Supplementary Information (SI) for ChemComm.

Supporting Information

Soft chiral-bridged binuclear Pt(II) complexes with cyclometalated N-heterocyclic carbene ligands for multicolor circularly polarized luminescence

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Section S1. Experimental Section

S1.1 Materials and Instruments

All reagents used in the experiment were purchased from ***J&K Scientific*** and ***Energy Chemical*** in this work.

The instrumental information used for characterizations in this work.

Characterization items	**Type**	**Manufacturer**
UV/Vis absorption spectra	U5100	Hitachi
Phosphorescence	F-7000 Fluorescence spectrophotometer	Hitachi
Phosphorescence quantum yield	Edinburgh FLS1000 Spectrofuorophotometer	Edinburgh analytical instrument
Phosphorescence lifetime	Edinburgh FLS1000	Edinburgh analytical instrument
^{1}H NMR and ^{13}C NMR	Nuclear Magnetic Resonance Spectrometer (400 MHz, AVANCE III HD)	Bruker, Germany
CD spectra	CD-250 Chirascan-plus spectrophotometer	Applied Photophysics Limited, U.K
Circularly Polarized Luminescence spectra	CPL-300	*J*ASCO, *J*apan
CCD X-ray single crystal diffractometer	Bruker D8 VENTURE	Bruker, Germany

S1.2 General Experimental Details

Materials and Instrumentation. All reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR (400 MHz) spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm using tetramethylsilane as the internal standard. UV/Vis absorption spectra were recorded on a U-5100 (Hitachi) spectrophotometer with quartz cuvettes of 1 cm path length. Fluorescence spectra were obtained on an F-7000 fluorescence spectrophotometer (Hitachi) at room temperature. Samples in solution and powder were contained in 1 cm path length quartz cuvettes (3.5 mL volume) and quartz tubes, respectively. Emission decay lifetime experiments were performed on an Edinburgh FLS1000 (Edinburgh Analytical Instruments). CD spectra were recorded on a CD-250 Chirascan Plus spectrophotometer at room temperature. CPL spectra were recorded on a JASCO CPL-300 spectrofluoropolarimeter at room temperature. High-resolution mass spectra (HR-MS) were obtained on a SCIEX X500R QTOF.

Measurement of Fluorescence Quantum Yield (Φ). The quantum yield was measured by an integrating sphere.

CPL measurements. Sample preparation: Dissolve 5 mg of the binuclear Pt(II) complex and 95 mg of PMMA in 4 ml of 1,2-dichloroethane by sonicating for 20 min. Each of the obtained solutions was uniformly coated onto a separate 2 cm × 2 cm × 1 mm quartz slide using a glass dropper. The solvent was allowed to evaporate overnight at ambient temperature to obtain the desired thin film samples. **Measurement parameters and procedure:** The quartz slide sample was horizontally attached to a cylindrical holder so that the light path passed perpendicularly through the quartz slide. The detailed measurement parameters are as follows: Ex wavelength 370 nm; Measure range 750 - 440 nm; Data pitch 0.1 nm; CD scale 10000 mdeg/1.0 dOD; D.I.T. 2 sec; Ex bandwidth 40.00 nm; Em bandwidth 20.00 nm; Scanning speed 200 nm/min.

Computational Details. DFT and TD-DFT calculations (PBE1PBE/6-31g*(C,H,N,O,S,F)/SDD(Pt)/PCM) were done by Gaussian 09 software. The ground-state geometry was optimized by DFT based on the X-ray single-crystal structure of Pt(II) complexes. After that, the optimized structure was used to calculate the UV/vis absorption by TD-DFT (DCM as the solvent, pcm method, 100 singlet-singlet transitions).

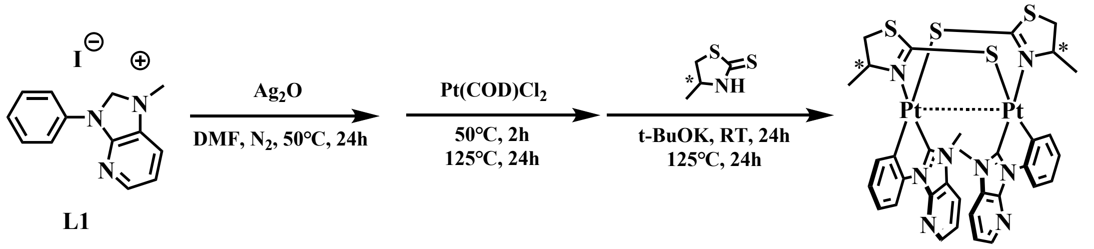
Chirality High-Performance Liquid Chromatography. Conditions for **(*R*,*Sp*,*R*)/(*S*,*Rp*,*S*)-PtF**: column: DAICEL Chiralpak IA; mobile phase: n-hexane / dichloromethane = 2 / 1; flow rate = 1.0 mL / min; temperature: 35℃. Conditions for **(*R*,*Sp*,*R*)/(*S*,*Rp*,*S*)-PtH** and **(*R*,*Sp*,*R*)/(*S*,*Rp*,*S*)-PtO**: column: DAICEL Chiralpak IA; mobile phase: n-hexane / dichloromethane = 1 / 1; flow rate = 1.0 mL / min; temperature: 35℃.

Preparation of a 5% PMMA films. Dissolve 5 mg of the binuclear Pt(II) complex and 95 mg of PMMA in 4 ml of 1,2-dichloroethane by sonicating for 20 min. Coat the resulting solution uniformly onto a 1×1 cm quartz slide and allow the solvent to evaporate overnight at ambient temperature to obtain the desired thin film sample.

Method for crystal growth. Dissolve 5 mg of the binuclear Pt(II) complex in 2 mL of dichloromethane in a test tube. Slowly add 10 mL of petroleum ether along the tube wall to form a solution boundary. Suitable crystal for testing is obtained via liquid-phase diffusion and solvent evaporation.

Section S2. Synthesis Characterizations

(*R*)/(*S*)-4-Methyl-2-thiazolidinethione, Imidazolium salt were synthesized according to the reported literature[1-4].



(*S,Rp,S*)-PtH / (*R,Sp,R*)-PtH

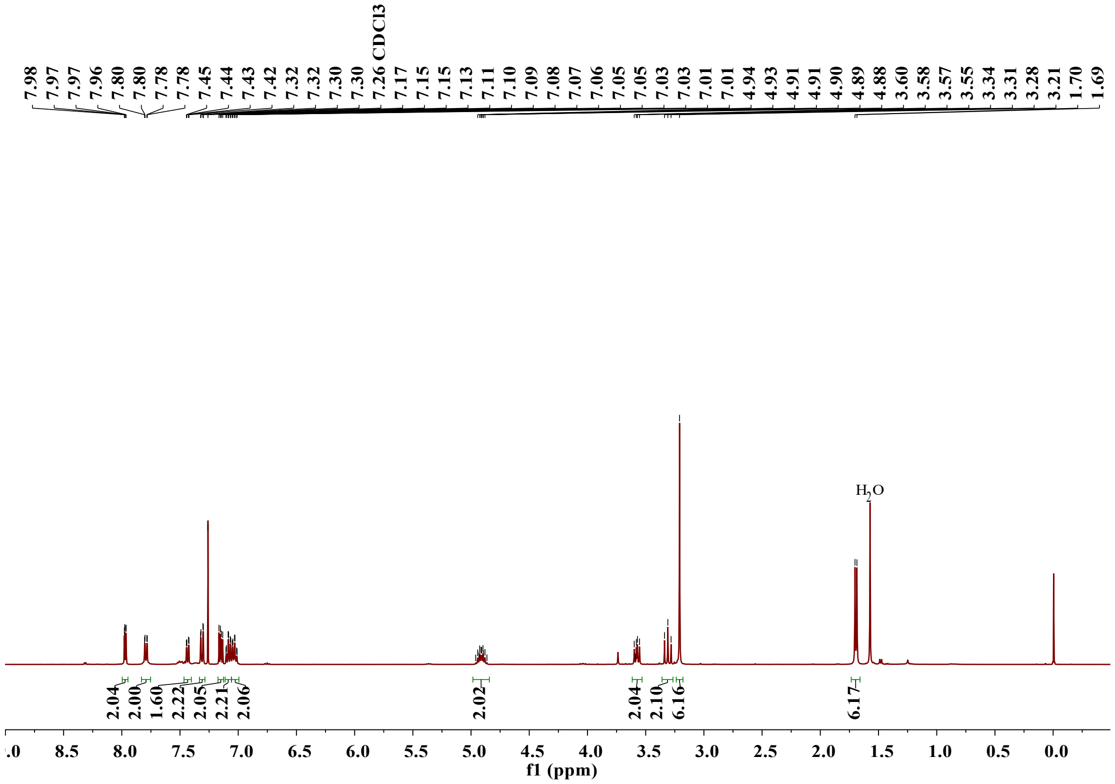
(*R,Sp,R*)-PtH: L1 (1.00 mmol, 0.34 g) and silver(I) oxide (0.60 mmol, 0.14g) were added to a 2-neck flask. After addition of dry DMF (10 mL), the reaction mixture was stirred under argon atmosphere for 24 h at 50 °C in the absence of light. 1,5-Cyclooctadieneplatinum(II) Dichloride (1.00 mmol, 0.37 g) was then added, and the mixture was stirred for a further 2 h at 50 °C, then for 24 h at 125 °C. Afterwards, potassium *tert*-butoxide (2.00 mmol, 0.22g) and (*R*)-4-Methyl-2-thiazolidinethione (2.00 mmol, 0.26 g) were added and the mixture was stirred for 24 h at room temperature and then for a further 24 h at 100 °C. After the reaction was cooled to room temperature, all volatiles were removed under reduced pressure. The crude product was purified by column chromatography (200-300 mesh silica gel powder, PE:DCM = 1:1 (v/v)) to afford pure products. The yields of **(*R,Sp,R*)-PtH** is 21% (112.46 mg, red powder).

(*R,Sp,R*)-PtH

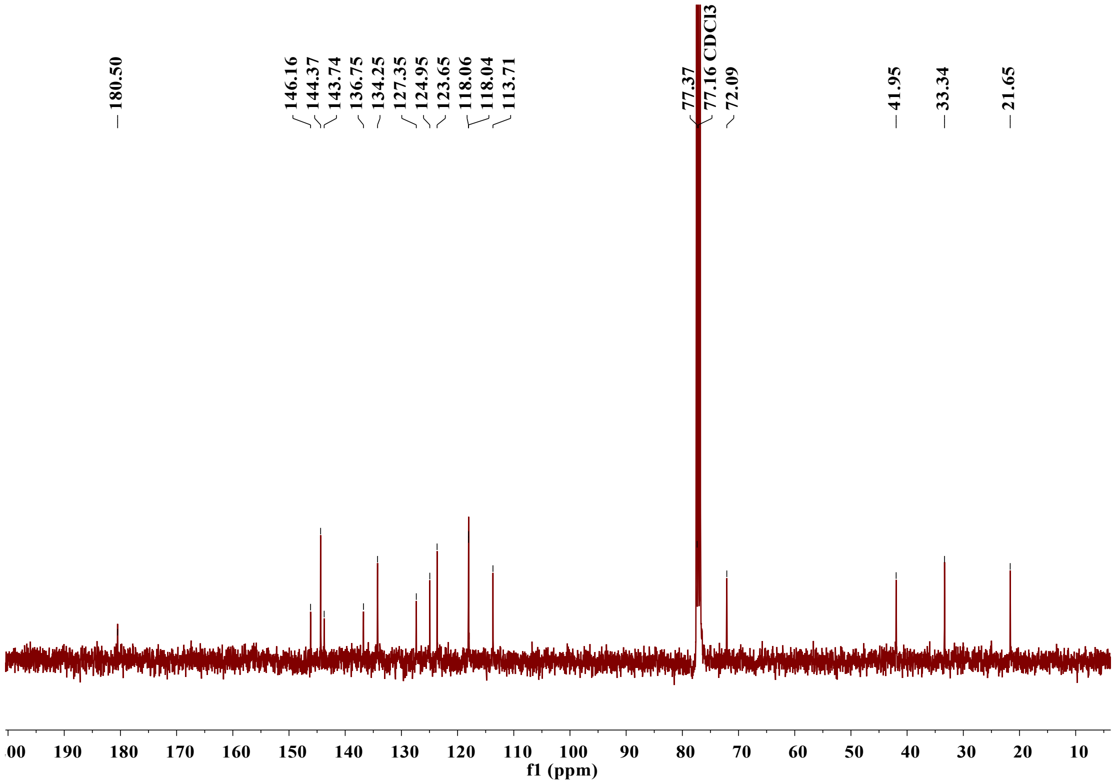
^{1}H NMR (400 MHz, Chloroform-d) δ 7.97 (dd, J = 4.8, 1.4 Hz, 2H), 7.79 (dd, J = 7.7, 1.5 Hz, 2H), 7.43 (dd, J = 7.3, 1.6 Hz, 2H), 7.31 (dd, J = 8.1, 1.4 Hz, 2H), 7.15 (dd, J = 8.1, 4.9 Hz, 2H), 7.08 (td, J = 7.4, 1.6 Hz, 2H), 7.03 (td, J = 7.3, 1.5 Hz, 2H), 4.91 (dp, J = 12.1, 6.7 Hz, 2H), 3.58 (dd, J = 10.9, 7.3 Hz, 2H), 3.31 (t, J = 11.2 Hz, 2H), 3.21 (s, 6H), 1.69 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 180.50, 146.16, 144.37, 143.74, 136.75, 134.25, 127.35, 124.95, 123.65, 118.06, 118.04, 113.71, 77.37, 72.09, 41.95, 33.34, 21.65.

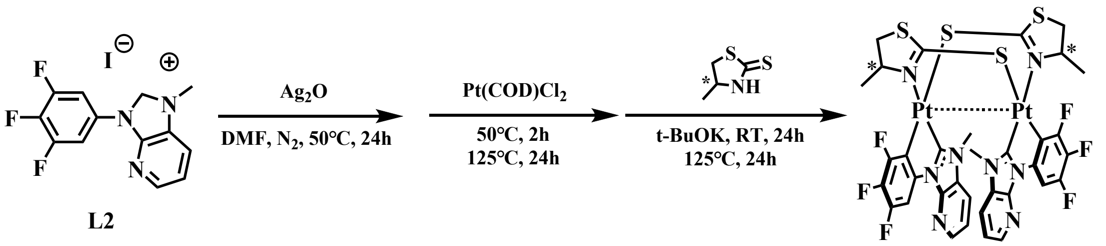
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{34}H_{33}N_8Pt_2S_4$ 1070.0907; Found 1070.0916



^{1}H NMR (400 MHz) of **(*R*,*Sp*,*R*)-PtH** in CDCl$_3$-d^1



^{13}C NMR (101 MHz) of **(*R*,*Sp*,*R*)-PtH** in CDCl$_3$-d^1



(*S*,*Rp*,*S*)-PtF/(*R*,*Sp*,*R*)-PtF

(*R*,*Sp*,*R*)-PtF: L2 (1.00 mmol, 0.39 g) and silver(I) oxide (0.60 mmol, 0.14g) were added to a 2-neck flask. After addition of dry DMF (10 mL), the reaction mixture was stirred under argon atmosphere for 24 h at 50 °C in the absence of light. 1,5-Cyclooctadieneplatinum(II) Dichloride (1.00 mmol, 0.37 g) was then added, and the mixture was stirred for a further 2 h at 50 °C, then for 24 h at 125 °C. Afterwards, potassium *tert*-butoxide (2.00 mmol, 0.22g) and (*R*)-4-Methyl-2-thiazolidinethione (2.00 mmol, 0.26 g) were added and the mixture was stirred for 24 h at room temperature and then for a further 24 h at 100 °C. After the reaction was cooled to room temperature, all volatiles were removed under reduced pressure. The crude product was purified by column chromatography (200-300 mesh silica gel powder, PE:DCM = 2:1 (v/v)) to afford pure products. The yields of **(*R*,*Sp*,*R*)-PtF** is 27% (158.90 mg, orange powder).

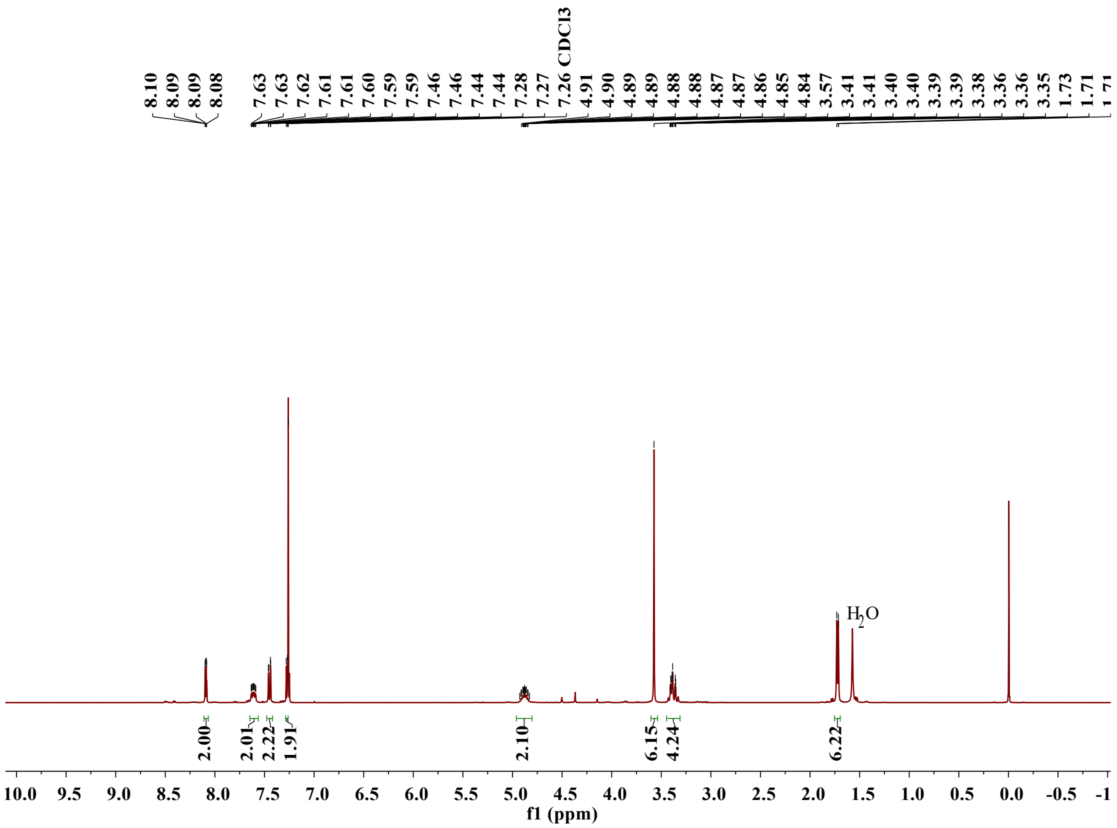
(*R*,*Sp*,*R*)-PtF

^{1}H NMR (400 MHz, Chloroform-d) δ 8.09 (dd, J = 4.9, 1.4 Hz, 2H), 7.61 (ddd, J = 10.7, 6.0, 2.0 Hz, 2H), 7.45 (dd, J = 8.2, 1.4 Hz, 2H), 7.27 (d, J = 4.9 Hz, 2H), 4.87 (dtt, J = 17.9, 7.7, 3.9 Hz, 2H), 3.57 (s, 6H), 3.42 – 3.33 (m, 4H), 1.72 (d, J = 6.4 Hz, 6H).

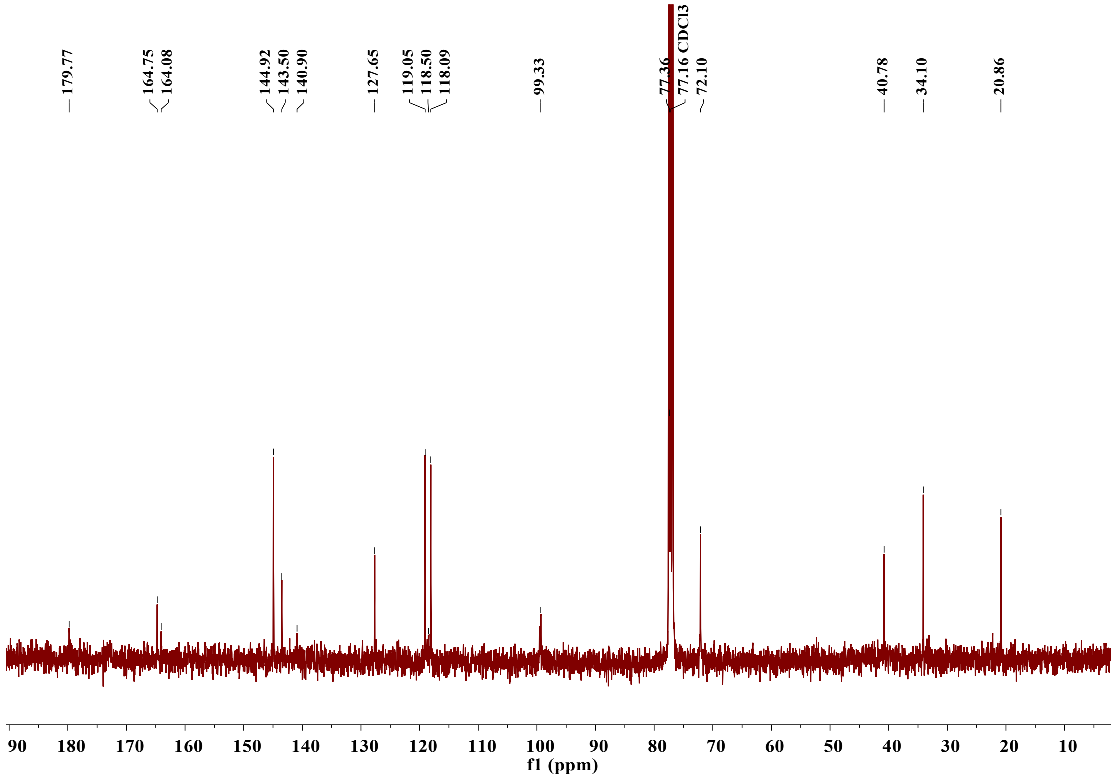
^{13}C NMR (101 MHz, Chloroform-d) δ 179.77, 164.75, 164.08, 144.92, 143.50, 140.90, 127.65, 119.05, 118.50, 118.09, 99.33, 77.36, 72.10, 40.78, 34.10, 20.86.

^{19}F NMR (376 MHz, Chloroform-d) δ -123.21 (d, J = 26.0 Hz), -138.75 – -145.51 (m), -160.08 – -169.78 (m).

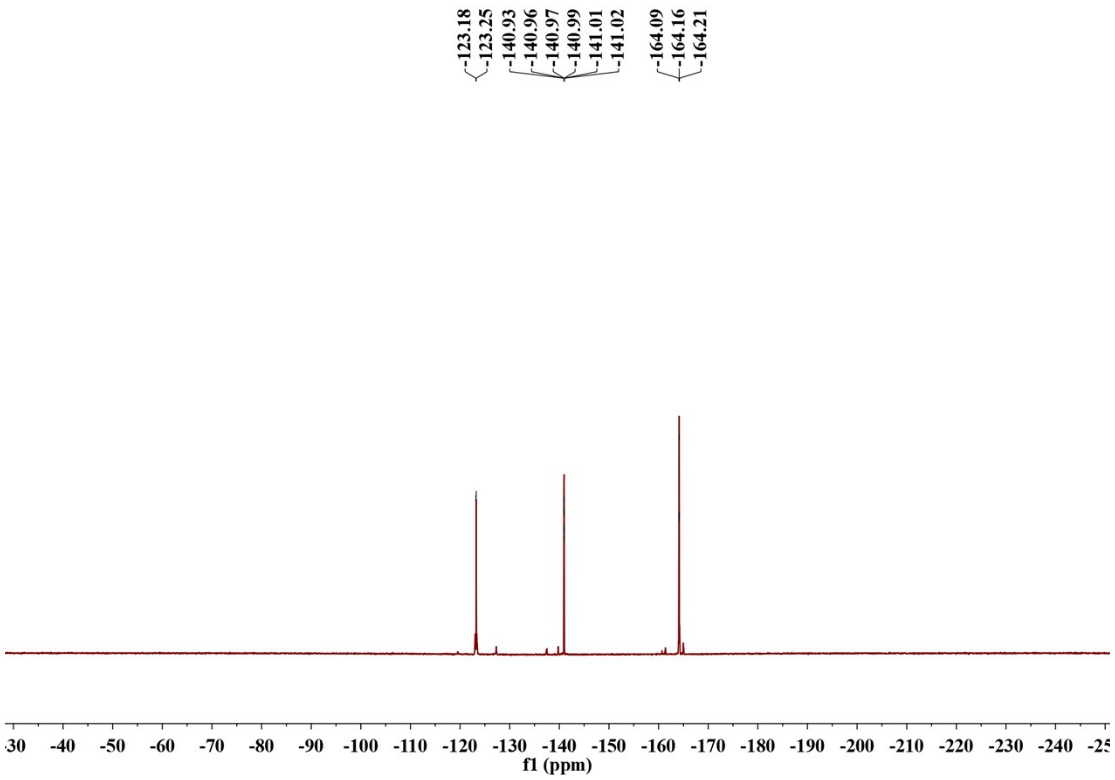
HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{34}H_{27}F_6N_8Pt_2S_4$ 1178.0342; Found 1178.0354



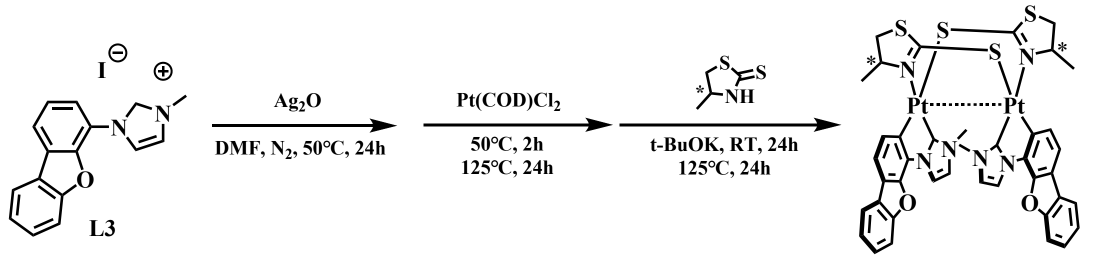
^{1}H NMR (400 MHz) of **(*R*,*Sp*,*R*)-PtF** in CDCl$_3$-d^1



^{13}C NMR (101 MHz) of **(*R*,*Sp*,*R*)-PtF** in CDCl$_3$-d^1



^{19}F NMR (376 MHz) of **(*R*,*Sp*,*R*)-PtF** in CDCl$_3$-d^1



(*S*,*Rp*,*S*)-PtO / (*R*,*Sp*,*R*)-PtO

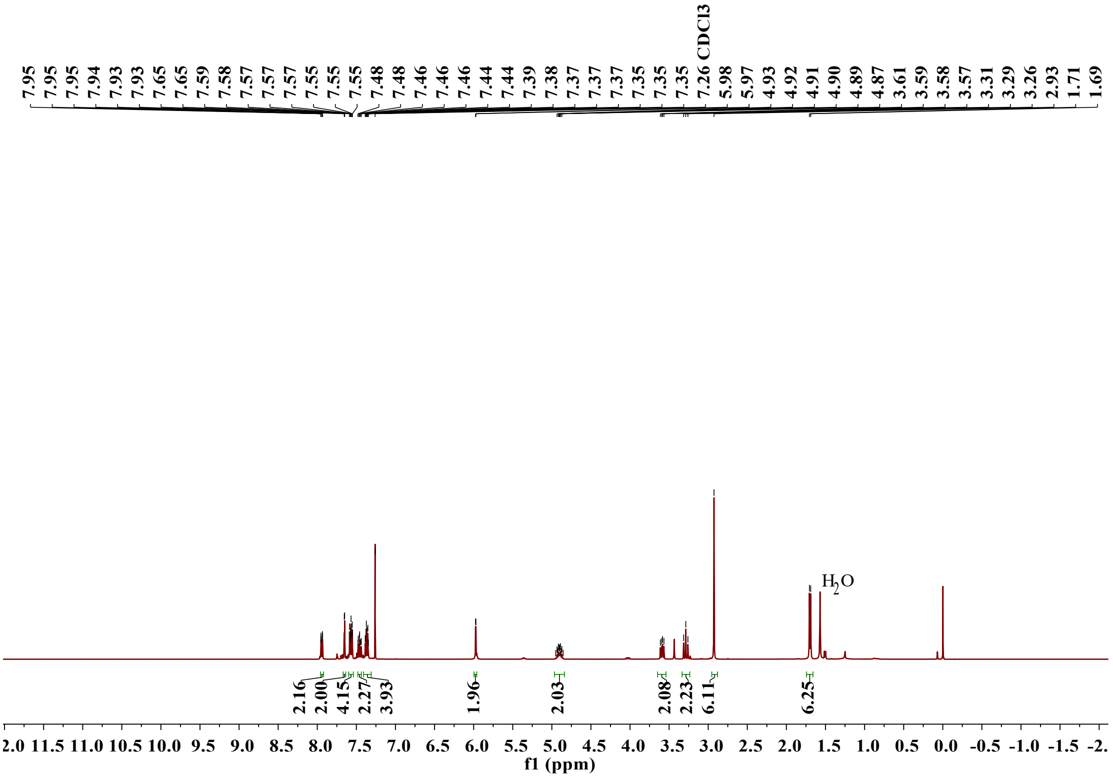
(*R*,*Sp*,*R*)-PtO: L3 (1.00 mmol, 0.38 g) and silver(I) oxide (0.60 mmol, 0.14g) were added to a 2-neck flask. After addition of dry DMF (10 mL), the reaction mixture was stirred under argon atmosphere for 24 h at 50 °C in the absence of light. 1,5-Cyclooctadieneplatinum(II) Dichloride (1.00 mmol, 0.37 g) was then added, and the mixture was stirred for a further 2 h at 50 °C, then for 24 h at 125 °C. Afterwards, potassium *tert*-butoxide (2.00 mmol, 0.22g) and (*R*)-4-Methyl-2-thiazolidinethione (2.00 mmol, 0.26 g) were added and the mixture was stirred for 24 h at room temperature and then for a further 24 h at 100 °C. After the reaction was cooled to room temperature, all volatiles were removed under reduced pressure. The crude product was purified by column chromatography (200-300 mesh silica gel powder, PE:DCM = 1:1 (v/v)) to afford pure products. The yields of ***(R,Sp,R)*-PtO** is 12% (68.94 mg, yellow powder).

***(R,Sp,R)*-PtO**

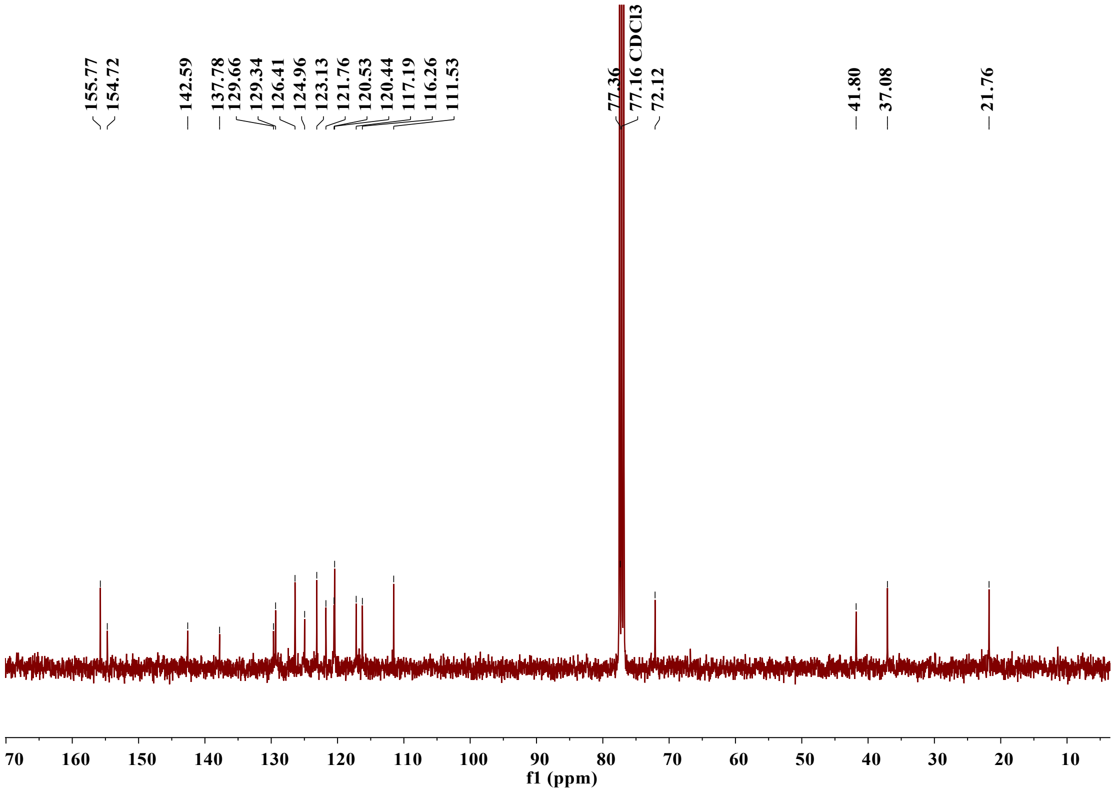
^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (dt, J = 7.2, 1.1 Hz, 2H), 7.65 (d, J = 2.0 Hz, 2H), 7.59 – 7.54 (m, 4H), 7.46 (ddd, J = 8.2, 7.2, 1.4 Hz, 2H), 7.39 – 7.34 (m, 4H), 5.97 (d, J = 2.0 Hz, 2H), 4.90 (dp, J = 10.7, 6.7 Hz, 2H), 3.59 (dd, J = 10.9, 7.3 Hz, 2H), 3.29 (t, J = 10.9 Hz, 2H), 2.93 (s, 6H), 1.70 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 155.73, 154.68, 142.56, 137.75, 129.62, 129.30, 126.38, 124.92, 123.10, 121.72, 120.49, 120.40, 117.15, 116.22, 111.50, 77.33, 72.08, 41.77, 37.05, 21.72.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{40}H_{37}N_6O_2Pt_2S_4$ 1150.1057; Found 1150.1073

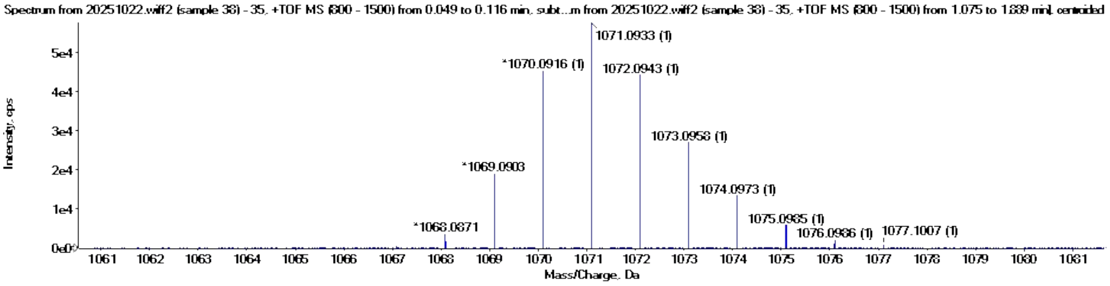


^{1}H NMR (400 MHz) of ***(R,Sp,R)*-PtO** in $CDCl_3$-d^1

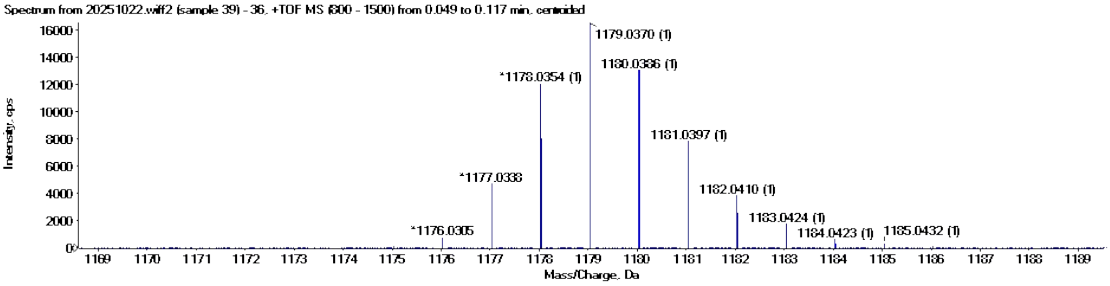


^{13}C NMR (101 MHz) of **(*R*,*Sp*,*R*)-PtO** in $CDCl_3$-d^1

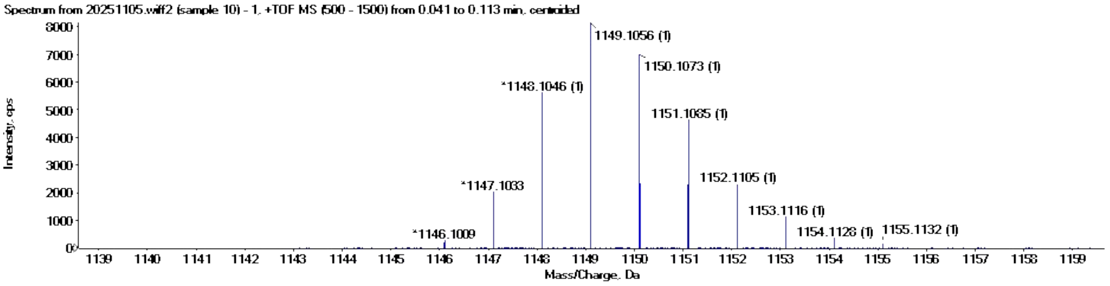
HR-ESI-MS spectra



HR-ESI-MS spectrum (positive ion mode) of **(*R*,*Sp*,*R*)-PtH**



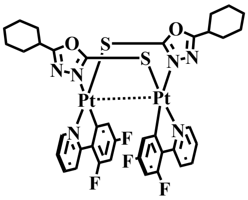
HR-ESI-MS spectrum (positive ion mode) of **(*R*,*Sp*,*R*)-PtF**



HR-ESI-MS spectrum (positive ion mode) of **(*R*,*Sp*,*R*)-PtO**

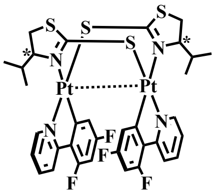
Section S3. Table in supporting information.

Table S1. Comparison of photophysical properties between binuclear Pt(II) complexes and mononuclear Pt(II) complexes.



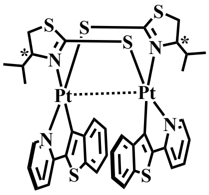
(*R*)-Cy-A

J. Am. Chem. Soc., **2022**, *144*, 2233-2244.



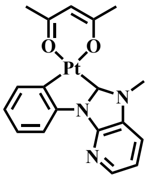
(*D*,*R*,*D*)Pt4a

Angew. Chemie Int. Ed., **2023**, *62*, e202302011.



(*S*,*R*,*S*)-PtII

Inorg. Chem., **2025**, *64*, 22513−22521.



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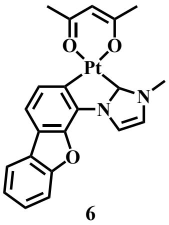
Organometallics **2016**, *35*, 673−680.



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Angew. Chem. Int. Ed., **2010**, *49*, 10214 −10216

Compounds	**medium**	**λ_{em} (nm)**	**FWHM (nm)**	**Φ (%)**	**τ (µs)**	**transition type**	**g_{lum} ×10^{-3}**
(*R*)-Cy-A	10 wt % in mCP	603	~100	83	3.22	MMLCT	2.4
(*D*,*R*,*D*)Pt4a	8 wt % in mCP	610	~100	100	3.01	MMLCT	1.8
(*S*,*R*,*S*)-PtII	5 wt % in PMMA	634, 676	~90	84	4.90	MMLCT	/
(*R*,*Sp*,*R*)-PtH	5 wt % in PMMA	**584**	**61**	66	**1.70**	MMLCT	1.1
(*R*,*Sp*,*R*)-PtF	5 wt % in PMMA	**567**	**53**	71	**1.54**	MMLCT	1.9
(*R*,*Sp*,*R*)-PtO	5 wt % in PMMA	**549**	**50**	36	**1.78**	MMLCT	1.7
4	2 wt % in PMMA	452, 458; 548	~180	64	4.8	MLCT	/
6	2 wt % in PMMA	463, 497	~50	90	23	MLCT	/

Table S2. Experimental g_{PL} values of binuclear Pt(II) complexes.

Compounds (5 wt% PMMA film)	$g_{\mathrm{lum}}\times10^{-3}$
(*R*,*Sp*,*R*)-PtH / (*S*,*Rp*,*S*)-PtH	1.07 / −1.33
(*R*,*Sp*,*R*)-PtF / (*S*,*Rp*,*S*)-PtF	1.90 / −2.33
(*R*,*Sp*,*R*)-PtO / (*S*,*Rp*,*S*)-PtO	1.71 / −1.70

Table S3: Crystallographic data for **(*Rac*)-PtH**.

Compound	**(*Rac*)-PtH**
CCDC #	2505760
Empirical formula	$C_{36}H_{36}Cl_4N_8Pt_2S_4$
Formula weight	1240.95
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	18.7524(2)
b/Å	15.8810(2)
c/Å	13.14550(10)
α/°	90
β/°	90.5210(10)
γ/°	90
Volume/Å^3	3914.66(7)
Z	4
ρ_{calc}g/cm^3	2.106
μ/mm^{-1}	18.013
F(000)	2384.0
Crystal size/mm^3	0.21×0.19×0.16
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.294 to 133.124
Index ranges	$-21 \leq h \leq 22$, $-15 \leq k \leq 18$, $-13 \leq l \leq 15$
Reflections collected	16034
Independent reflections	3415 [R_{int} = 0.0543, R_{sigma} = 0.0291]
Data/restraints/parameters	3415/54/247
Goodness-of-fit on F^2	1.159
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.1058
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.1064
Largest diff. peak/hole / e Å^{-3}	1.46/-2.34

Table S4: Crystallographic data for **(*R*,*Sp*,*R*)-PtF**.

Compound	**(*R*,*Sp*,*R*)-PtF**
CCDC #	2505761
Empirical formula	$C_{35}H_{28}Cl_2F_6N_8Pt_2S_4$
Formula weight	1263.97
Temperature/K	150
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.7069(7)
b/Å	18.5912(15)
c/Å	28.355(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4062.7(6)
Z	4
ρ_{calc}g/cm^3	2.066
μ/mm^{-1}	16.413
F(000)	2408
Crystal size/mm^3	0.08×0.06×0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.684 to 138.178
Index ranges	$-8 \leq h \leq 7, -21 \leq k \leq 22, -34 \leq l \leq 33$
Reflections collected	41358
Independent reflections	7227 [R_{int} = 0.0544, R_{sigma} = 0.0370]
Data/restraints/parameters	7227/3/492
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0320, wR_2 = 0.0782
Final R indexes [all data]	R_1 = 0.0343, wR_2 = 0.0786
Largest diff. peak/hole / e Å^{-3}	0.72/-1.21

Table S5: Crystallographic data for **(*S*,*Rp*,*S*)-PtO**.

Compound	**(*S*,*Rp*,*S*)-PtO**
CCDC #	2505762
Empirical formula	$C_{41}H_{36}N_6O_2S_4Cl_2Pt_2$
Formula weight	1234.08
Temperature/K	99.9(4)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.5038(2)
b/Å	10.2969(2)
c/Å	19.7181(3)
α/°	90
β/°	104.793(2)
γ/°	90
Volume/$Å^3$	2061.95(7)
Z	2
$\rho_{calc}g/cm^3$	1.988
μ/mm^{-1}	15.957
F(000)	1188
Crystal size/mm^3	0.15×0.11×0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.636 to 154.486
Index ranges	$-13 \leq h \leq 10$, $-12 \leq k \leq 12$, $-24 \leq l \leq 24$
Reflections collected	16926
Independent reflections	16926 [$R_{int} = 0.1045$, $R_{sigma} = 0.0210$]
Data/restraints/parameters	16926/65/547
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	$R_1 = 0.0828$, $wR_2 = 0.2236$
Final R indexes [all data]	$R_1 = 0.0847$, $wR_2 = 0.2266$
Largest diff. peak/hole / e $Å^{-3}$	2.76/-2.30

Section S4. Figures in supporting information.

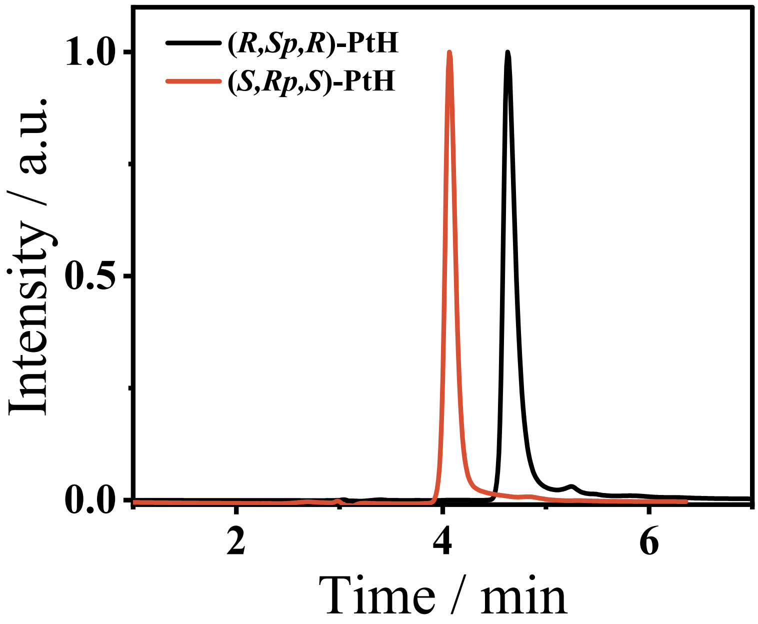

Figure S1. Chiral HPLC traces of **(*R*,*Sp*,*R*)/(*S*,*Rp*,*S*)-PtH**.

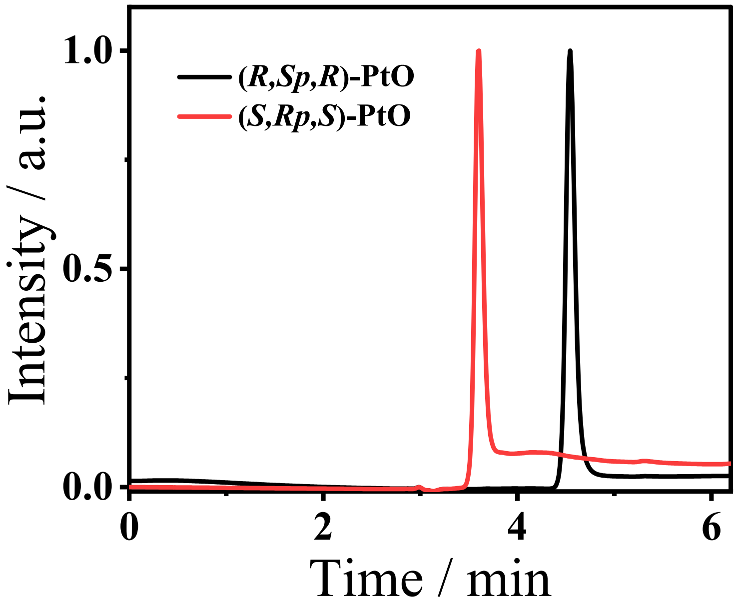

Figure S2. Chiral HPLC traces of **(*R*,*Sp*,*R*)/(*S*,*Rp*,*S*)-PtO**.

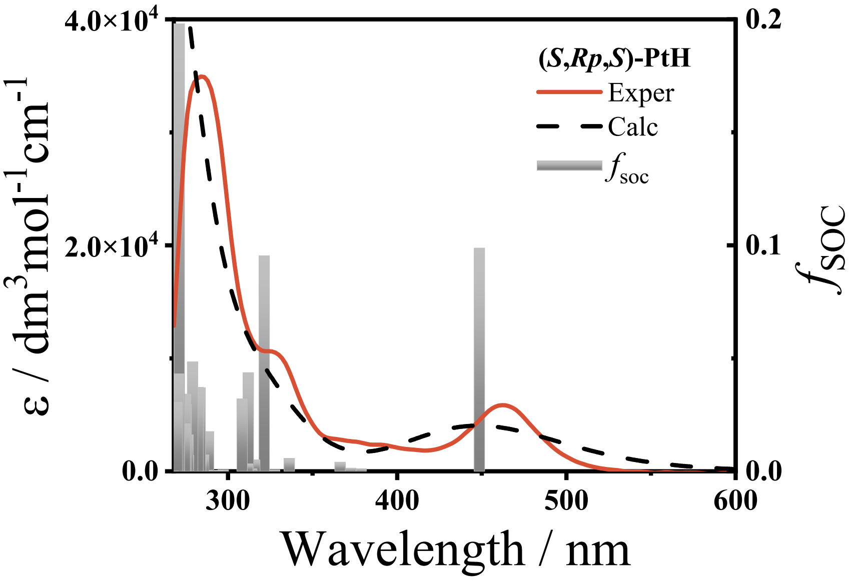

Figure S3. Experimental absorption (3.0×10^{-5} mol dm^{-3}) and calculated absorption spectrum of ***(S,Rp,S)*-PtH** in DCM.

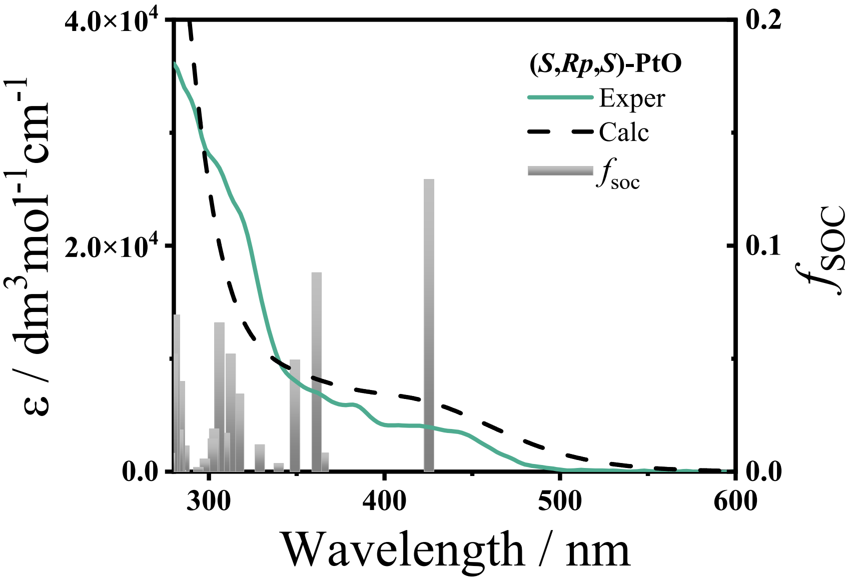

Figure S4. Experimental absorption (3.0×10^{-5} mol dm^{-3}) and calculated absorption spectrum of ***(S,Rp,S)*-PtO** in DCM.

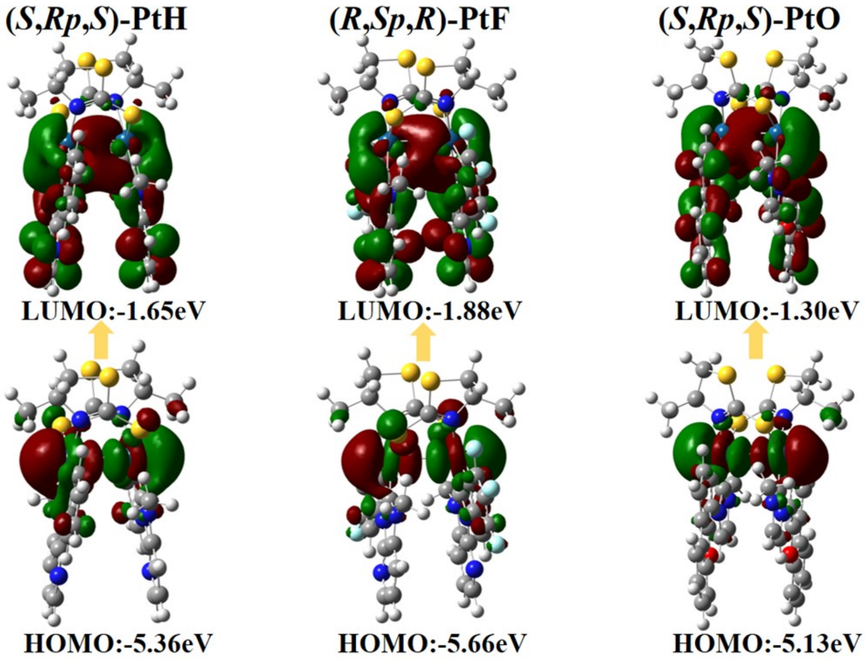

Figure S5. Energy level diagram and frontier molecular orbitals of **(*S*,*Rp*,*S*)-PtH**, **(*R*,*Sp*,*R*)-PtF** and **(*S*,*Rp*,*S*)-PtO** in DCM.

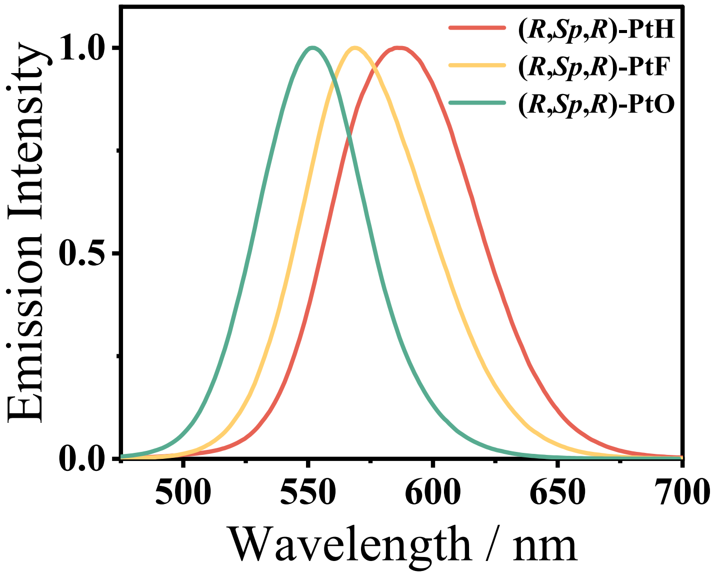

Figure S6. Normalized emission spectra of binuclear Pt(II) complexes in DCM (3.0 × 10^{-5} mol dm^{-3}).

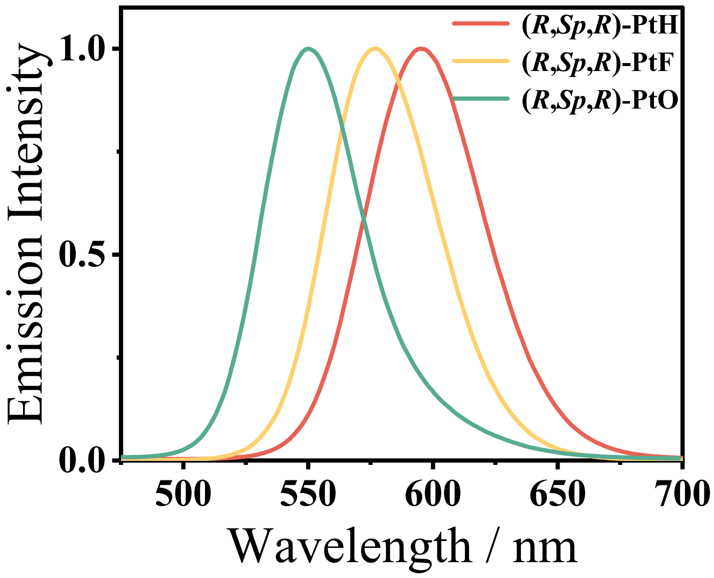

Figure S7. Normalized emission spectra of binuclear Pt(II) complexes in powder.

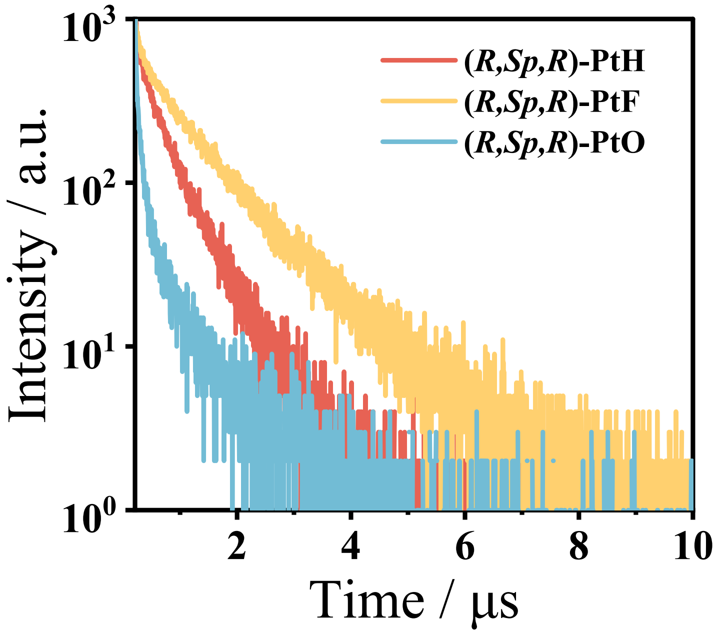

Figure S8. PL decay spectra of binuclear Pt(II) complexes in DCM (3.0×10^{-5} mol dm^{-3}).

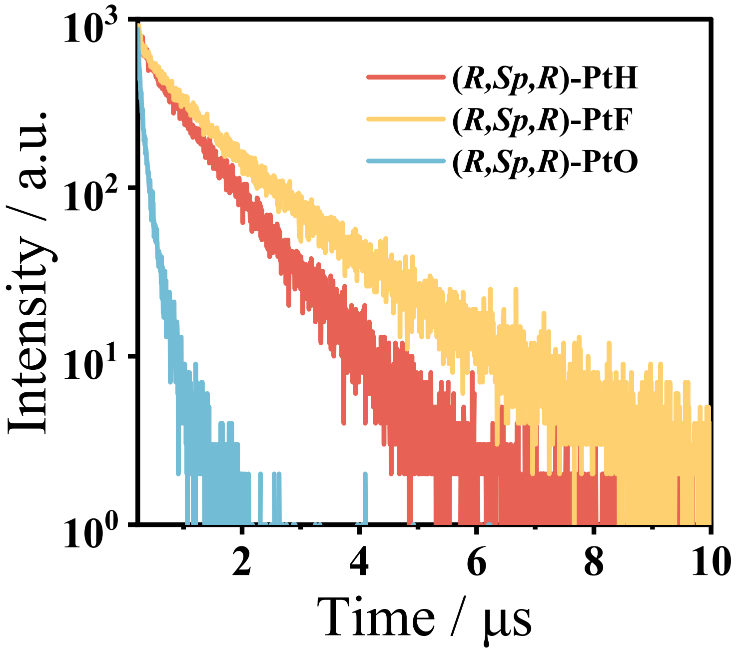

Figure S9. PL decay spectra of binuclear Pt(II) complexes in power.

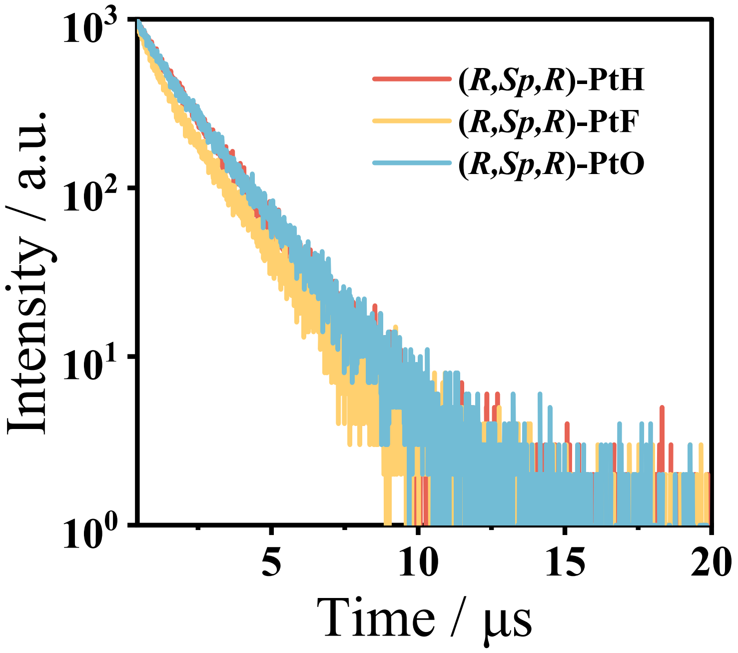

Figure S10. PL decay spectra of binuclear Pt(II) complexes in 5%-doped PMMA films.

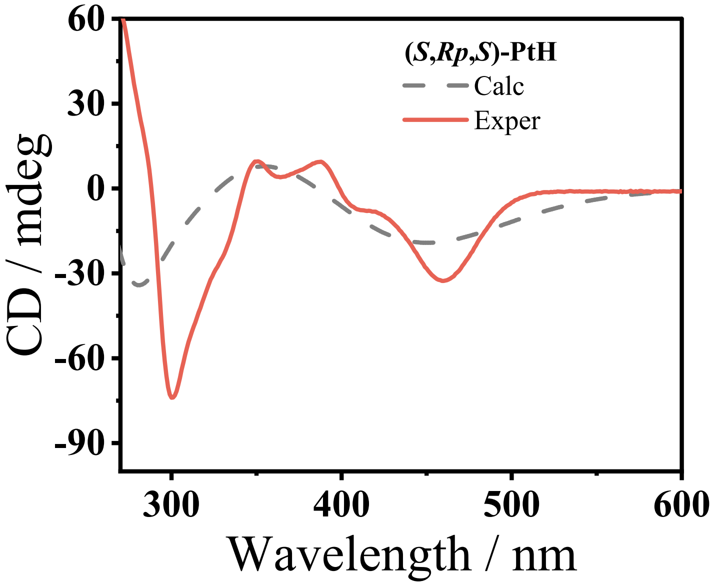

Figure S11. CD spectra of **(*S*,*Rp*,*S*)-PtH** in DCM (3.0 × 10^{-5} mol dm^{-3}) and calculated CD spectra of **(*S*,*Rp*,*S*)-PtH** in DCM.

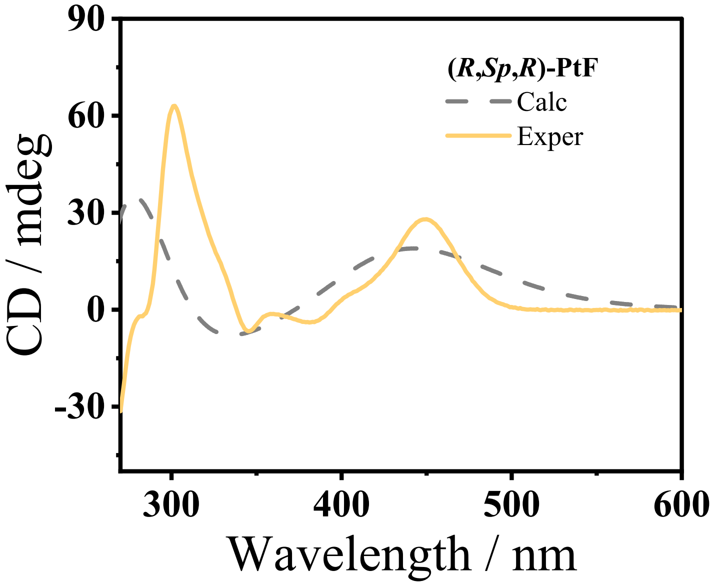

Figure S12. CD spectra of **(*R*,*Sp*,*R*)-PtF** in DCM (3.0 × 10^{-5} mol dm^{-3}) and calculated CD spectra of **(*R*,*Sp*,*R*)-PtF** in DCM.

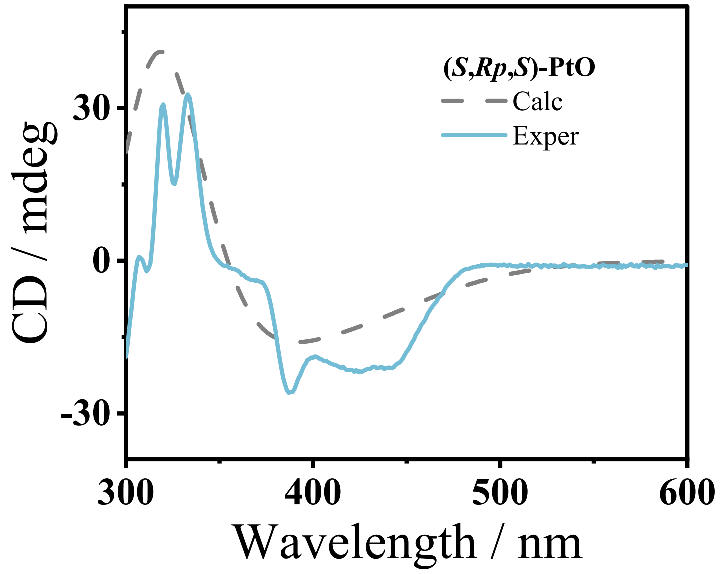

Figure S13. CD spectra of **(*S*,*Rp*,*S*)-PtO** in DCM (3.0 × 10^{-5} mol dm^{-3}) and calculated CD spectra of **(*S*,*Rp*,*S*)-PtO** in DCM.

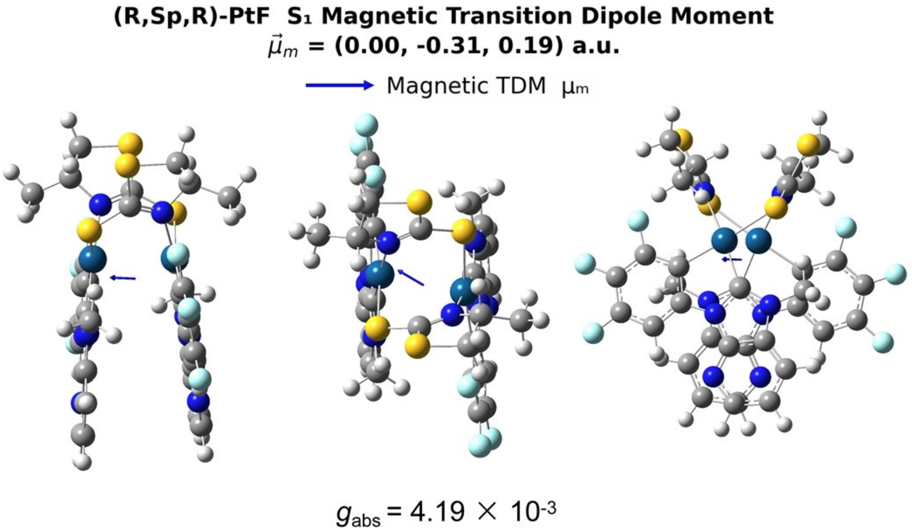

Figure S14. The magnetic transition dipole moment of **(*R*,*Sp*,*R*)-PtF** and the theoretical calculation of g_{abs}.

Reference

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