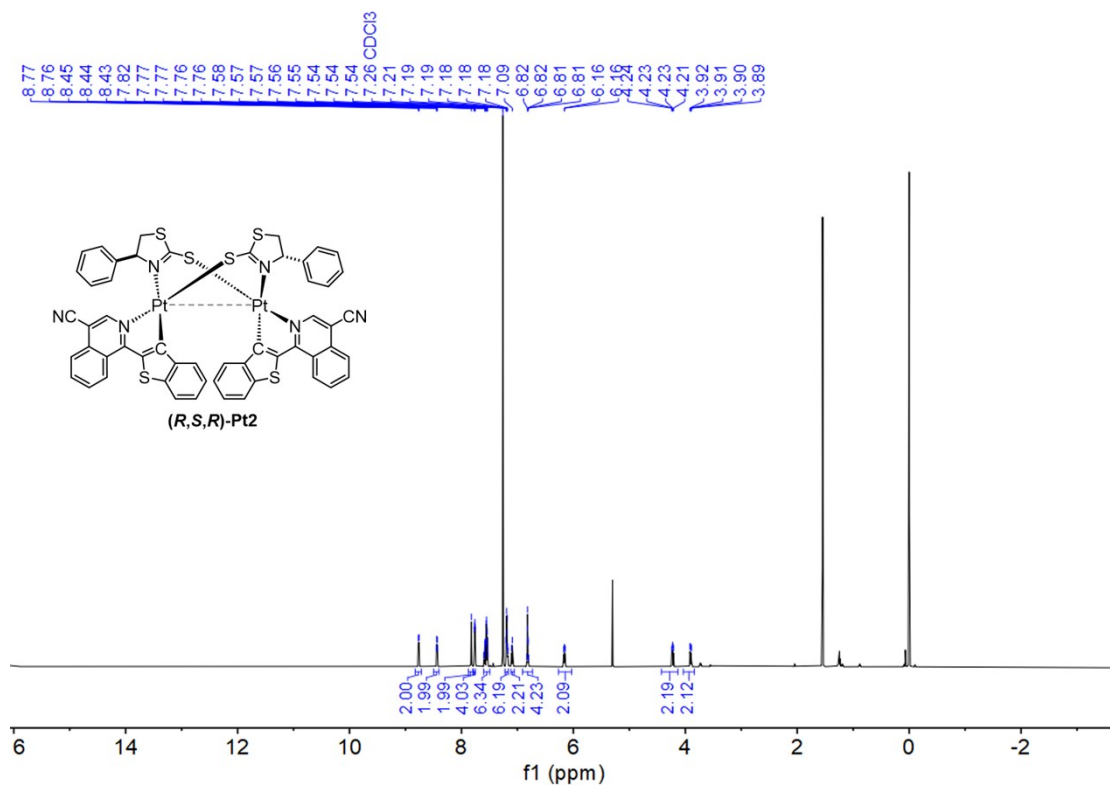


Figure S21. ¹H NMR spectrum for **(R,S,R)-Pt2** in CDCl₃ at room temperature.

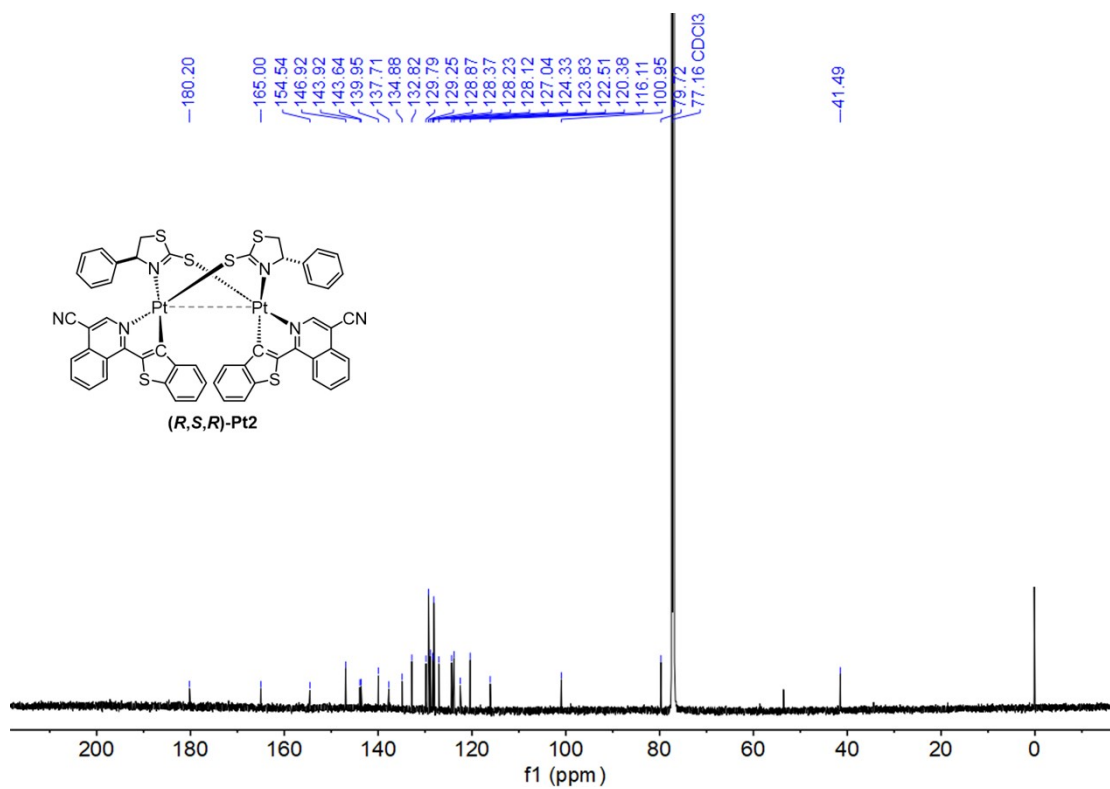


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $(R,S,R)\text{-Pt}2$ in CDCl_3 at room temperature.

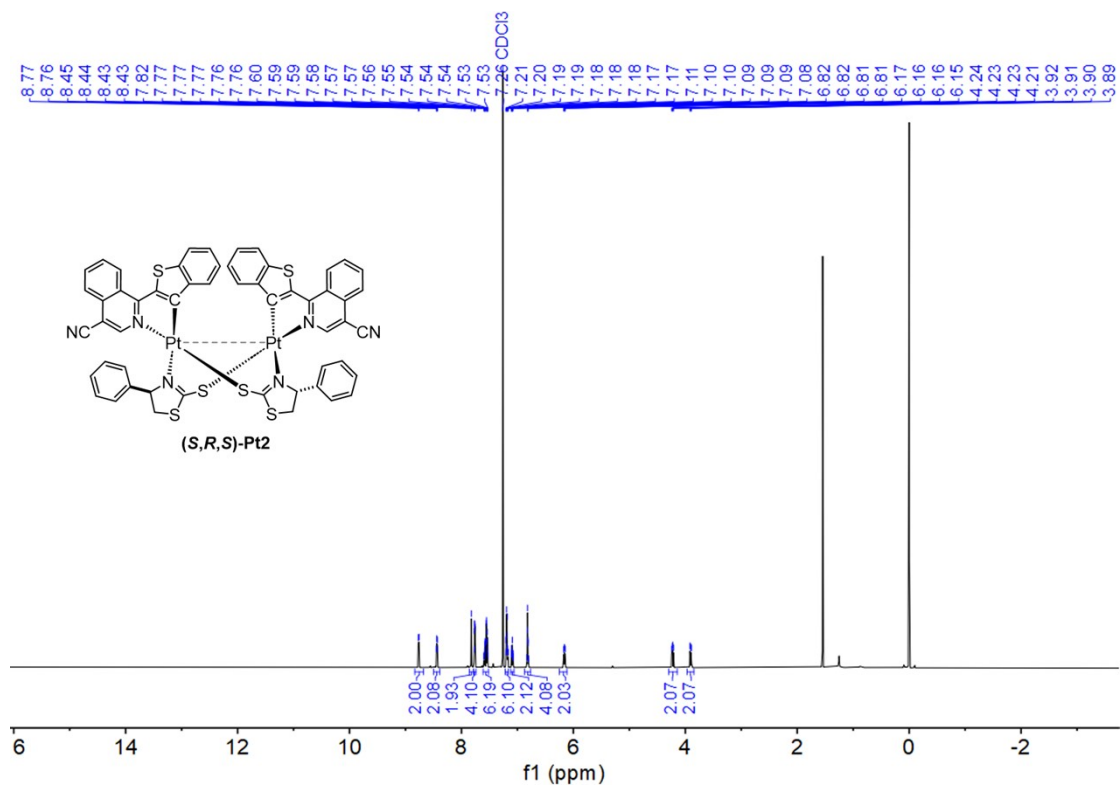


Figure S23. ¹H NMR spectrum for (S,R,S)-Pt₂ in CDCl₃ at room temperature.

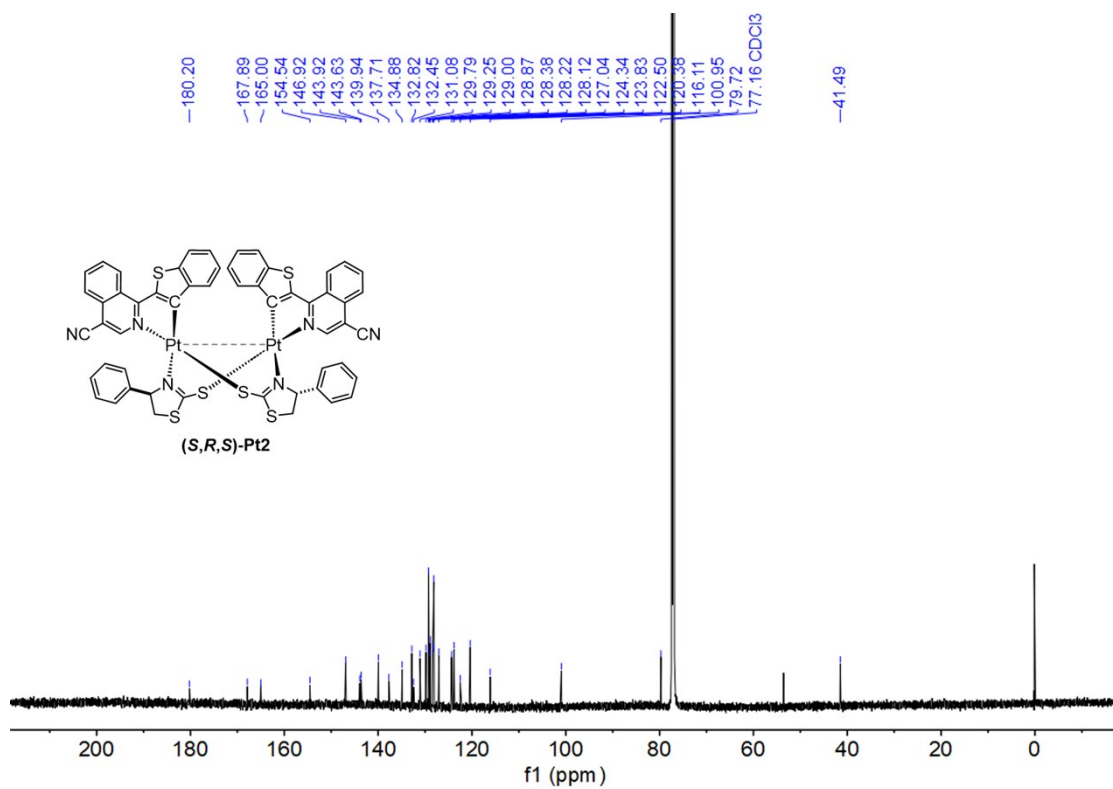


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **(S,R,S)-Pt2** in CDCl_3 at room temperature.

Spectrum Plot Report



| | | | | | | | |
|----------------|-----|--------------|---------|------------|-----------------|-------------------|----------------------|
| Name | 0 | Rack Pos. | | Instrument | Instrument 1 | Operator | |
| Inj. Vol. (ul) | 2 | Plate Pos. | | IRM Status | All ions missed | Acq. Time (Local) | 4/2/2026 10:38:41 AM |
| Data File | F.d | Method (Acq) | ceshi.m | Comment | | (UTC+08:00) | |

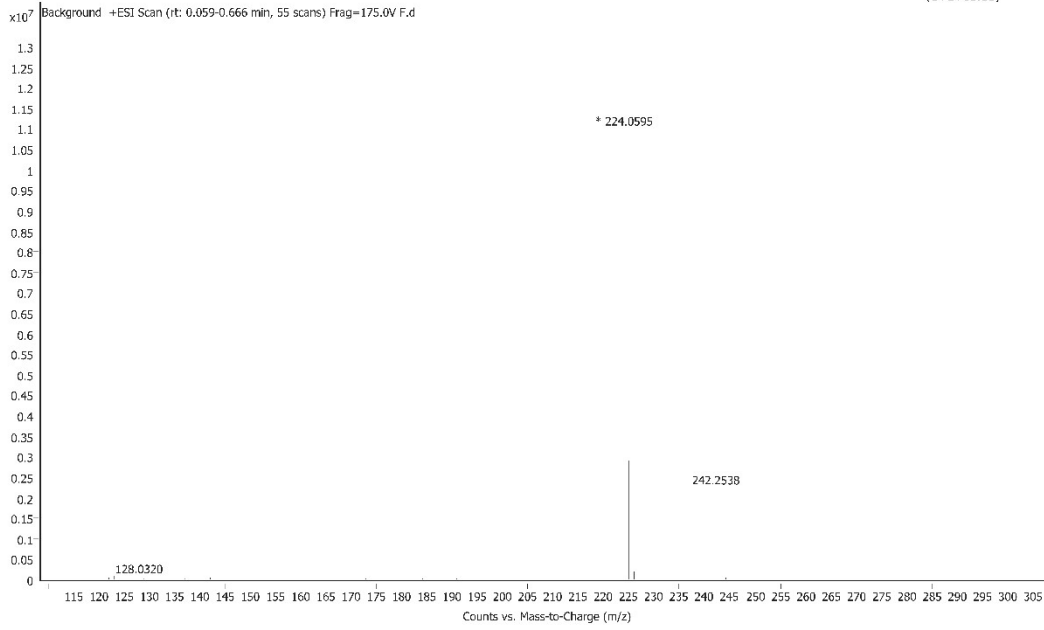


Figure S25. The mass spectrum for **F-Hpiq**.

Spectrum Plot Report



| | | | | | | | |
|----------------|-------|--------------|---------|------------|-----------------|-------------------|----------------------|
| Name | 0 | Rack Pos. | | Instrument | Instrument 1 | Operator | |
| Inj. Vol. (ul) | 2 | Plate Pos. | | IRM Status | All ions missed | Acq. Time (Local) | 4/2/2026 10:40:54 AM |
| Data File | CNT.d | Method (Acq) | ceshi.m | Comment | | (UTC+08:00) | |

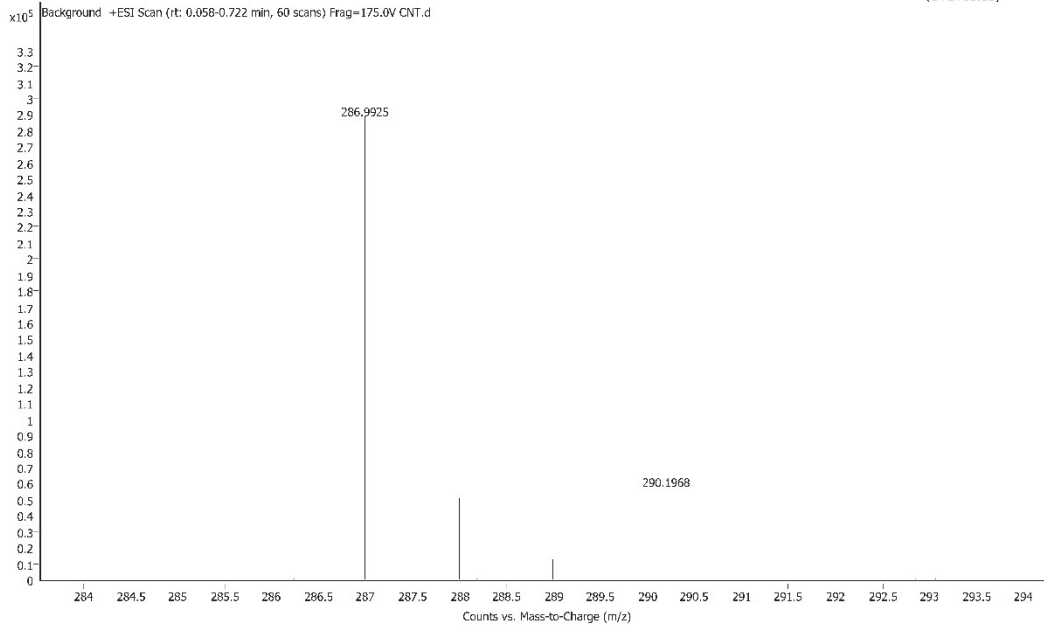


Figure S26. The mass spectrum for CN-Hiqbt.

Spectrum Plot Report



| | | | | | | | |
|----------------|-------|--------------|---------|------------|--------------|-------------------|-----------------------------------|
| Name | 0 | Rack Pos. | | Instrument | Instrument 1 | Operator | |
| Inj. Vol. (ul) | 2 | Plate Pos. | | IRM Status | Success | Acq. Time (Local) | 3/25/2026 10:20:08 AM (UTC+08:00) |
| Data File | 2-1.d | Method (Acq) | ceshi.m | Comment | | | |

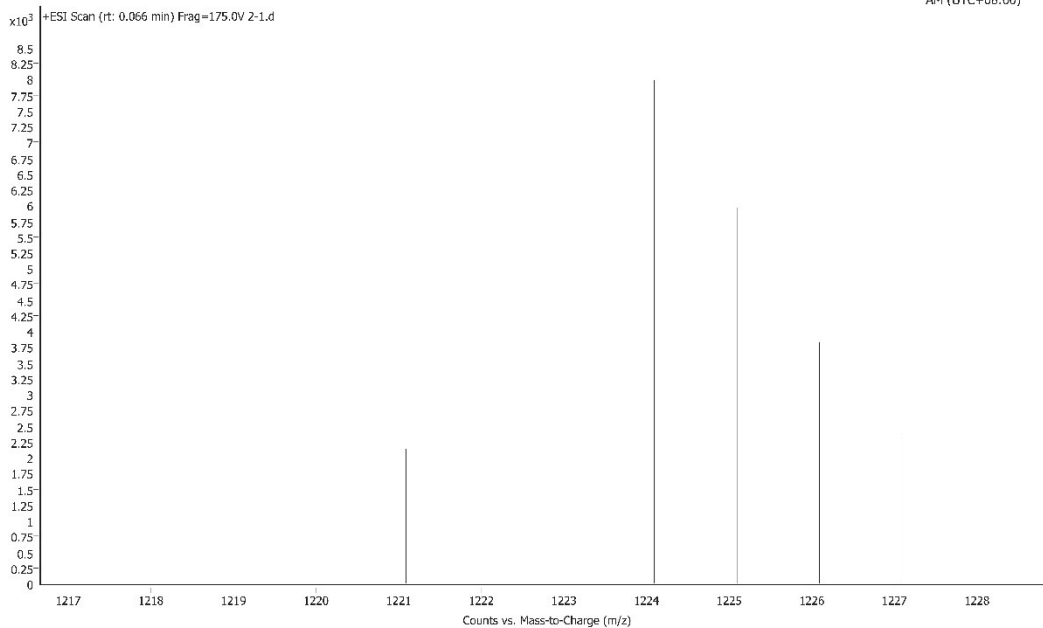


Figure S27. The mass spectrum for *(R,S,R)*-Pt1.

Spectrum Plot Report



| | | | | | | | |
|----------------|-------|--------------|---------|------------|--------------|-------------------|-----------------------------------|
| Name | 0 | Rack Pos. | | Instrument | Instrument 1 | Operator | |
| Inj. Vol. (ul) | 2 | Plate Pos. | | IRM Status | Success | Acq. Time (Local) | 3/25/2026 10:53:05 AM (UTC+08:00) |
| Data File | 2-2.d | Method (Acq) | ceshi.m | Comment | | | |

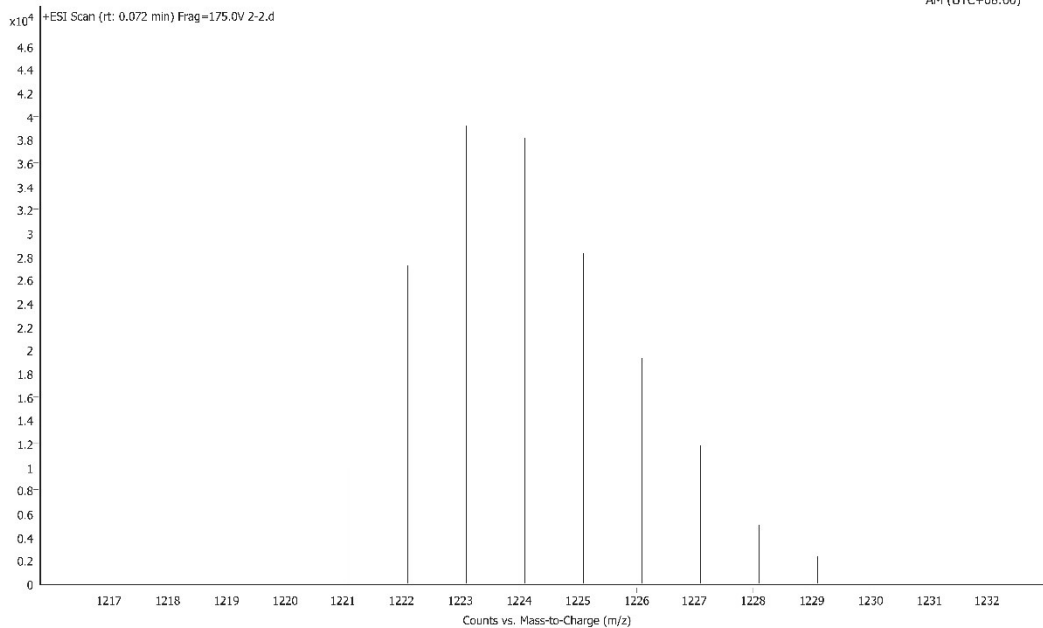


Figure S28. The mass spectrum for **(S,R,S)-Pt1**.

Spectrum Plot Report



| | | | | | | | |
|----------------|---------|--------------|---------|------------|--------------|-------------------|----------------------|
| Name | 0 | Rack Pos. | | Instrument | Instrument 1 | Operator | |
| Inj. Vol. (ul) | 2 | Plate Pos. | | IRM Status | Success | Acq. Time (Local) | 3/25/2026 3:41:04 PM |
| Data File | 2-4-1.d | Method (Acq) | ceshi.m | Comment | | (UTC+08:00) | |

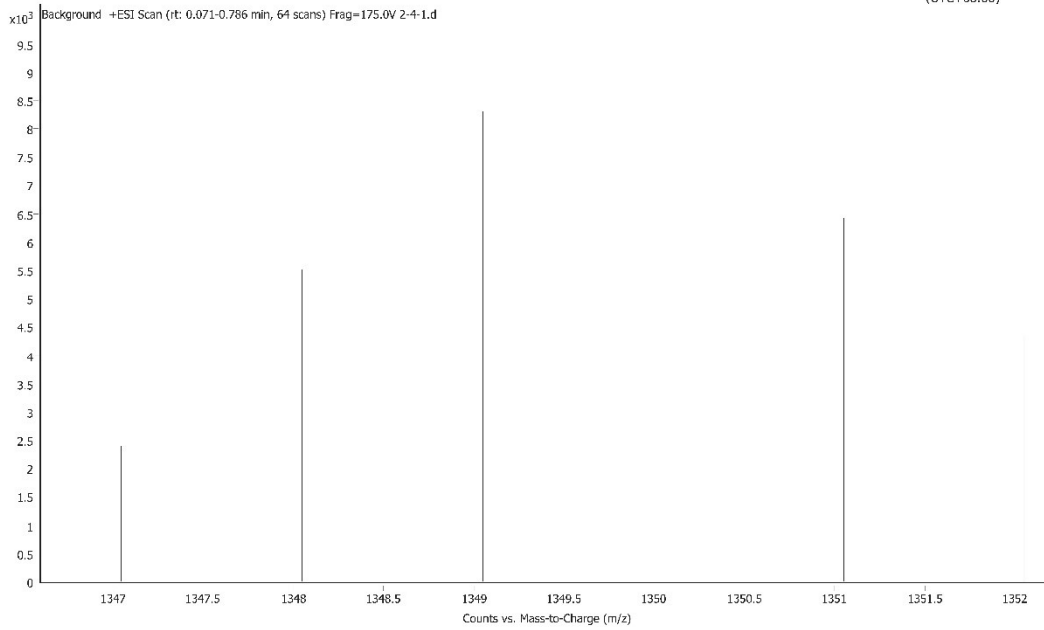


Figure S29. The mass spectrum for **(R,S,R)-Pt2**.

Spectrum Plot Report



| | | | | | | | |
|----------------|-------|--------------|---------|------------|--------------|-------------------|-----------------------------------|
| Name | 0 | Rack Pos. | | Instrument | Instrument 1 | Operator | |
| Inj. Vol. (ul) | 2 | Plate Pos. | | IRM Status | Success | | |
| Data File | Z-4.d | Method (Acq) | ceshi.m | Comment | | Acq. Time (Local) | 3/25/2026 10:59:57 AM (UTC+08:00) |

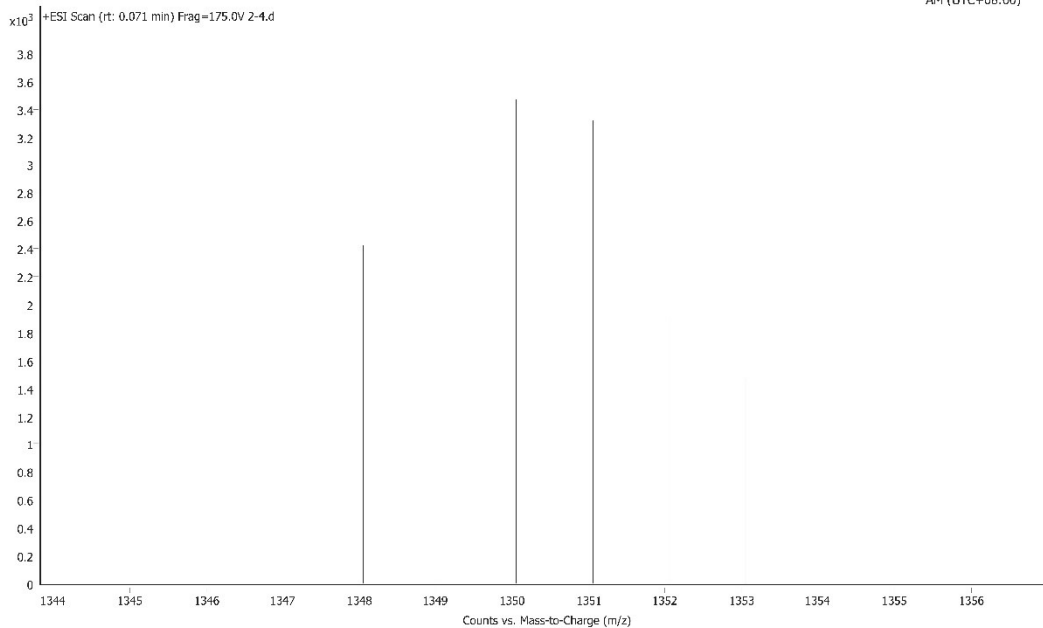


Figure S30. The mass spectrum for **(S,R,S)-Pt2**.

Supplementary References

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