Supporting information

Potential Switchable Circularly Polarized Luminescence from Chiral Cyclometalated Platinum(II) Complexes

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Synthesis and characterization of complexes (+)-**1**, (+)-**2** and (+)-**3**

[Pt((+)-L_1)(Dmpi)]Cl ((+)-**1**). To a vigorously stirred solution of Pt((+)-L_1)Cl (1 mmol, 560 mg) in 20 mL dichloromethane pre-covered by 40 mL water, a small excess of 2,6-dimethylphenylisocyanide (1.05 mmol, 138 mg) dissolved in 8 mL dichloromethane was added. After reaction for 1 hour at room temperature, the aqueous phase was separated and the solvents were evaporated and red powders were obtained (95%). The pure product was obtained after several recrystallizations in MeOH/H_2O solution. MS (ESI) (m/z): $[M]^+$ calcd for $C_{32}H_{30}N_3Pt$, 651.2; found, 651.3. Anal. Calcd for $C_{32}H_{30}ClN_3Pt$ ((+)-**1**): C, 55.93; H, 4.40; N, 6.12%. Found: C, 55.89; H, 4.38; N, 6.08%. ^{1}H NMR (600 MHz, MeOD-d4, RT): δ 7.83 [s, 1H], 7.68 [t, *J* = 7.8 Hz, 1H], 7.60 [s, 1H], 7.59 [d, *J* = 7.8 Hz, 1H], 7.26 [d, *J* = 7.8 Hz, 1H], 7.13 [d, *J* = 7.2 Hz, 1H], 6.94 [d, *J* = 7.2 Hz, 2H], 6.90 [d, *J* = 7.2 Hz, 1H], 6.76 [d, *J* = 6.6 Hz, 1H], 6.65 [t, *J* = 6.6 Hz, 1H], 6.43 [t, *J* = 6.6 Hz, 1H], 3.14 [d, *J* = 18.0 Hz, 2H], 2.85-2.89 [m, 1H], 2.60 [t, *J* = 5.4 Hz, 1H], 2.38-2.41 [m, 1H], 1.95 [s, 6H], 1.46 [s, 3H], 1.22 [d, *J* = 10.8 Hz, 1H], 0.64 [s, 3H]. ^{13}C NMR (151 MHz, MeOD-d4, RT): δ 165.0, 156.0, 155.7, 153.3, 150.1, 148.0, 147.8, 144.1, 139.7, 137.9, 136.4, 136.0, 132.5, 132.0, 130.0, 127.3, 127.1, 127.0, 125.9, 121.3, 121.1, 46.0, 40.7, 40.1, 34.4, 32.2, 25.9, 22.1, 19.8.

[Pt((+)-L_2)(Dmpi)]Cl ((+)-**2**). To a vigorously stirred solution of Pt((+)-L_2)Cl (1 mmol, 650 mg) in 50 mL dichloromethane, an equivalent amount of 2,6-dimethylphenylisocyanide (1 mmol, 131 mg) dissolved in 30 mL dichloromethane was slowly added over 1 hour. After the reaction mixture was stirred at room temperature for 4 hours, the solvent was removed under reduced pressure, and the residue was purified by

flash chromatography on Al_2O_3 column with DCM/MeOH (20/1, v/v) as eluent to give a yellow solid (70%). MS (ESI) (m/z): $[M]^+$ calcd for $C_{39}H_{40}N_3Pt$, 745.3; found, 745.5. Anal. Calcd for $C_{39}H_{40}ClN_3Pt$ ((+)-**2**): C, 59.95; H, 5.16; N, 5.38%. Found: C, 59.93; H, 5.13; N, 5.35%. ^{1}H NMR (600 MHz, CD_2Cl_2-d2, RT): δ 8.25 [s, 2H], 7.67 [s, 2H], 7.55 [d, *J* = 7.8 Hz, 2H], 7.45 [t, *J* = 7.8 Hz, 1H], 7.36 [t, *J* = 7.8 Hz, 1H], 7.32 [d, *J* = 7.8 Hz, 2H], 3.18-3.21 [m, 4H], 2.81-2.83 [m, 2H], 2.77-2.80 [m, 2H], 2.60 [s, 6H], 2.38-2.41 [m, 2H], 1.44 [s, 6H], 1.28 [d, *J* = 10.2 Hz, 2H], 0.71 [s, 6H]. ^{13}C NMR (151 MHz, CD_2Cl_2-d2, RT): δ 168.5, 166.3, 152.1, 150.2, 145.6, 144.7, 136.2, 131.3, 129.1, 127.2, 126.1, 124.1, 121.0, 45.0, 39.9, 39.6, 33.9, 31.8, 25.8, 21.6, 19.5. The compound (+)-**2**-OTf was obtained by replacement Cl with OTf anion. An aqueous solution (10 mL) of silver trifluoromethanesulfonate (0.22 mmol, 56.5 mg) was added into a 20 mL dichloromethane solution of (+)-**2** (0.2 mmol, 156.2 mg). After vigorously stirring for 15 minutes, the organic phase was separated and evaporated under vacuum.

$[Pt_3((+)\text{-}L_2)_2(Dmpi)_4](ClO_4)_4$ ((+)-**3**). A mixture of (+)-**2** (1 mmol, 781 mg) and excess 2,6-dimethylphenylisocyanide (2 mmol, 262 mg) was stirred in 40 mL dichloromethane at room temperature. After stirring vigorously for 24 hours, an aqueous solution of $AgClO_4$ (2 mmol, 414 mg) was added and reacted for another 24 hours. The organic layer was separated, and the aqueous phase was extracted twice with dichloromethane (20 mL×2). The organic layer was combined and washed twice with water, then dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was washed with n-hexane twice, and green-yellow crystals were isolated by recrystallization in chloroform at 273K (50%). MS (ESI) (m/z): $[M]^{4+}$ calcd for $C_{96}H_{98}N_8Pt_3$, 487.0; found, 487.5. Anal. Calcd for $C_{96}H_{98}Cl_4N_8O_{16}Pt_3$ ((+)-**3**): C, 49.13; H, 4.21; N, 4.77%.

Found: C, 49.10; H, 4.17; N, 4.75%. ^{1}H NMR (400 MHz, CD_2Cl_2-d2, 273.15 K): δ 9.29 [s, 2H], 7.79 [s, 2H], 7.73 [d, *J* = 7.6 Hz, 2H], 7.39-7.44 [m, 8H], 7.25 [d, *J* = 7.6 Hz, 4H], 7.21 [t, *J* = 7.6 Hz, 2H], 7.04 [d, *J* = 7.6 Hz, 4H], 6.52 [d, *J* = 7.2 Hz, 2H], 3.36-3.41 [m, 2H], 3.20-3.25 [m, 2H], 2.71-2.75 [m, 6H], 2.46 [s, 12H], 2.42-2.44 [m, 2H], 2.22-2.32 [m, 6H], 2.17 [s, 12H], 1.98-2.02 [m, 2H], 1.33 [s, 6H], 1.11 [s, 6H], 1.06-1.09 [m, 2H], 0.57 [s, 6H], 0.33 [s, 6H], -0.53 [m, 2H]. ^{13}C NMR (100 MHz, CD_2Cl_2-d2, 273.15 K): δ 164.2, 160.0, 152.6, 149.5, 148.2, 148.0, 147.7, 147.2, 145.0, 144.5, 143.0, 142.8, 136.6, 136.0, 131.9, 131.5, 131.1, 129.1, 128.7, 127.9, 127.1, 125.2, 124.7, 123.4, 122.3, 119.4, 44.5, 43.9, 39.6, 39.2, 39.0, 38.8, 34.0, 33.1, 32.0, 30.1, 25.6, 25.2, 22.1, 21.4, 19.2, 18.8.

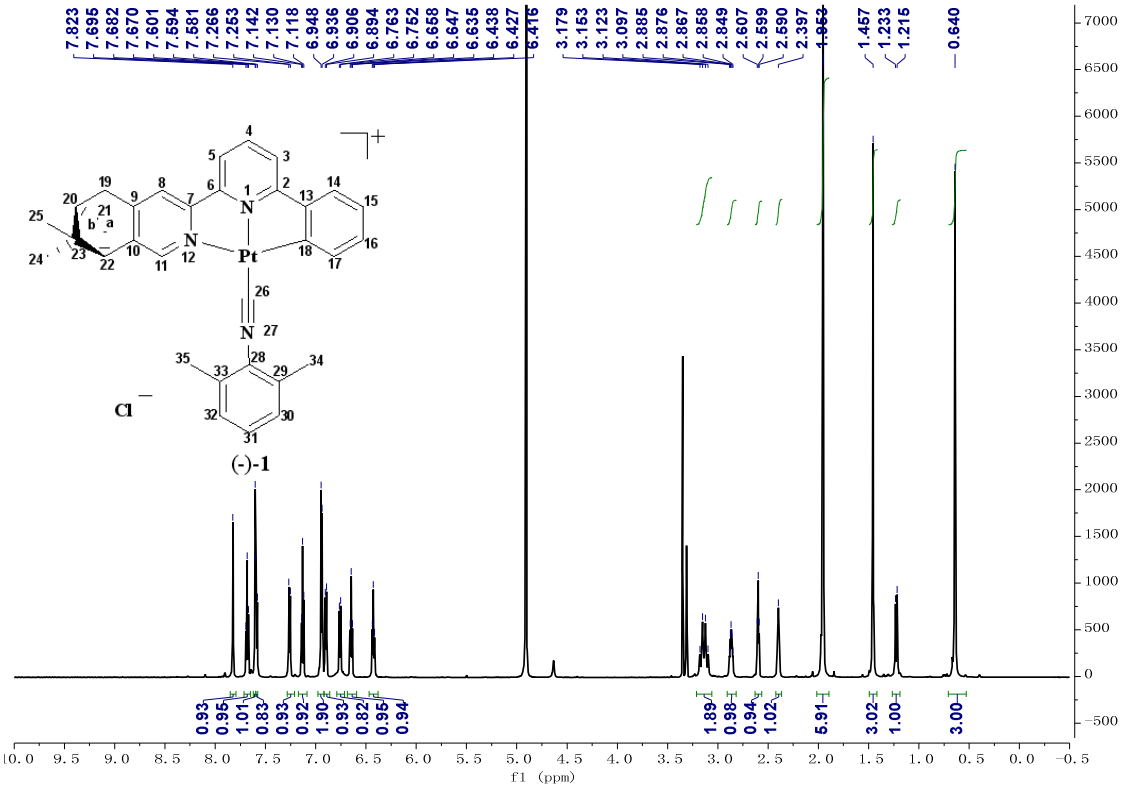

Figure S1. The ^{1}H NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

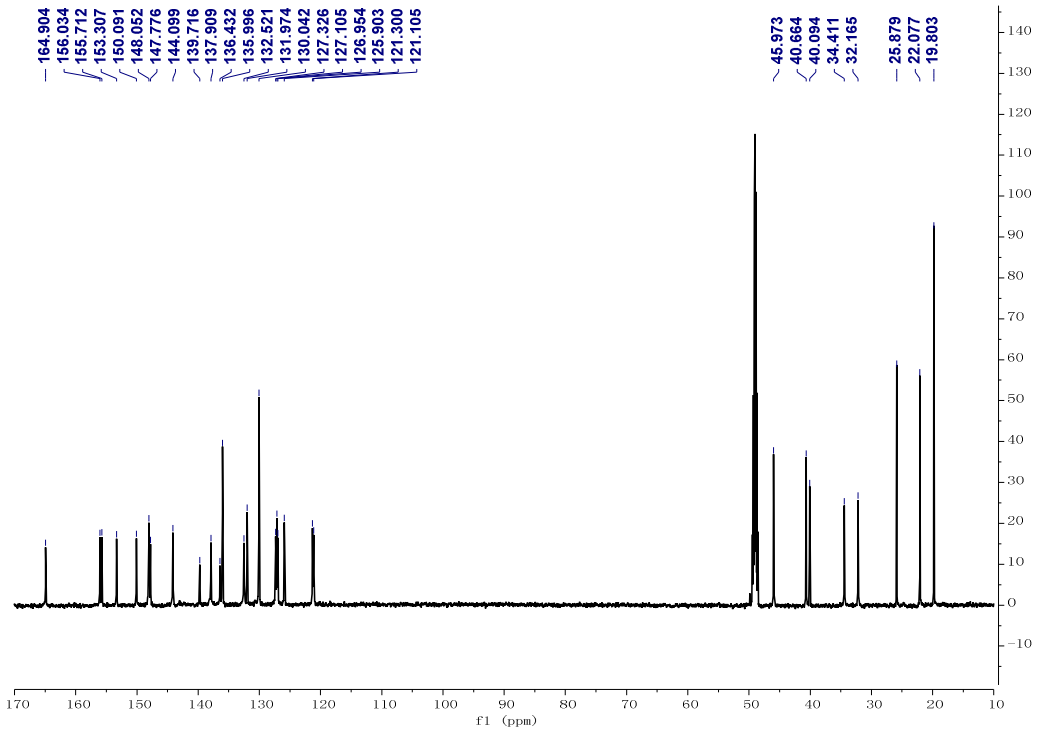

Figure S2. The ^{13}C NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

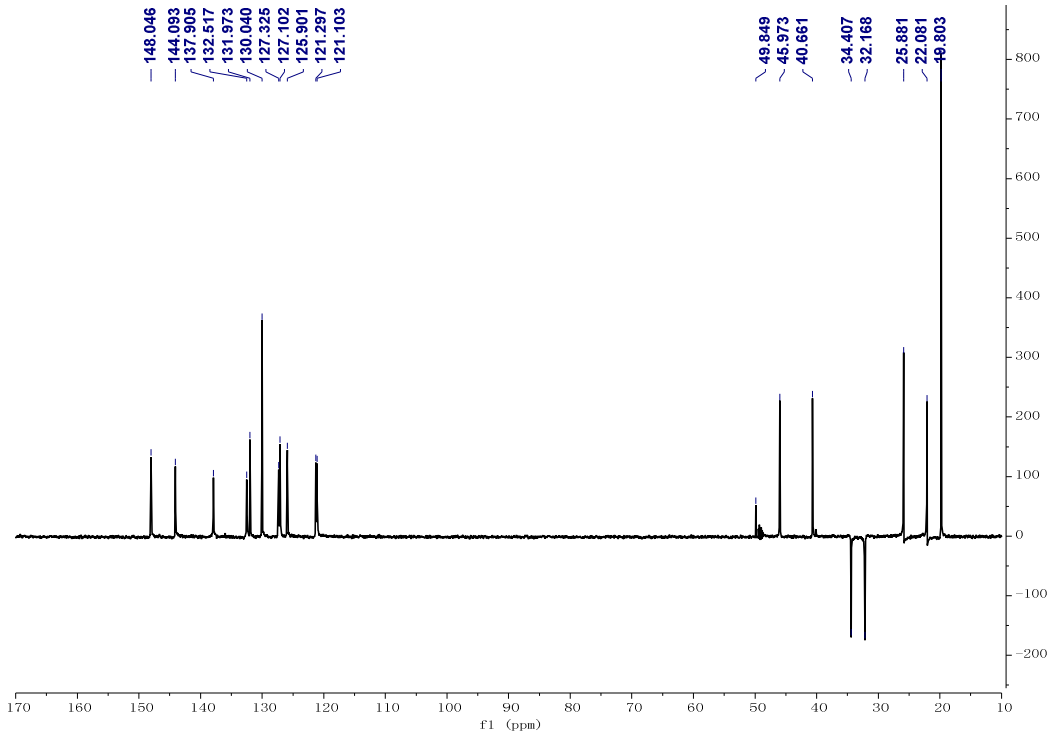

Figure S3. The ^{13}C/DEPT 135º NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

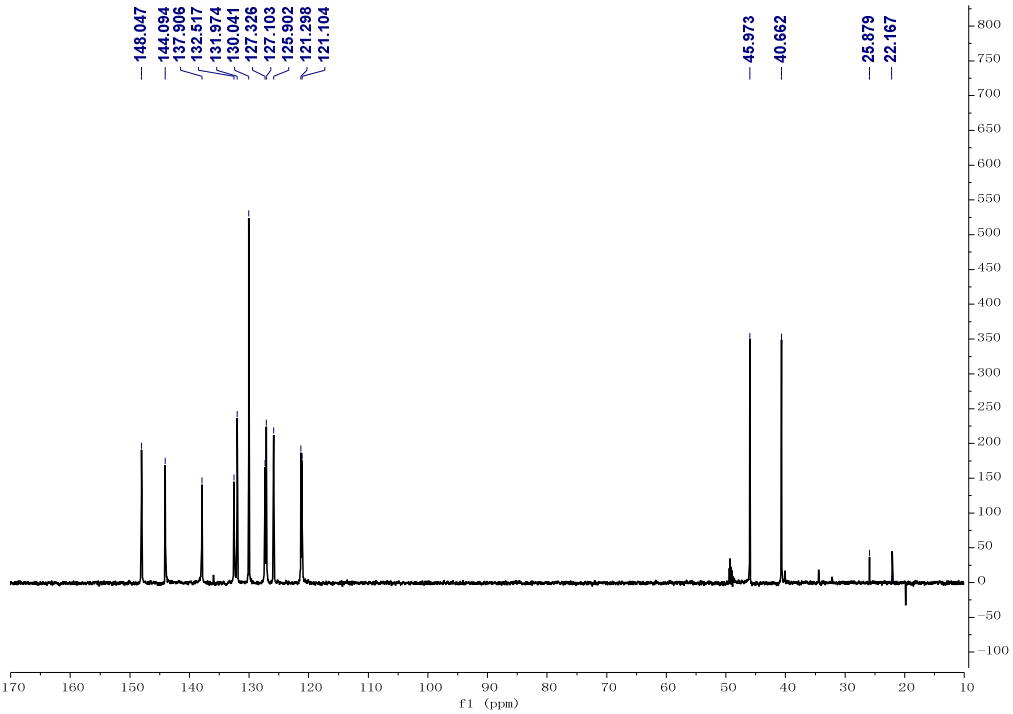

Figure S4. The ^{13}C/DEPT 90º NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

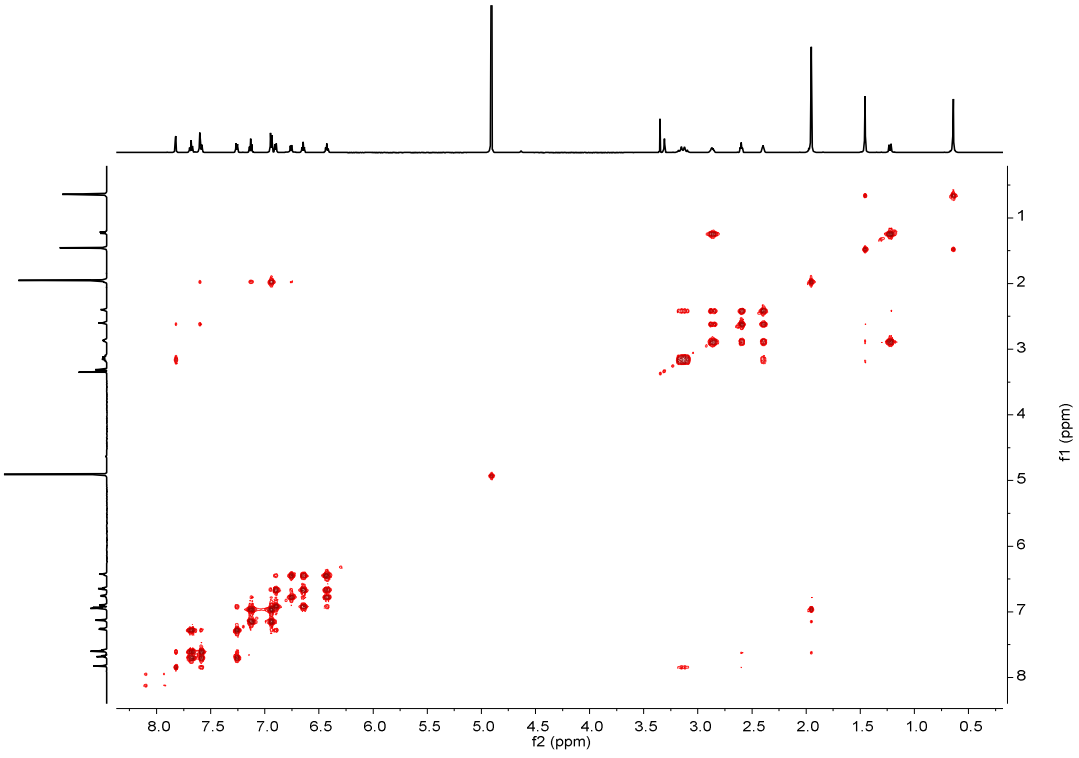

Figure S5. The ^{1}H − ^{1}H COSY NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

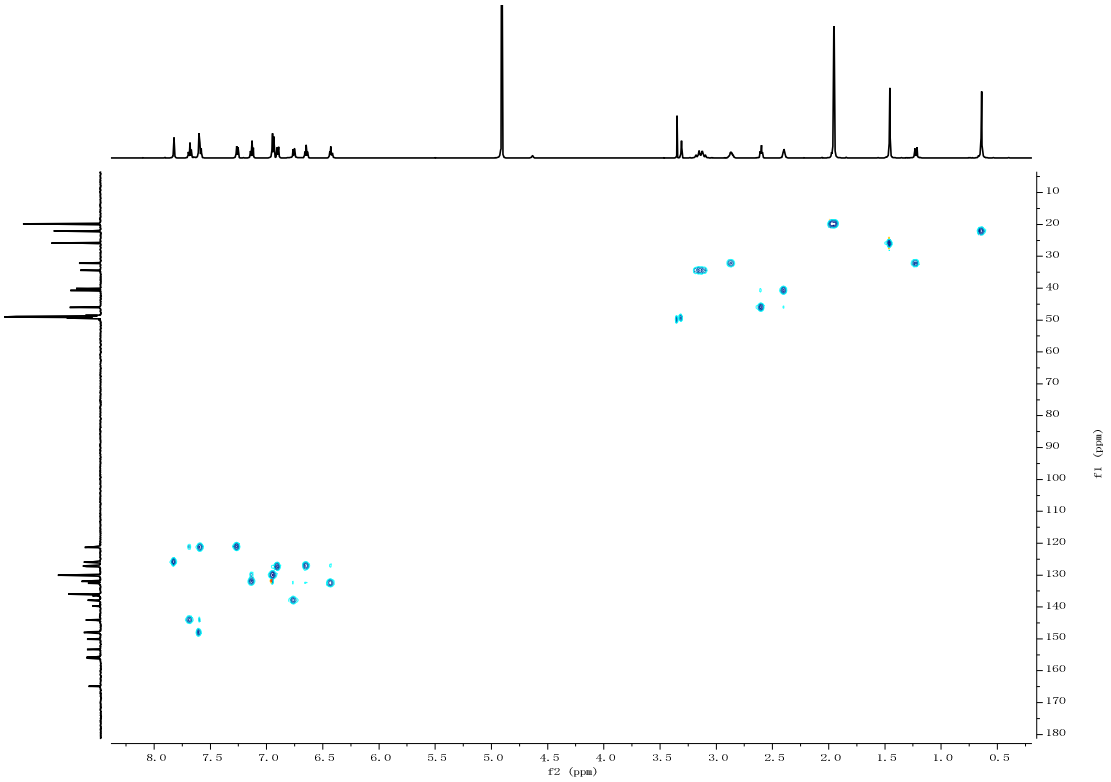

Figure S6. The HSQC NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

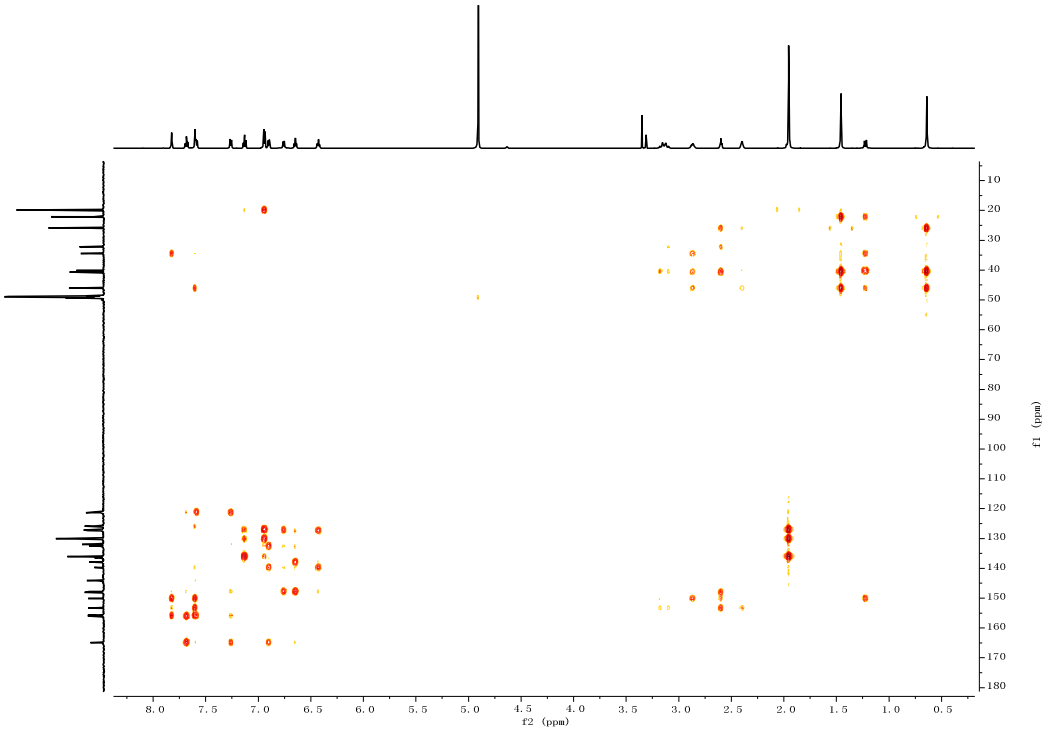

Figure S7. The HMBC NMR spectrum of (−)-**1** (Bruker DRX-600, RT).

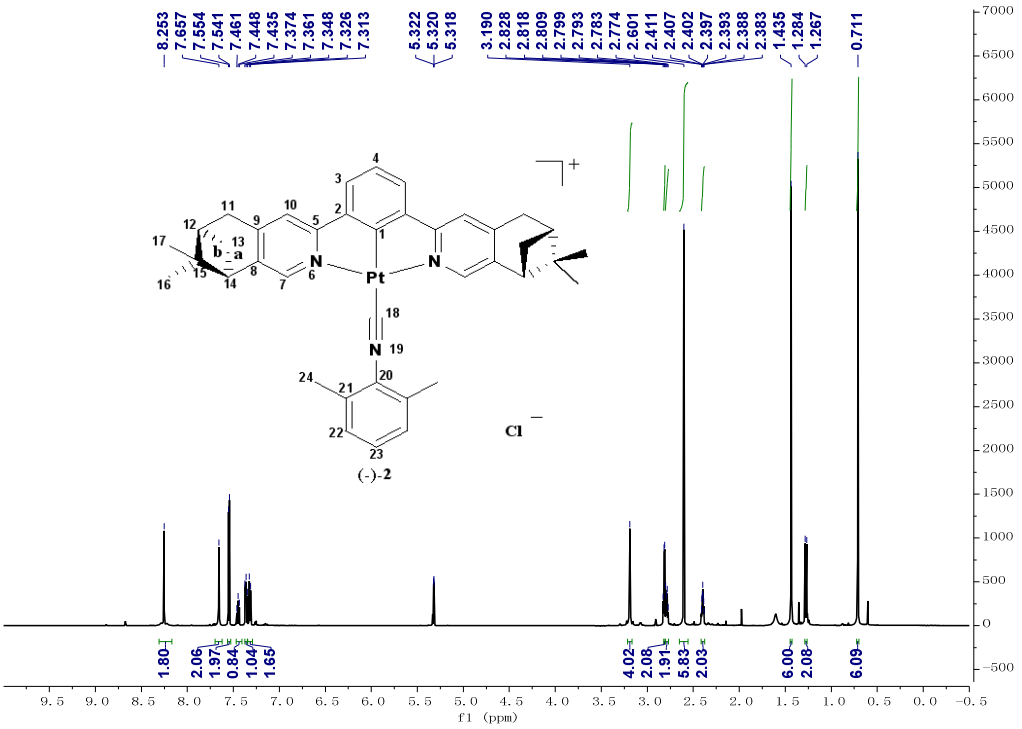

Figure S8. The ^{1}H NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

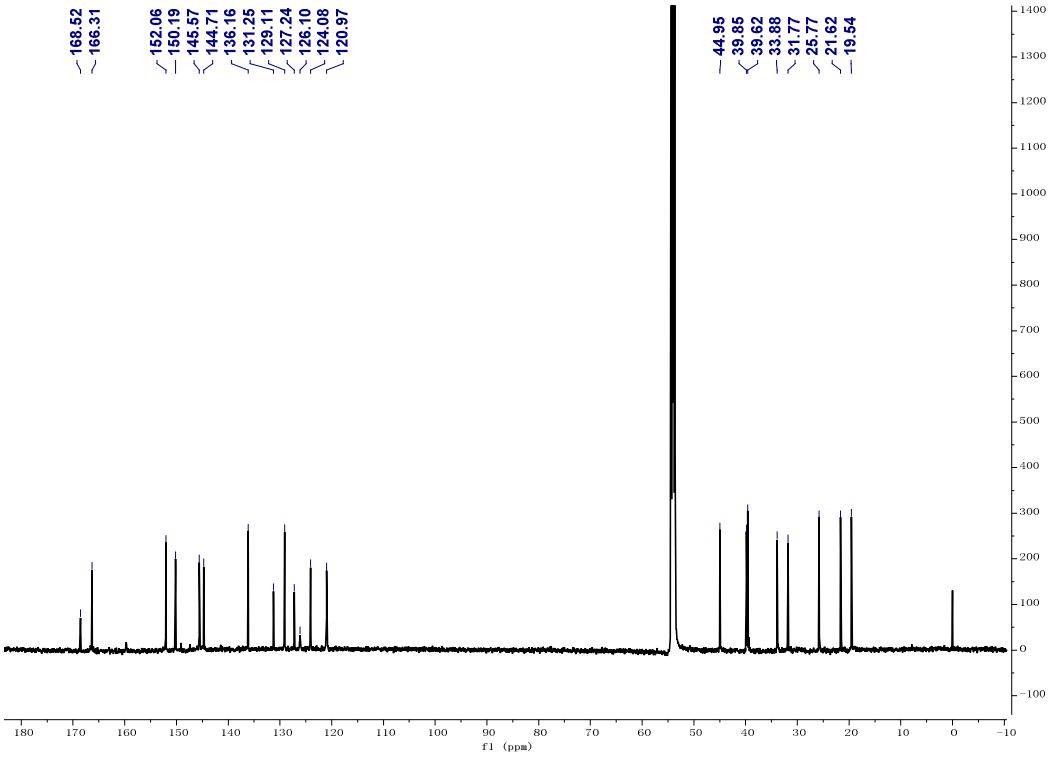

Figure S9. The ^{13}C NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

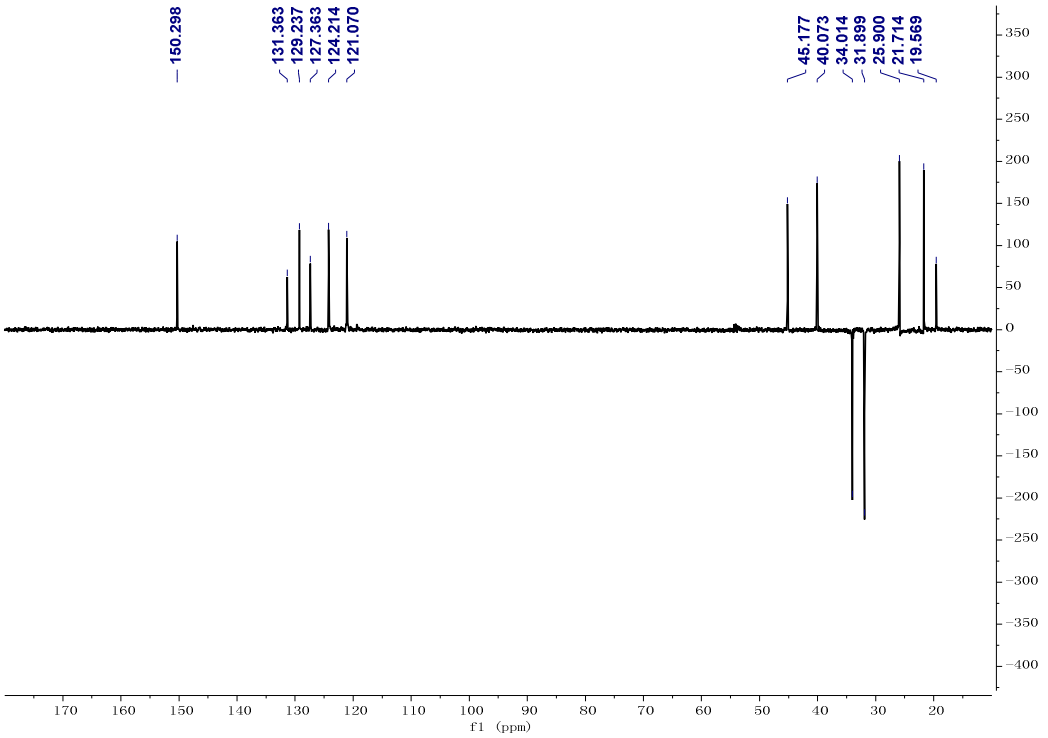

Figure S10. The ^{13}C/DEPT 135º NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

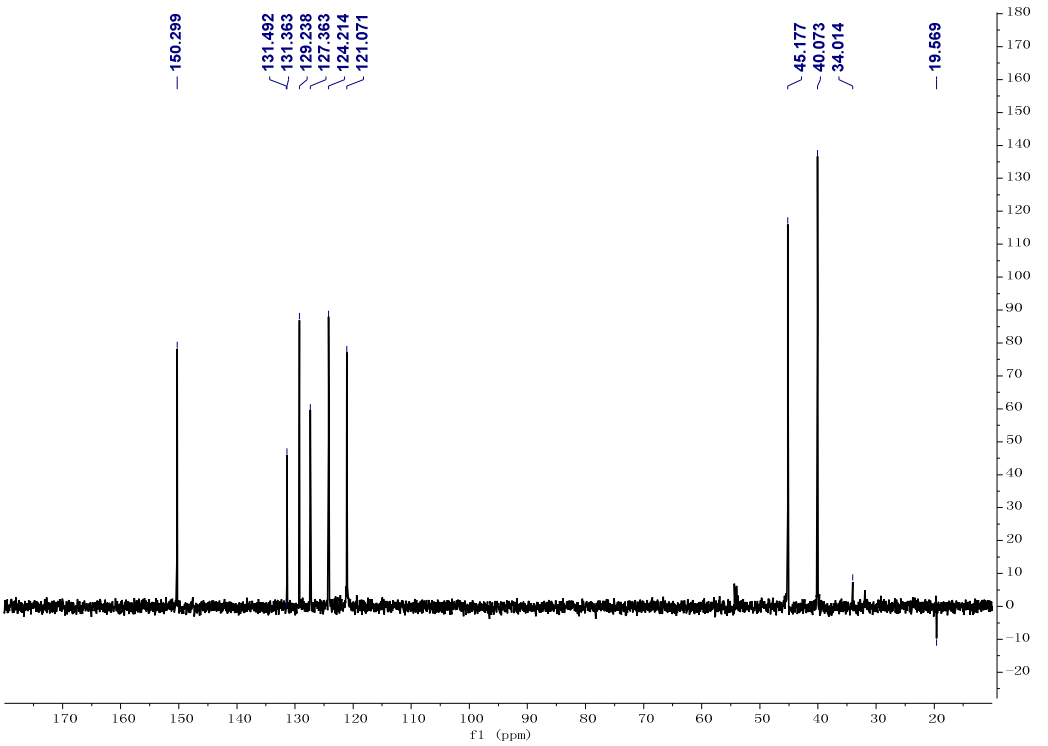

Figure S11. The ^{13}C/DEPT 90º NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

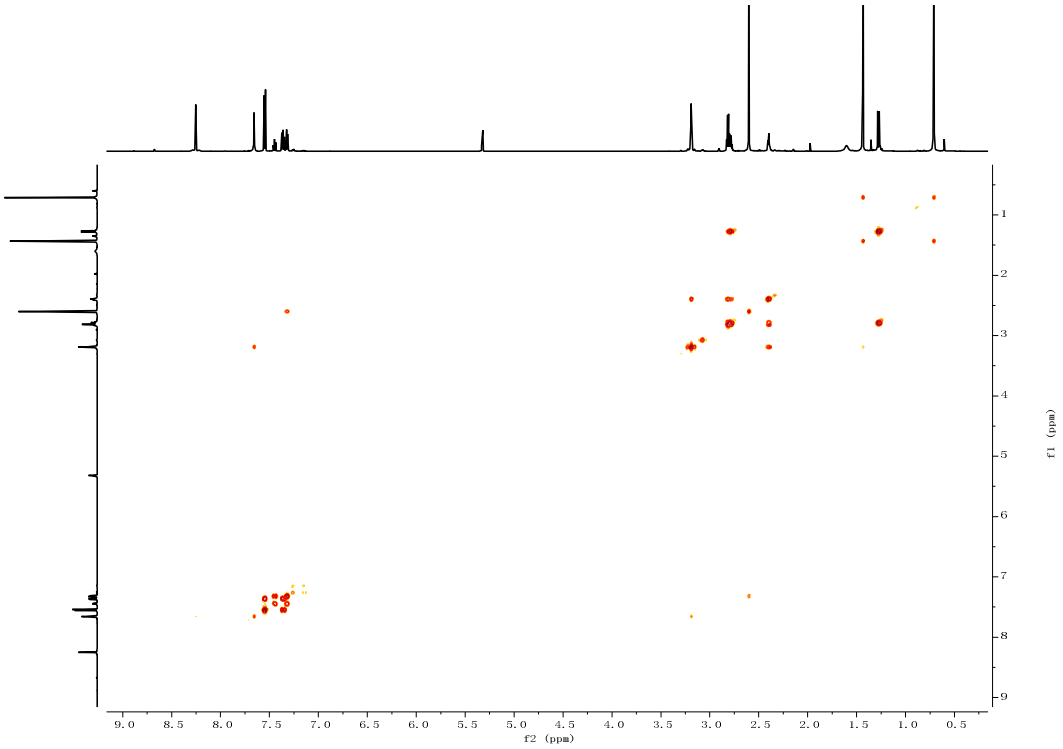

Figure S12. The $^{1}H - {}^{1}H$ COSY NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

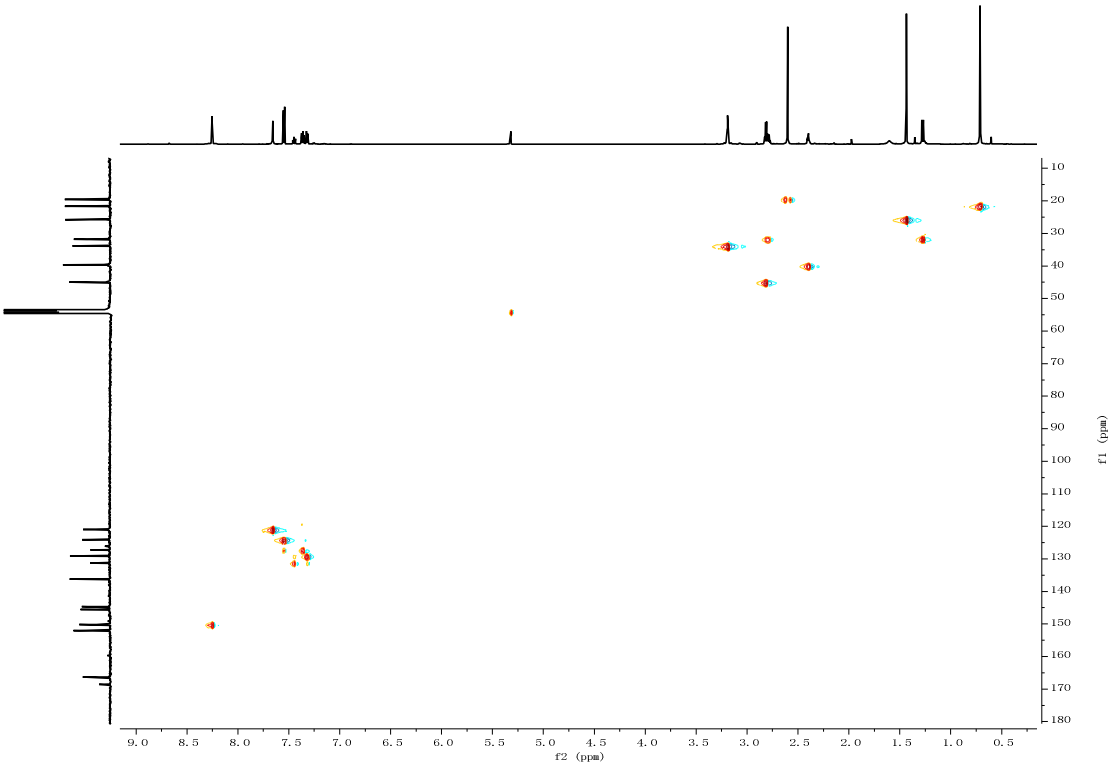

Figure S13. The HSQC NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

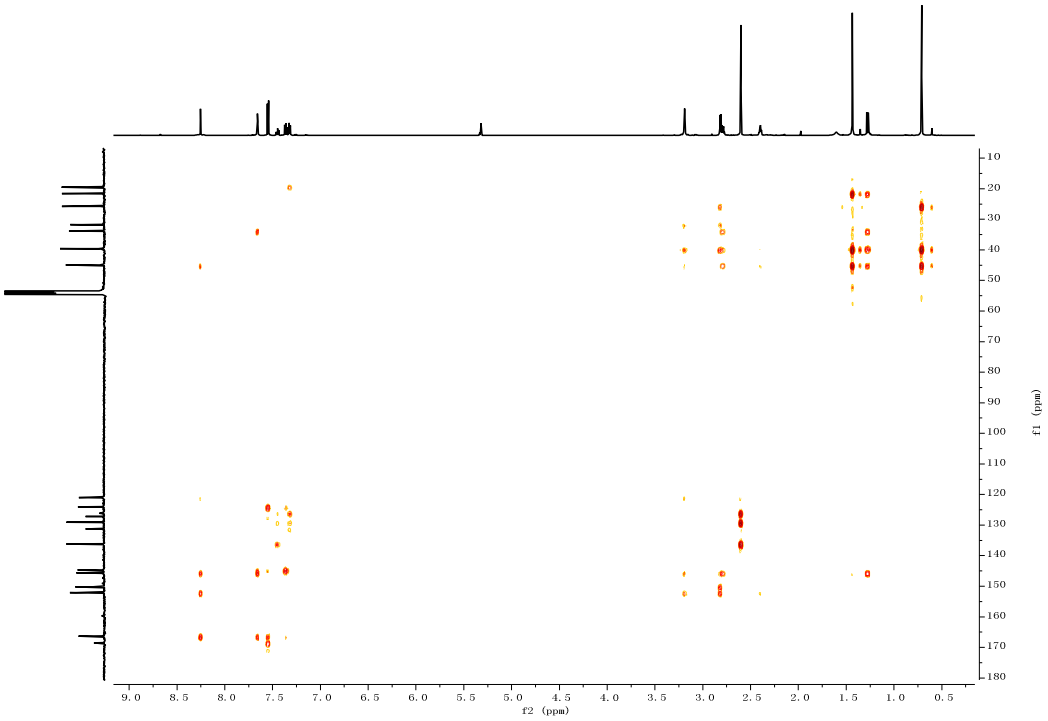

Figure S14. The HMBC NMR spectrum of (−)-**2** (Bruker DRX-600, RT).

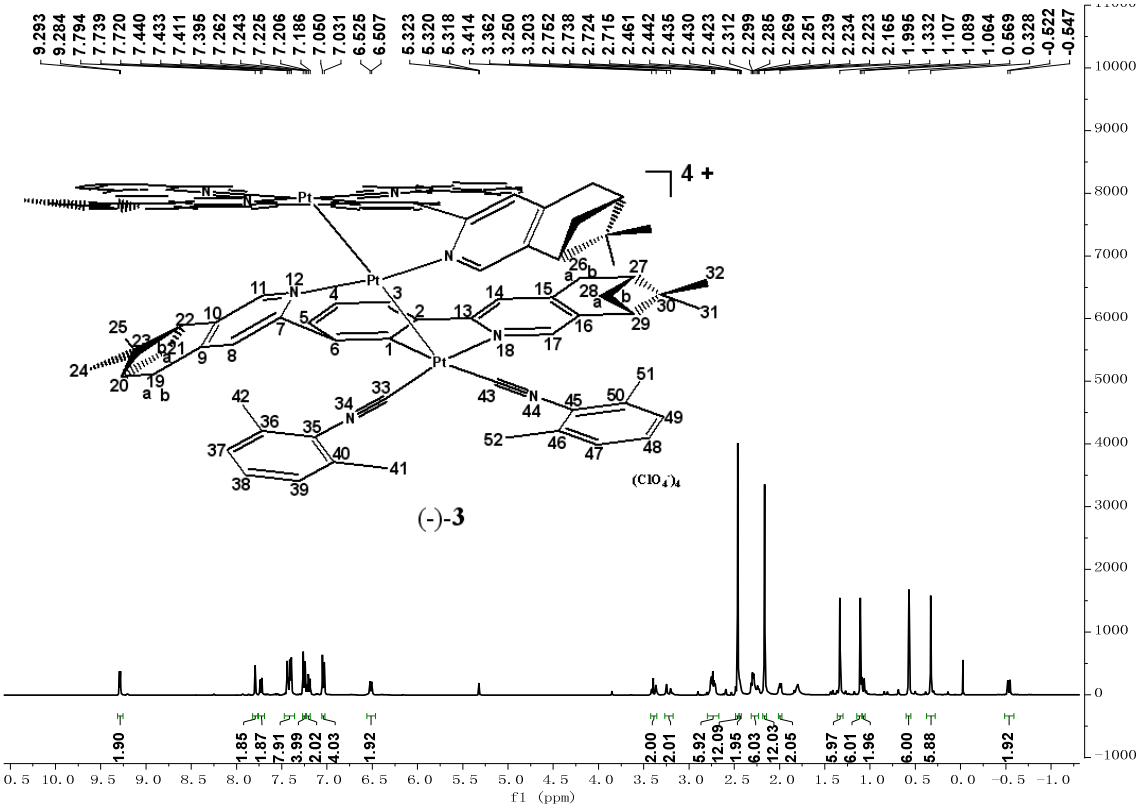

Figure S15. The ^{1}H NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

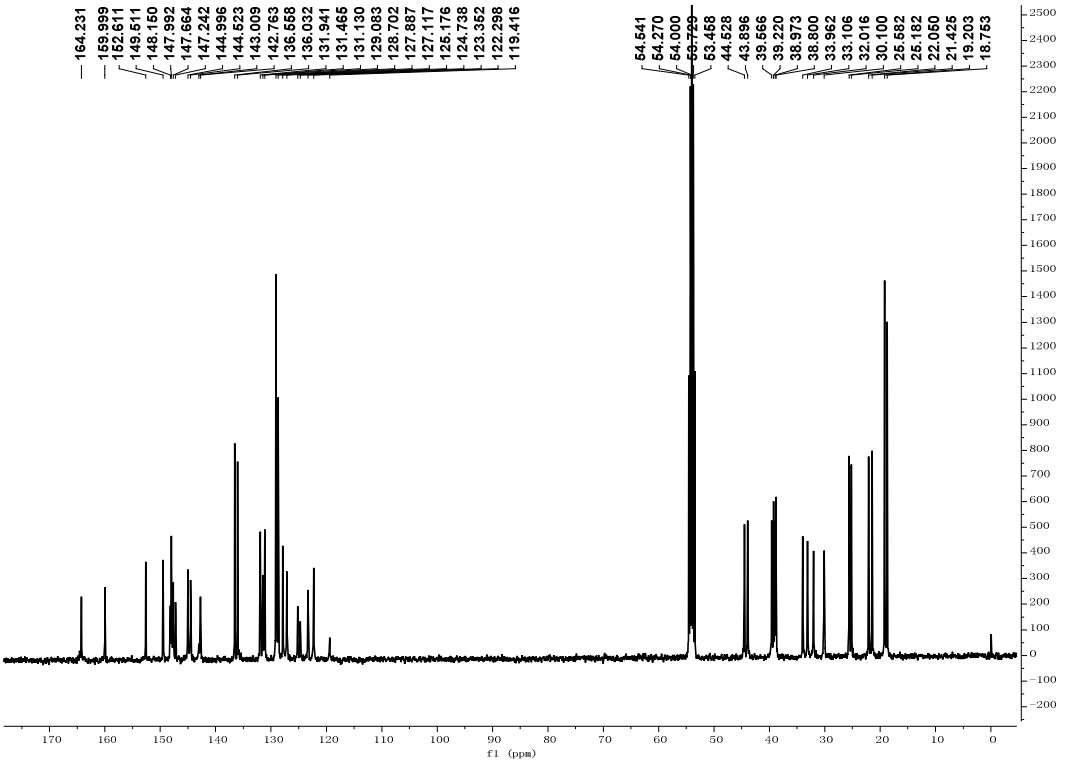

Figure S16. The ^{13}C NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

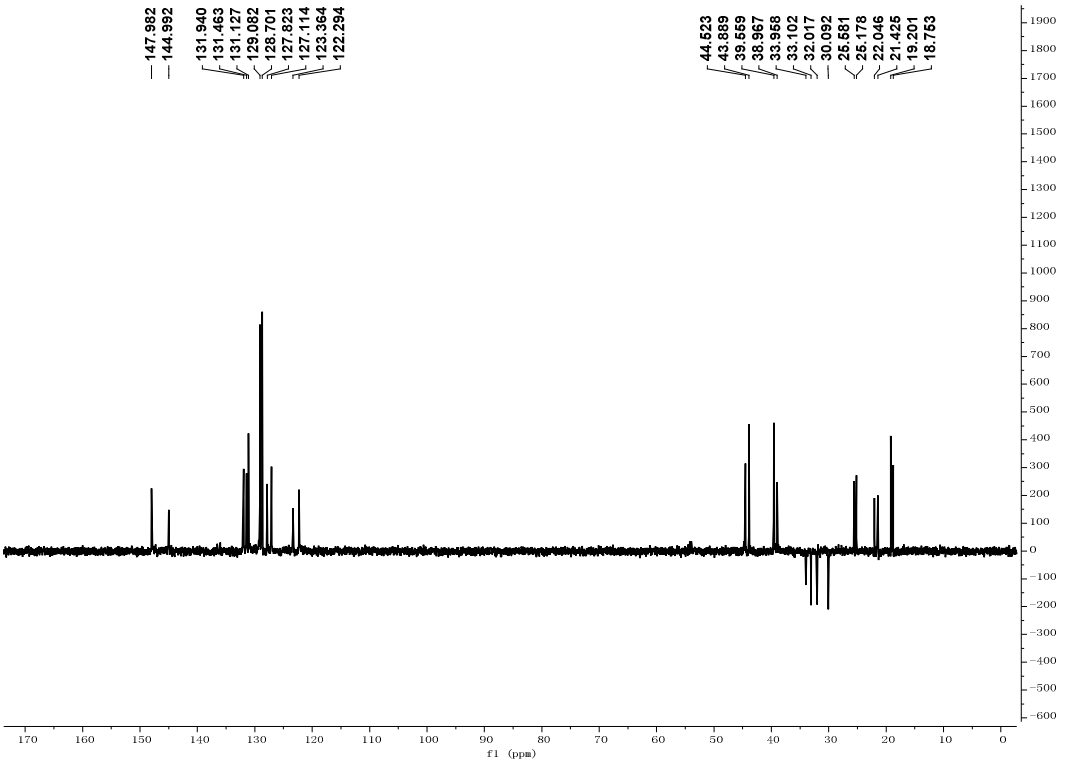

Figure S17. The ^{13}C/DEPT 135º NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

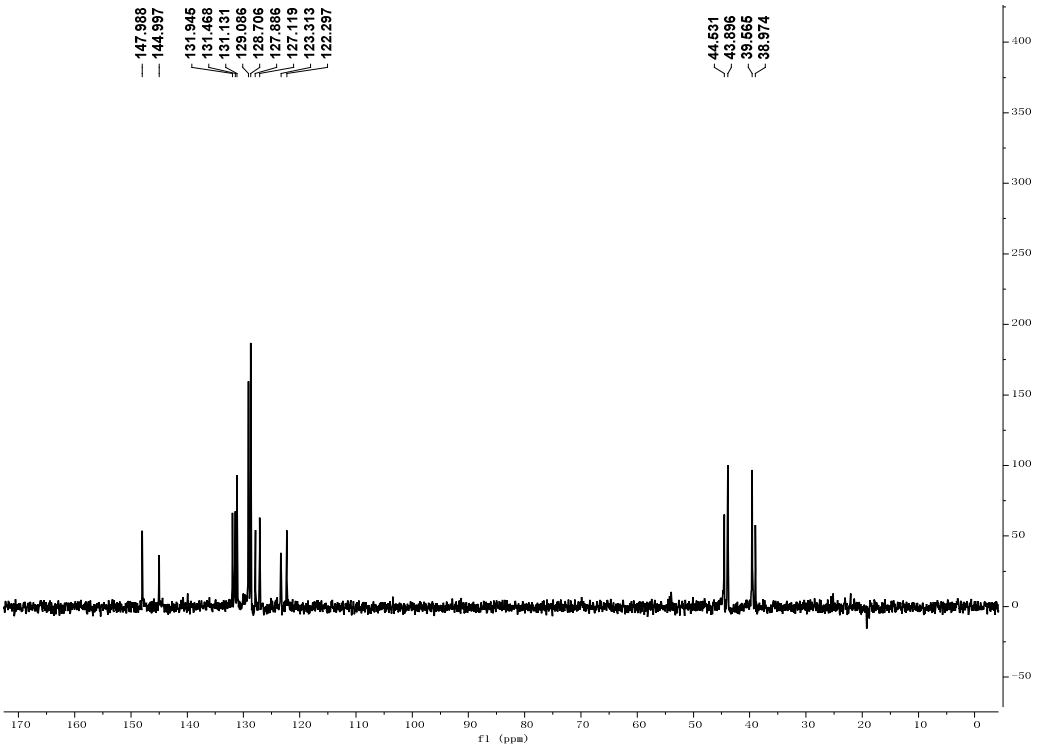

Figure S18. The ^{13}C/DEPT 90º NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

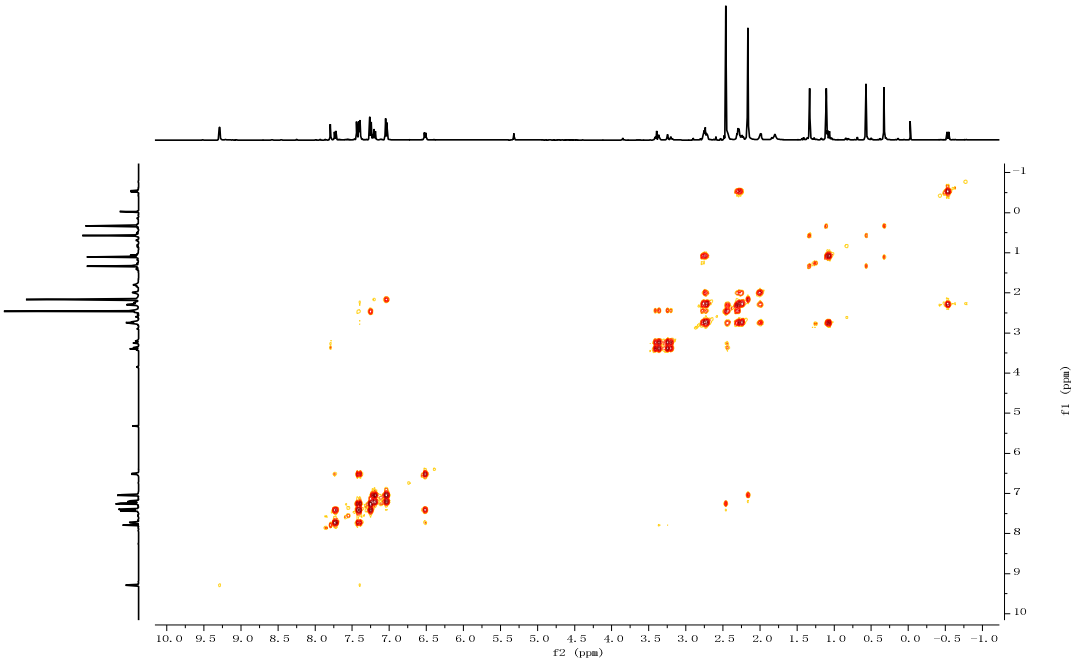

Figure S19. The ^{1}H − ^{1}H COSY NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

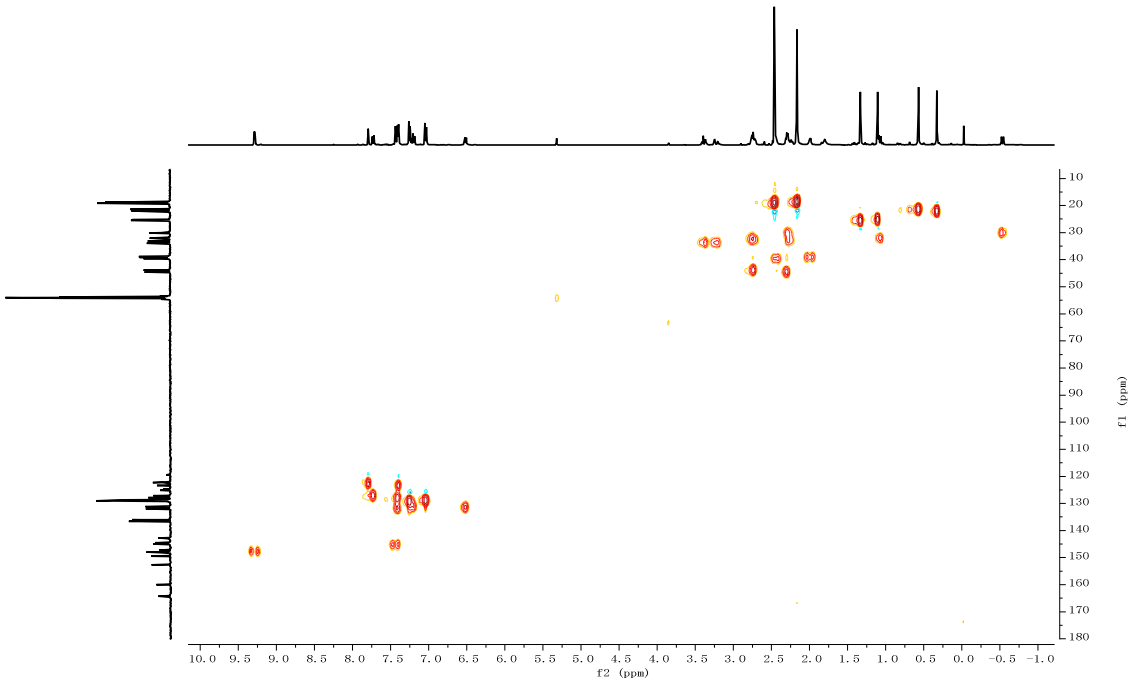

Figure S20. The HSQC NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

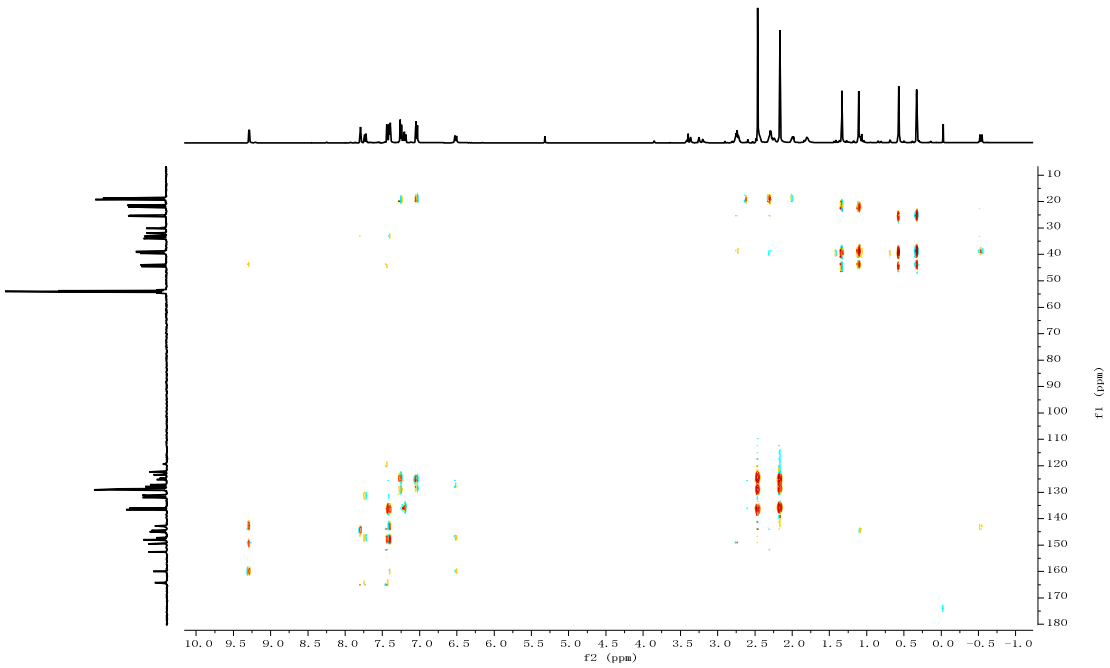

Figure S21. The HMBC NMR spectrum of (−)-**3** (Bruker DRX-400, 273.15 K).

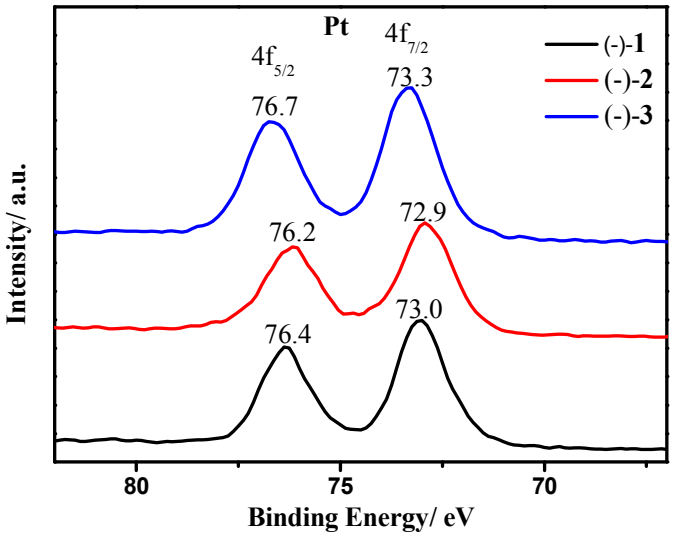

Figure S22. Pt $4f_{5/2}$ and $4f_{7/2}$ core levels of XPS for complexes (−)-**1**, (−)-**2** and (−)-**3**.

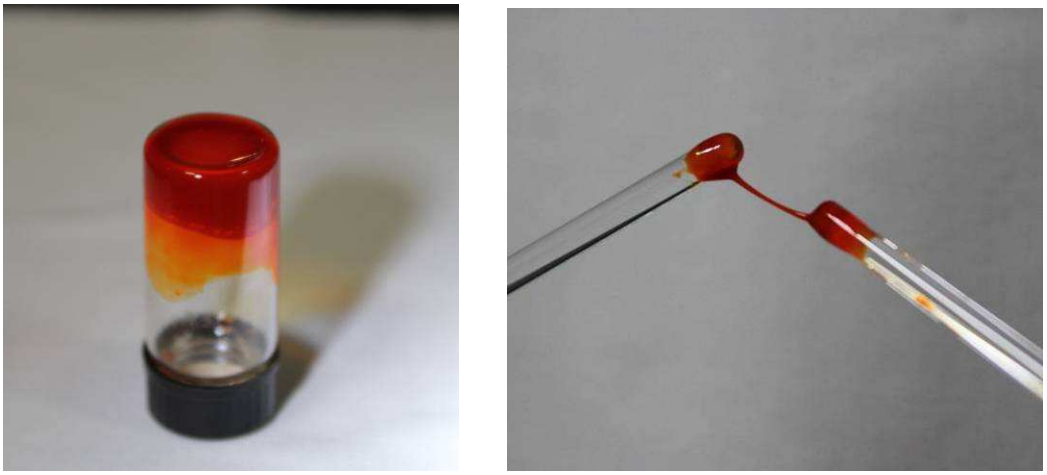

Figure S23. Photograph of hydrogels of (−)-**1**.

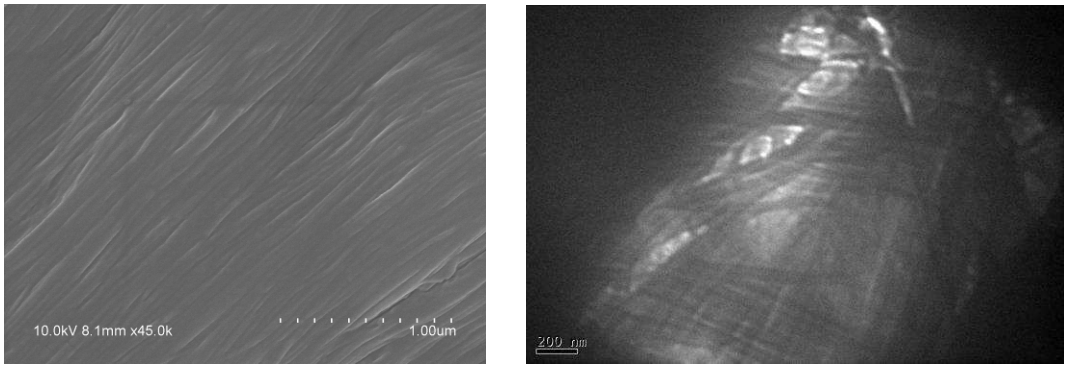

Figure S24. SEM (left) and TEM (right) of hydrogels of (−)-**1**.

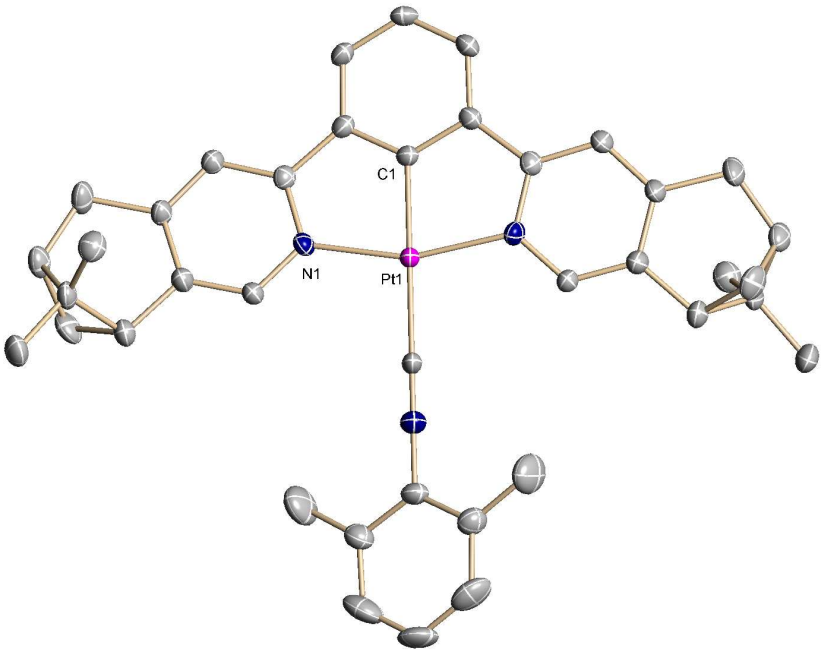

Figure S25. X-ray crystal structure of **2**-OTf**.** H atoms as well as anions are omitted for clarity, and the percentage of thermal ellipsoid probability is 30%.

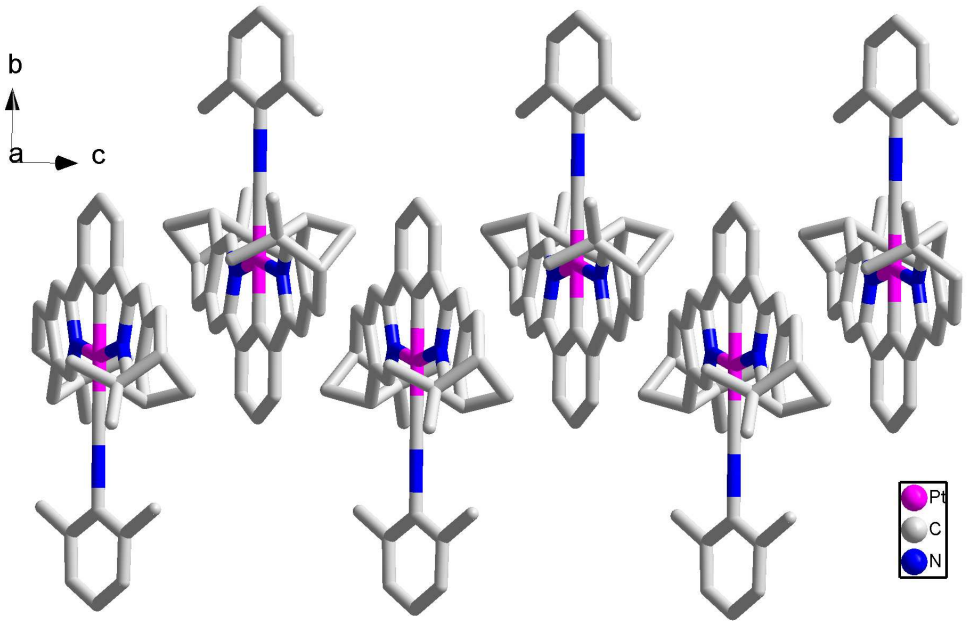

Figure S26. Crystal packing diagram of complex **2**-OTf. H atoms and anions are omitted for clarity.

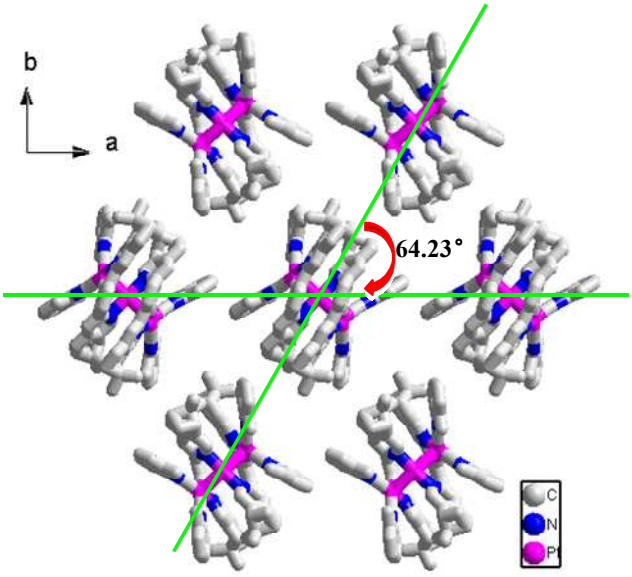

Figure S27. Crystal packing diagram of complex (−)-**3**. H atoms, solvent molecules and anions are omitted for clarity.

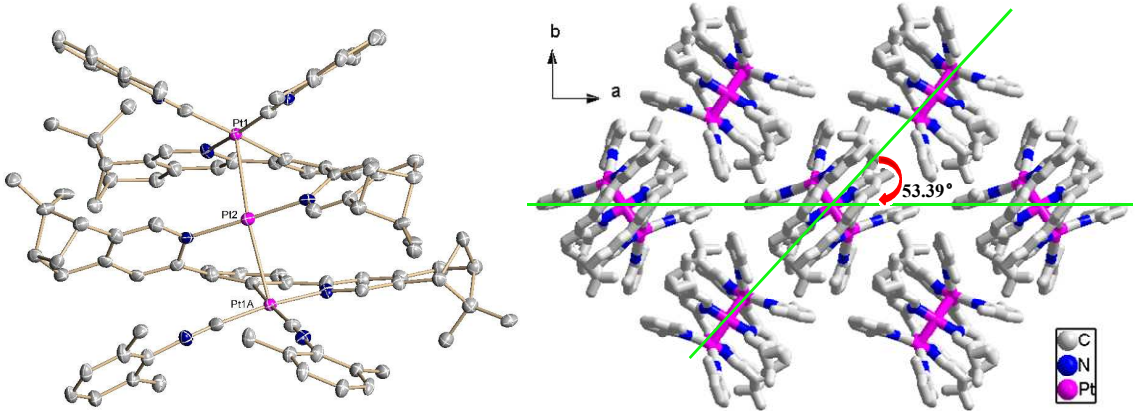

Figure S28. X-ray crystal structure (left) and crystal packing diagram (right) of (−)-**3′**. H atoms, solvent molecules as well as anions are omitted for clarity, and the percentage of thermal ellipsoid probability is 30%.

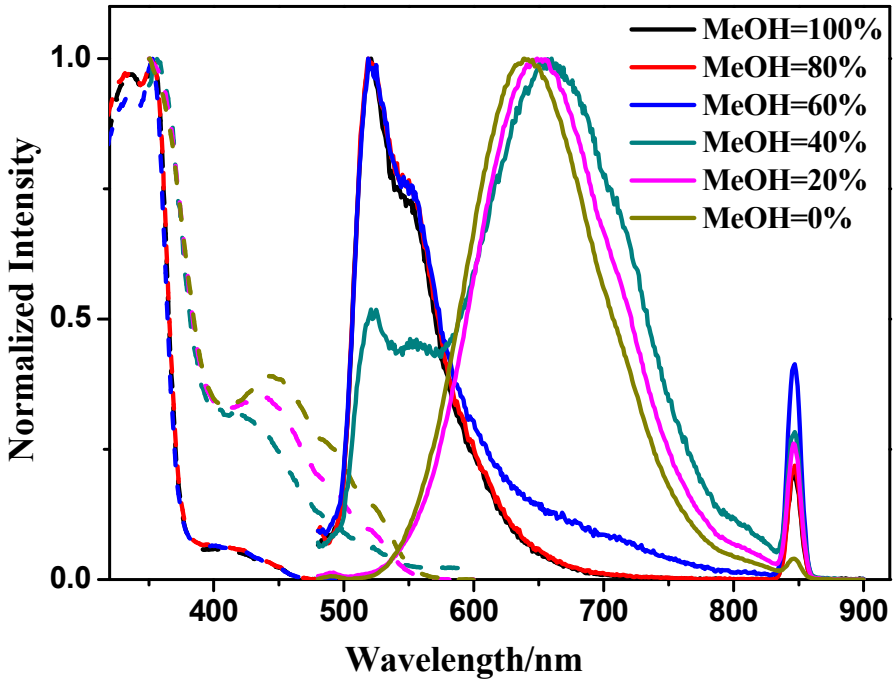

Figure S29. Excitation (dash line) and emission (solid line, λ_{ex} = 420 nm) spectra of (−)-**1** (5×10^{-5} mol·L^{-1}) in mixed solution of MeOH and H_2O in the ratios shown. * indicates artifacts

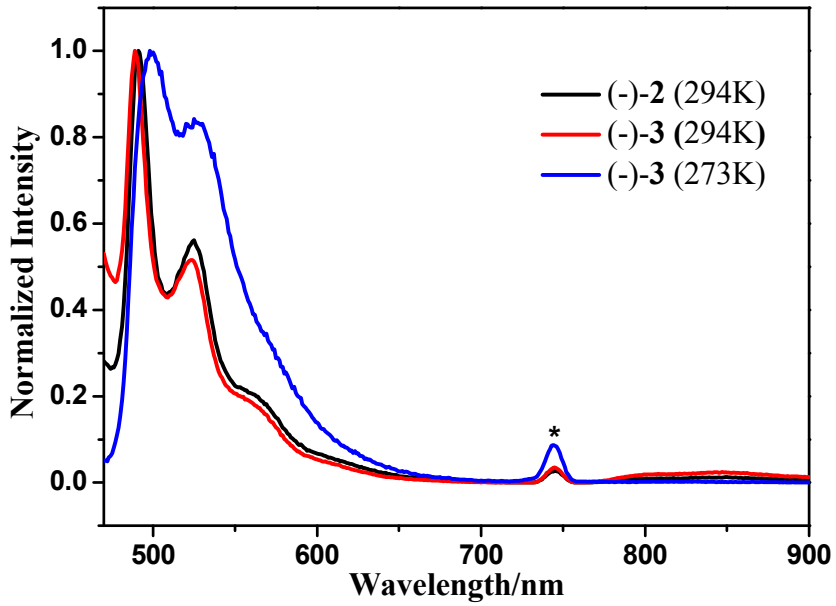

Figure S30. Emission spectra of (−)-**2** (5×10^{-5} mol·L^{-1}) and (−)-**3** (2.5×10^{-5} mol·L^{-1}) in dichloromethane solution (λ_{ex} = 370 nm). * indicates artifacts.

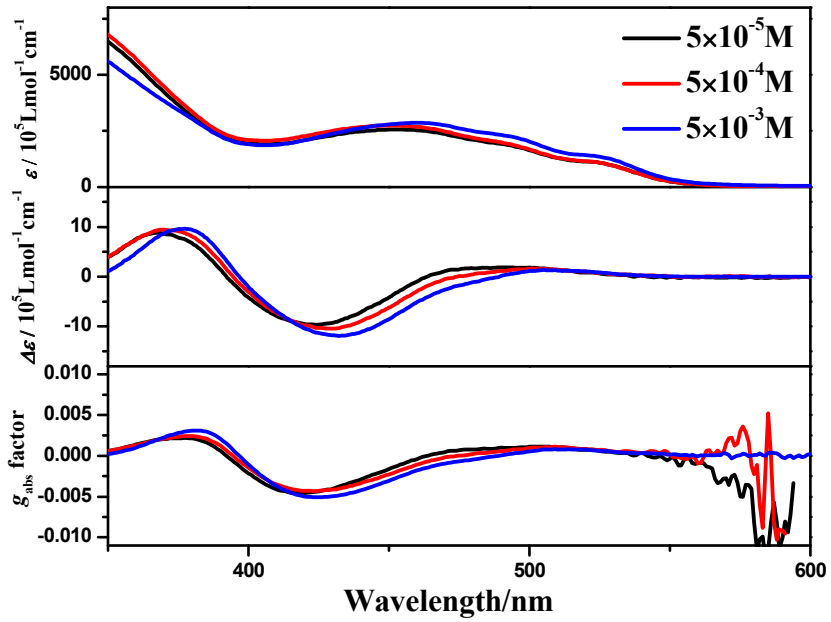

Figure S31. UV-Vis absorption, ECD spectra and g_{abs} factor of (−)-**1** with different concentrations in water.

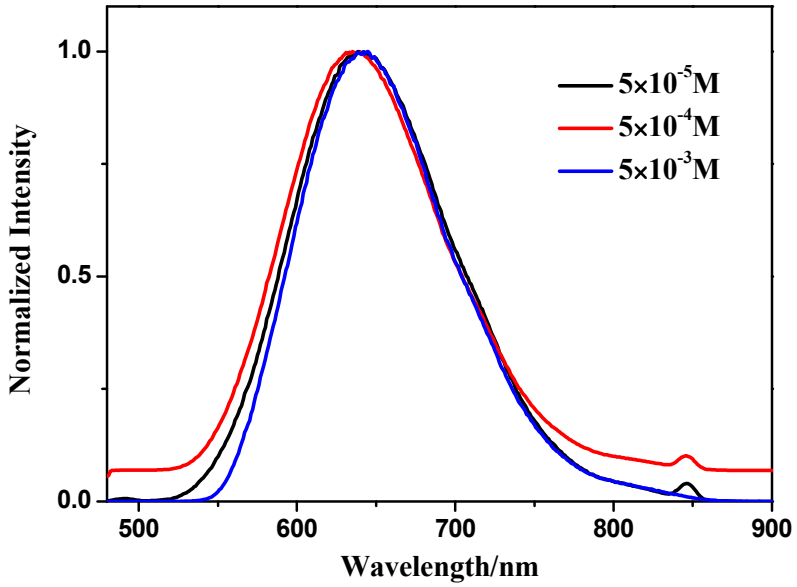

Figure S32. Emission spectra of (−)-**1** with different concentrations in water.

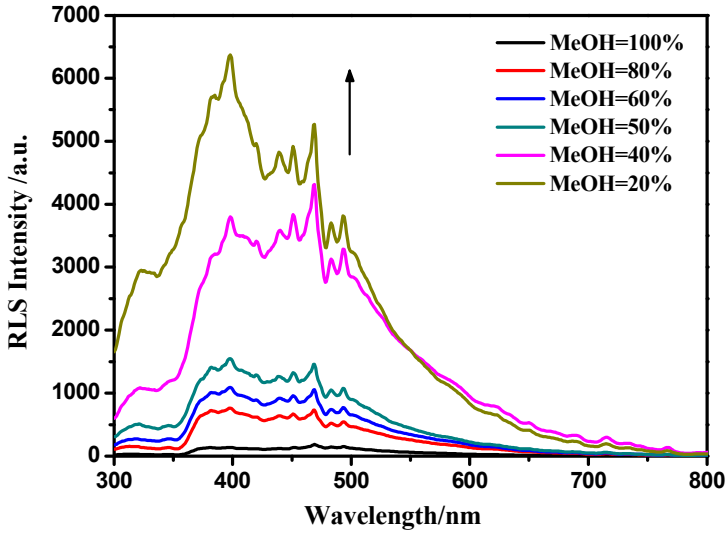

Figure S33. Resonance light scattering (RLS) spectra of (−)-**1** (5×10^{-5} mol·L^{-1}) in mixed solution of MeOH and H_2O in the ratios shown.

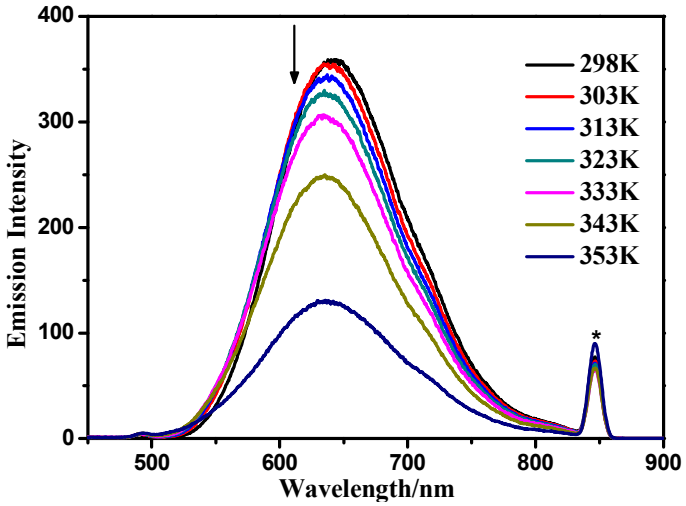

Figure S34. Emission spectra of (−)-**1** (5×10^{-5} mol·L^{-1}) in H_2O (λ_{ex} = 420 nm) with different temperatures. * indicates artifacts.

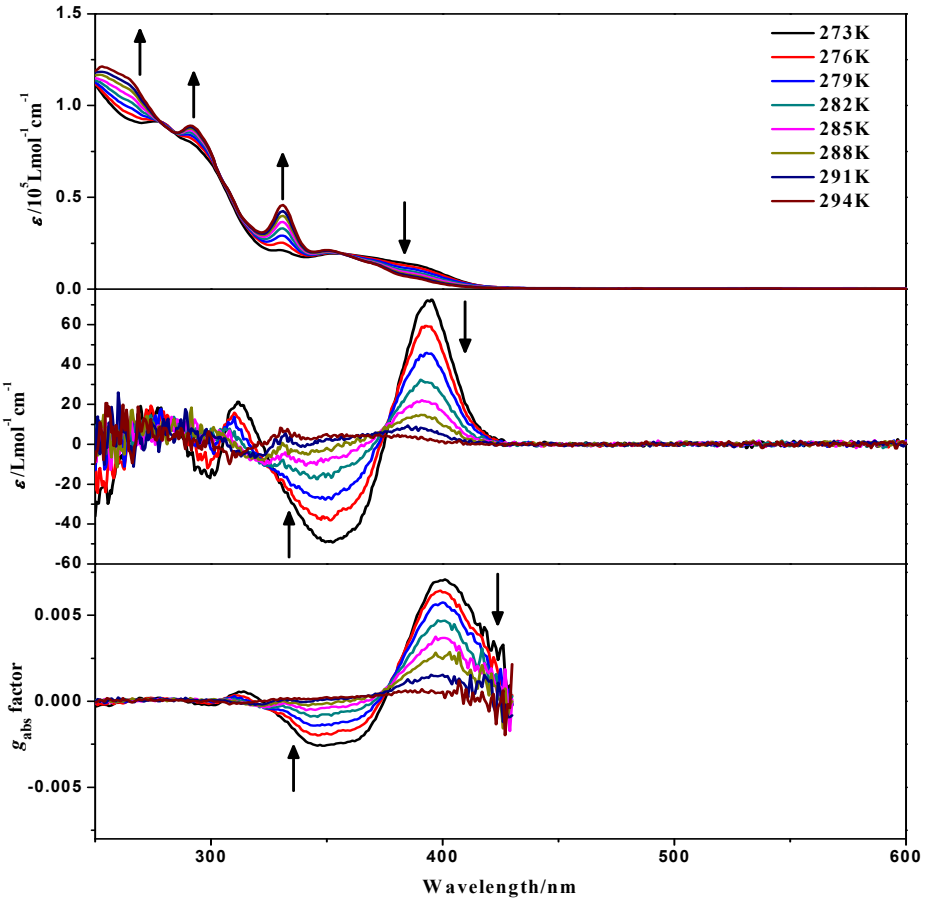

Figure S35. UV-Vis, ECD spectra and g_{abs} factor of (−)-**3** in dichloromethane at 2.5×10^{-5} mol·L^{-1} with different temperatures.

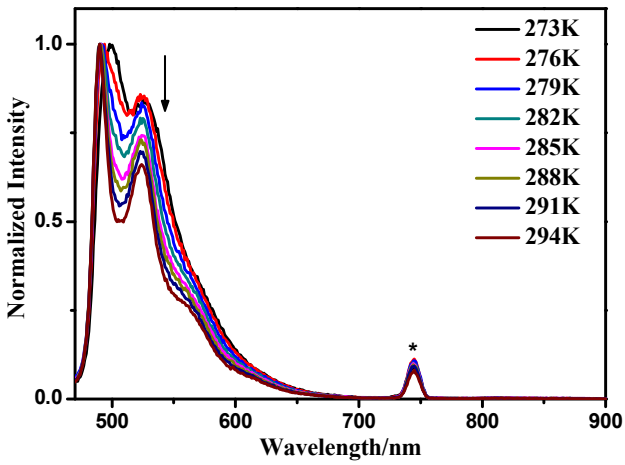

Figure S36. Emission spectra of (−)-**3** (2.5×10^{-5} mol·L^{-1}) in dichloromethane solution (λ_{ex} = 370 nm) with different temperatures. * indicates artifacts.

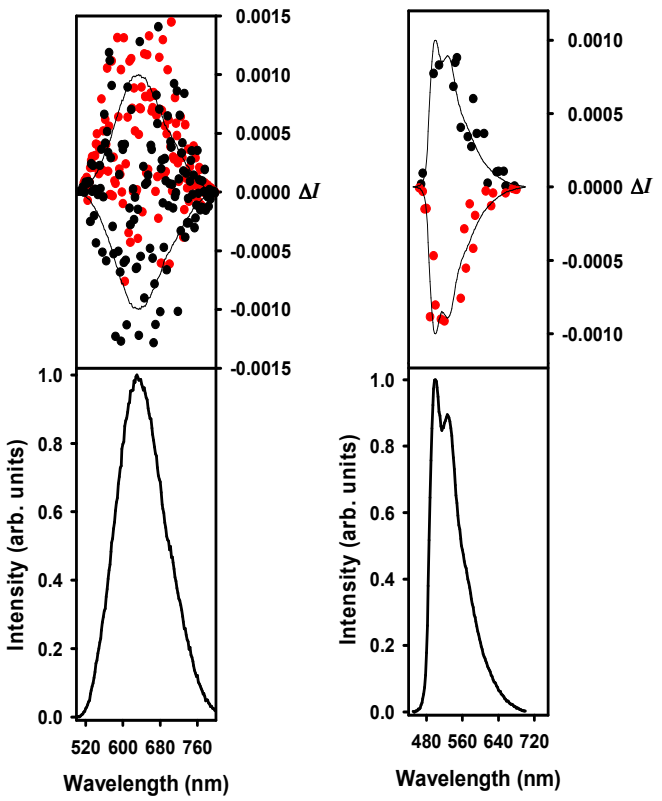

Figure S37. (a) Circularly polarized luminescence (upper curves) and total luminescence (lower curves) spectra of (−)-**1** and (+)-**1** (left panel) in 1 mM aqueous solutions at 353K, and (b) (−)-**3** and (+)-**3** (right panel) in 1 mM MeOH solutions at 295 K.

Table S1. Structural parameters of complexes (−)-**1**, **2**-OTf, (−)-**3**, (+)-**3** and (−)-**3′** determined by X-ray single crystal diffraction.

Bond Length	(−)-**1**	**2**-OTf	Bond Length	(−)-**3**	(+)-**3**	(−)-**3′**
Pt1−C1	2.018(15)	1.960(10)	Pt1−C1	2.004(8)	2.012(7)	2.062(8)
Pt1−C2	1.87(3)	2.035(10)	Pt1−C31	2.028(9)	2.033(7)	1.937(9)
Pt1−N1	1.915(15)	2.039(5)	Pt1−C40	1.976(9)	1.977(8)	2.007(9)
Pt1−N2 (N1A)	2.12(3)	2.039(5)	Pt1−N1	2.017(7)	2.033(6)	2.048(7)
Pt2−C3	2.016(10)		Pt2−N2	2.144(6)	2.157(6)	2.182(7)
Pt2−C4	1.86(3)		Pt1− Pt2	2.8862(3)	2.8909(3)	2.8749(3)
Pt2−N3	1.923(9)					
Pt1−N4	2.106(8)					
Bond Angles	(−)-**1**	**2**-OTf	Bond Angles	(−)-**3**	(+)-**3**	(−)-**3′**

C1−Pt1−C2	97.7(13)	180.000(1)	C1−Pt1−C31	94.7(2)	95.2(3)	94.8(4)
C1−Pt1−N1	81.5(9)	79.84(16)	C1−Pt1−C40	174.7(2)	174.1(2)	175.1(4)
C1−Pt1−N2 (N1A)	160.1(10)	79.84(16)	C1−Pt1−N1	79.9(2)	79.2(2)	80.5(3)
C2−Pt1−N1	177.6(12)	100.16(16)	C1−Pt1−Pt2	69.00(18)	69.09(16)	69.5(2)
C2−Pt1−N2 (N1A)	102.1(15)	100.16(16)	C31−Pt1−C40	90.5(3)	90.4(2)	89.9(4)
N1−Pt1−N2 (N1A)	78.7(10)	159.7(3)	C31−Pt1−N1	171.4(3)	171.0(2)	169.9(3)
C3−Pt2−C4	96.6(14)		C31−Pt1− Pt2	93.4(2)	93.78(18)	94.6(2)
C3−Pt2−N3	81.9(5)		C40−Pt1−N1	94.8(3)	95.0(2)	94.6(3)
C3−Pt2−N4	161.2(5)		C40−Pt1− Pt2	112.1(3)	112.2(2)	111.9(3)
C4−Pt2−N3	178.2(13)		N1−Pt1− Pt2	90.97(18)	90.79(16)	92.13(19)
C4−Pt2−N4	102.1(14)		N2−Pt2− Pt1	87.55(16)	87.22(14)	86.97(17)
N3−Pt2−N4	79.4(3)		N2−Pt2− N2’	176.8(4)	176.5(3)	173.2(4)
			Pt1−Pt2− Pt1’	158.47(2)	158.53(2)	160.74(2)

Table S2. Absorption and emission data of (−)-**1**, (−)-**2** and (−)-**3** in solution.

	294K	273K
Absorption λ_{max}/nm (ε /Lmol^{-1}cm^{-1}) of (-)-**1** in methanol	248 (41800), 269 (36900), 336 (16000), 354 (17400), 410 (700)	
Absorption λ_{max}/nm (ε /Lmol^{-1}cm^{-1}) of (-)-**1** in water	242 (22100), 262(19200), 335 (7390), 450 (2570), 491(1910), 523 (1120)	
Absorption λ_{max}/nm (ε /Lmol^{-1}cm^{-1}) of (-)-**2** in CH_2Cl_2	263 (43300), 292 (28900), 330 (19100), 350 (7790), 371sh (5170), 404sh (1340)	
Absorption λ_{max}/nm (ε /Lmol^{-1}cm^{-1}) of (-)-**3** in CH_2Cl_2	254 (121000), 291 (89300), 331 (45400), 350 (21500), 369sh (14200), 388sh (6270)	276 (92300), 293sh (78800), 330 (21300), 354 (19500), 390sh (12600)
Emission λ_{max} /nm of (−)-**1** in methanol [a]	521, 550 (sh)	
Emission λ_{max} /nm of (−)-**1** in water [a]	640	
Emission λ_{max} /nm of (−)-**2** in CH_2Cl_2 [b]	489, 524, 563 (sh)	
Emission λ_{max} /nm of (−)-**3** in CH_2Cl_2 [c]	489, 524, 563 (sh)	499, 527

[a] (−)-**1**: λ_{ex} = 420 nm. [b] (−)-**2**: λ_{ex} = 370 nm. [c] (−)-**3**: λ_{ex} = 370 nm.