

Supporting Info

A Unique Class of Neutral Cyclometalated Platinum(II) Complexes with π -bonded Benzenedithiolate: Synthesis, Molecular Structures and Tuning of Luminescence Properties

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Table of Contents

| | |
|--|-----|
| General experimental methods | S2 |
| Synthesis of [Na][Cp*Ru(η -C ₆ H ₄ S ₂)] (Na-1) | S2 |
| Synthesis of Synthesis of [(ppy)Pt(Cp*Ru(η -C ₆ H ₄ S ₂))] (2) | S3 |
| Synthesis of [(dfppy)Pt(Cp*Ru(η -C ₆ H ₄ S ₂))] (3) | S3 |
| Synthesis of [(bzq)Pt(Cp*Ru(η -C ₆ H ₄ S ₂))] (4) | S3 |
| X-ray Structural determination of complexes 2-3 | S4 |
| Optical spectroscopy | S4 |
| References | S5 |
| ¹ H NMR spectrum of Na-(1) | S6 |
| ¹ H and ¹³ C NMR spectra of (2) | S7 |
| ¹ H and ¹³ C NMR spectra of (3) | S8 |
| ¹⁹ F NMR spectrum of (3) | S9 |
| ¹ H and ¹³ C NMR spectra of (4) | S10 |
| Excitation spectra of 2-4 | S11 |

General experimental methods

^1H NMR spectra were recorded at 300 MHz in CD_2Cl_2 and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CD_2Cl_2 \square 5.33 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration. ^{13}C NMR spectra were recorded at 75.4 MHz in CD_2Cl_2 and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CD_2Cl_2 \square 53.84 ppm), multiplicity with respect to proton (deduced from DEPT experiments). Glassware was oven-dried prior to use. All reactions were carried out under an argon atmosphere. THF and diethyl ether were distilled from sodium–benzophenone. CH_2Cl_2 was distilled from CaH_2 . Other reagents were obtained from commercial suppliers and used as received. Infra-red spectra were measured using Tensor 27 (ATR diamond) Bruker spectrometer. IR data are reported as characteristic bands (cm^{-1}).

Synthesis of $[\text{Na}][\text{Cp}^*\text{Ru}(\eta\text{-C}_6\text{H}_4\text{S}_2)]$ (**Na-1**).

A Schlenk flask under argon was charged with sodium hydrosulfide (293 mg, 5.22 mmol), $[\text{Cp}^*\text{Ru}(\eta\text{-1,2-dichlorobenzene})][\text{OTf}]$ (95 mg, 0.18 mmol) and 1.5 mL of $\text{DMSO-}d_6$. This reaction mixture turned immediately to blue-green and was heated at 175°C for 1h, during which the color turned to brown. An aliquot of the reaction mixture was removed by syringe and dissolved in $\text{DMSO-}d_6$ for ^1H NMR measurement. ^1H NMR indicated complete conversion of $[\text{Cp}^*\text{Ru}(\eta\text{-1,2-dichlorobenzene})][\text{OTf}]$ to **Na-1**. The solvent was removed under reduced pressure, and the residue was extracted with CH_3CN (40 mL) and filtered through a plug of Celite. Partial evaporation of the filtrate (4 mL) led to a brown solution of **Na-1**.

^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 5.43 (m, 2H, diene), 4.90 (m, 2H, diene), 1.62 (s, 15H, Cp^*). This compound was air- and moisture-sensitive and hence no ^{13}C NMR spectrum neither microanalytical data could be obtained. However it was used *in-situ* to prepare the cyclometallated platinum complexes **2-4**.

General procedure for $(\text{C}^{\wedge}\text{N})\text{Pt}(\eta\text{-S}^{\wedge}\text{S})$ complexes.

Cyclometallated platinum dimer $[(\text{C}^{\wedge}\text{N})\text{Pt}(\mu\text{-Cl})_2]$ (0.06 mmol) and silver triflate (32 mg, 0.13 mmol) were introduced into a Schlenk tube containing 10 mL of acetonitrile. The reaction mixture was stirred in the dark, at room temperature for two hours, then it was filtered on a plug of celite, and concentrated to 2 mL. To the resulting solution presumably $[(\text{C}^{\wedge}\text{N})\text{Pt}(\text{MeCN})_2][\text{OTf}]$ was added $[\text{Na}][\text{Cp}^*\text{Ru}(\eta\text{-C}_6\text{H}_4\text{S}_2)]$ (**Na-1**) in 4 mL of CH_3CN to give immediately a precipitate, which was filtered off and washed with 2 mL of acetonitrile followed by 4 mL of diethylether. This solid was then dissolved in 10 mL of dichloromethane and filtered through a plug of celite. The filtrate was evaporated and the microcrystalline powder was dried under vacuum providing the neutral cyclometallated $(\text{C}^{\wedge}\text{N})\text{Pt}(\eta\text{-S}^{\wedge}\text{S})$ compounds (**2-4**) in good yields.

Synthesis of [(ppy)Pt(Cp**Ru*(η -C₆H₄S₂))] (2)

Starting with 46 mg of [(ppy)Pt(μ -Cl)]₂, compound **2** was isolated as a yellow microcrystalline solid. Yield (56 mg, 51%). ¹H NMR (400 MHz, CD₂Cl₂) δ : 9.03 (dd, J =5.1, 0.8 Hz, J_{H-Pt} =34.1 Hz, 1H, ppy), 7.83 (td, J =10.8, 2 Hz, 1H, ppy), 7.76 (m, 2H, ppy), 7.58 (dd, J =8.4, 3.6 Hz, 1H, ppy), 7.08 (m, 3H, ppy), 5.73 (m, 2H, H π -arene), 5.05 (m, 2H, H π -arene), 1.76 (s, 15H, Cp*). ¹³C NMR (100 MHz, CD₂Cl₂) δ : 150.2, 144.8, 137.4, 134.1, 130.7, 124.1, 122.9, 122.6, 19.3, 92.2, 88.6, 87.3, 82.3, 81.8, 30.1, 9.4. IR (ATR, cm⁻¹): 3039, 3905, 3849, 1602, 1581, 1476, 1404, 1376, 1347, 1266, 1204, 1160, 1080, 1029, 754, 731, 661, 505, 447, 355. Anal. Calcd for C₂₇H₂₇NS₂RuPt C, 44.68; H, 3.75. Found: C, 44.86; H, 4.10.

Synthesis of [(dfppy)Pt(Cp**Ru*(η -C₆H₄S₂))] (3)

Using 52 mg of [(dfppy)Pt(μ -Cl)]₂ compound **3** was obtained as a light yellow solid. Yield (17 mg, 18%).

¹H NMR (400 MHz, CD₂Cl₂) δ : 9.08 (d, J =5.2 Hz, J_{H-Pt} =33.6 Hz, 1H, dfppy), 8.12 (d, J =7.2 Hz, 1H, dfppy), 7.86 (t, J =7.8 Hz, 1H, dfppy), 7.35 (dd, J =8.8, 2.4 Hz, J_{H-Pt} =53.6 Hz, 1H, dfppy), 7.08 (t, J =6.4 Hz, 1H, dfppy), 6.56 (td, J_{H-F} =11.0 Hz, J_{H-H} =2.4 Hz, 1H, dfppy), 5.73 (m, 2H, π -arene), 5.07 (m, 2H, π -arene), 1.75 (s, 15H, Cp*). ¹⁹F NMR (375 MHz, CD₂Cl₂) δ : -109.3 (d, J_{F-F} =7.5 Hz, J_{F-Pt} =60.2 Hz), -111.5 (d, J_{F-F} =7.5 Hz, J_{F-Pt} =37.7 Hz). ¹³C NMR (100 MHz, CD₂Cl₂) δ : 150.3, 138.0, 123.0, 116.7, 115.5, 98.3, 92.3, 88.5, 87.3, 82.4, 82.0, 30.1, 9.39. IR (ATR, cm⁻¹): 2960, 2917, 2849, 1599, 1567, 1475, 1399, 1382, 1259, 1243, 1165, 10082, 1010, 795, 755, 704, 661, 506, 378, 313. Anal. Calcd for C₂₇H₂₅F₂NS₂RuPt.2(C₄H₁₀O).0.5H₂O C, 44.77; H, 4.87. Found: C, 44.61; H, 4.91.

Synthesis of [(bzq)Pt(Cp**Ru*(η -C₆H₄S₂))] (4)

Using 49 mg of [(bzq)Pt(μ -Cl)]₂. Compound **4** was obtained as a brown-yellow solid. Yield (49 mg, 55%).

¹H NMR (400 MHz, CD₂Cl₂) δ : 9.27 (dd, J =4.9, 1.2 Hz, J_{H-Pt} =34.2 Hz, 1H, bq), 8.33 (dd, J =8.0, 1.2 Hz, 1H, bq), 7.95 (dd, J =6.9, 0.8 Hz, J_{H-Pt} =41.8 Hz, 1H, bq), 7.78 (d, J =8.8 Hz, 1H, bq), 7.59 (t, J =9.0 Hz, 2H, bq), 7.51 (t, J =7.6 Hz, 1H, bq), 7.43 (t, J =6.8, 2.4 Hz, 1H, bq), 5.79 (m, 2H, π -arene), 5.08 (m, 2H, π -arene), 1.77 (s, 15H, Cp*). ¹³C NMR (100 MHz, CD₂Cl₂) δ : 157.4, 153.6, 148.4, 136.4, 134.5, 130.8, 130.3, 129.8, 123.5, 122.3, 122.1, 120.6, 92.2, 88.6, 87.3, 82.3, 81.9, 9.4. IR (ATR, cm⁻¹): 3032, 2917, 2851, 1616, 1562, 1444, 1404, 1375, 1327, 1203, 1080, 1030, 832, 760, 715, 661, 504, 443, 355. Anal. Calcd for C₂₉H₂₇NS₂RuPt.0.5H₂O. C, 45.90; H, 3.72 Found: C, 46.02; H, 4.10.

X-ray Structural determination of compounds 2-3

Suitable crystals for X-ray diffraction study were grown through slow evaporation of diethyl ether into a saturated CH_2Cl_2 solution of the desired compound. A single crystal was selected, mounted and transferred in a cold nitrogen gas stream. Intensity data for compounds **2** and **3** was collected with Bruker Kappa-APEX2 systems using Cu-K α micro-source and Mo-K α fine-focus sealed tube radiations respectively. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.¹ The structures were solved using SIR92² and refined anisotropically by full-matrix least-squares methods using SHELXL-2013.³ Both structures contain a combination of the two enantiomers depending on the coordination of the cyclometalated ligand, whereby the cyclometalated carbon center and the nitrogen atom are disordered over two positions. Refinement of the corresponding site occupancy factors led to ratios of 50:50 (**2**) and 67:33 (**3**). Crystallographic data (excluding structure factors) for these structures was deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 996068 (**2**) and 996069 (**3**). Data can be obtained free of charge via www.ccdc.cam.ac.uk.

Crystal data for **2** : yellow crystal, $\text{C}_{58}\text{H}_{64}\text{N}_2\text{OPt}_2\text{Ru}_2\text{S}_4$, monoclinic, P 2₁/n, a = 9.4042(3) , b = 32.3818(12), c = 17.4083(6) Å, β = 95.707(2) °, V = 5275.0(3) Å³, Z = 4, T = 200(1) K, μ = 16.044 mm⁻¹, 35960 reflections measured, 9289 independent (R_{int} = 0.0439), 7644 observed [$I > 2\sigma(I)$], 634 parameters, final R indices R1 [$I > 2\sigma(I)$] = 0.0279 and wR2 (all data) = 0.0627, GOF(on F²) = 1.051, max/min residual electron density 1.025/-0.586 e.Å⁻³.

Crystal data for **3** : yellow crystal, $\text{C}_{27}\text{H}_{25}\text{F}_2\text{NPtRuS}_2$, monoclinic, P 2₁/c, a = 7.9705(2) , b = 12.8005(3), c = 23.7135 Å, β = 96.8710(10) °, V = 2402.03(10) Å³, Z = 4, T = 200(1) K, μ = 6.653 mm⁻¹, 37344 reflections measured, 7358 independent (R_{int} = 0.0207), 6912 observed [$I > 2\sigma(I)$], 330 parameters, final R indices R1 [$I > 2\sigma(I)$] = 0.0331 and wR2 (all data) = 0.0849, GOF(on F²) = 1.289, max/min residual electron density 2.914/-2.645 e.Å⁻³.

Optical spectroscopy

Absorption spectra of dilute CH_2Cl_2 solutions (c = 2×10⁻⁵ M) for the determination of the absorption coefficients were obtained using PerkinElmer Lambda 950 UV/vis/ NIR spectrophotometer. Steady-state photoluminescence spectra were measured in de-aerated solutions at rt, using an Edinburgh FLS920 fluorimeter, equipped with a Peltier-cooled R928 (200–850 nm) Hamamatsu PMT at the excitation wavelength of λ_{ex} = 425 nm. Luminescence quantum yields at rt were evaluated by comparing wavelength integrated intensities of the corrected emission spectra with reference $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (ϕ = 0.028 in air-equilibrated water). [Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press, Taylor & Francis: Boca Raton, FL, 2006.] The concentration was adjusted to obtain

absorbance values $A \leq 0.1$ at the excitation wavelengths. Band maxima and relative luminescence intensities are obtained with uncertainties of 2 nm and 10%, respectively.

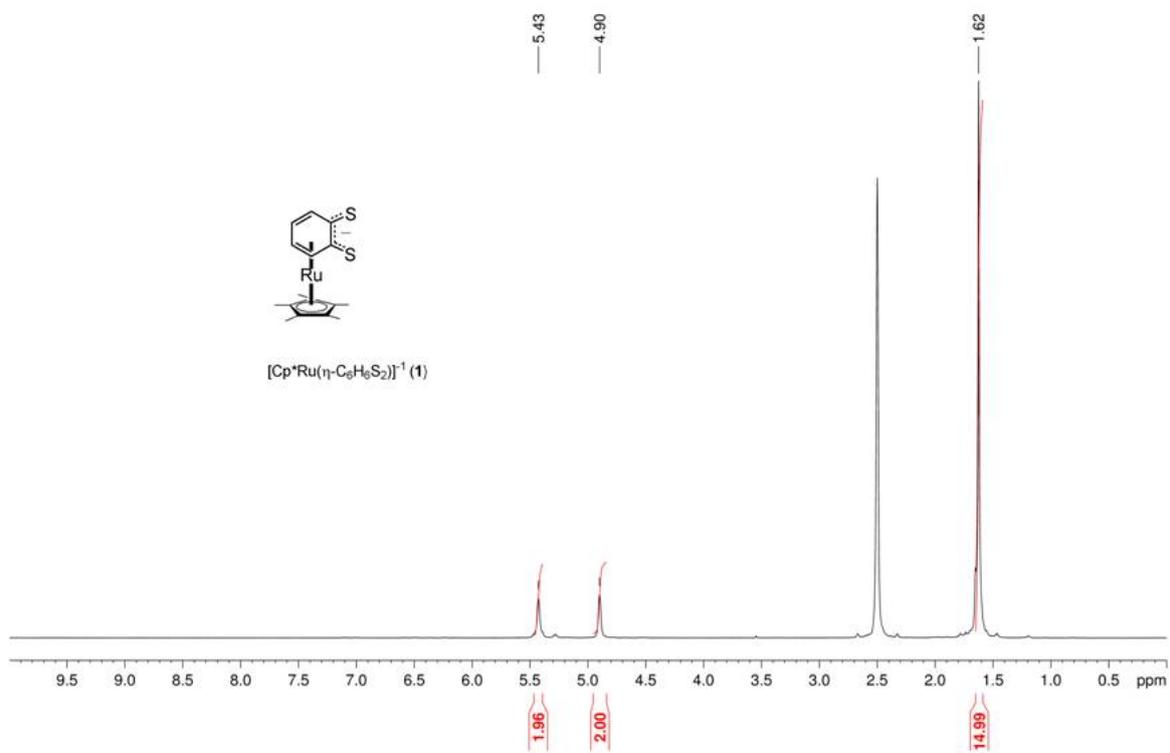
Luminescence lifetimes were obtained using a Jobin-Yvon IBH 5000F TCSPC apparatus equipped with a TBX Picosecond Photon Detection Module and NanoLED pulsed excitation sources ($\lambda_{\text{ex}} = 370$ nm). Analysis of luminescence decay profiles against time was accomplished using the Decay Analysis Software DAS6 provided by the manufacturer. The lifetime values were obtained with an estimated uncertainty of 10%.

Luminescence measurements of $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (1:1) glassy solutions at 77 K were performed by employing quartz capillary tubes immersed in liquid nitrogen and hosted within homemade quartz coldfinger dewar.

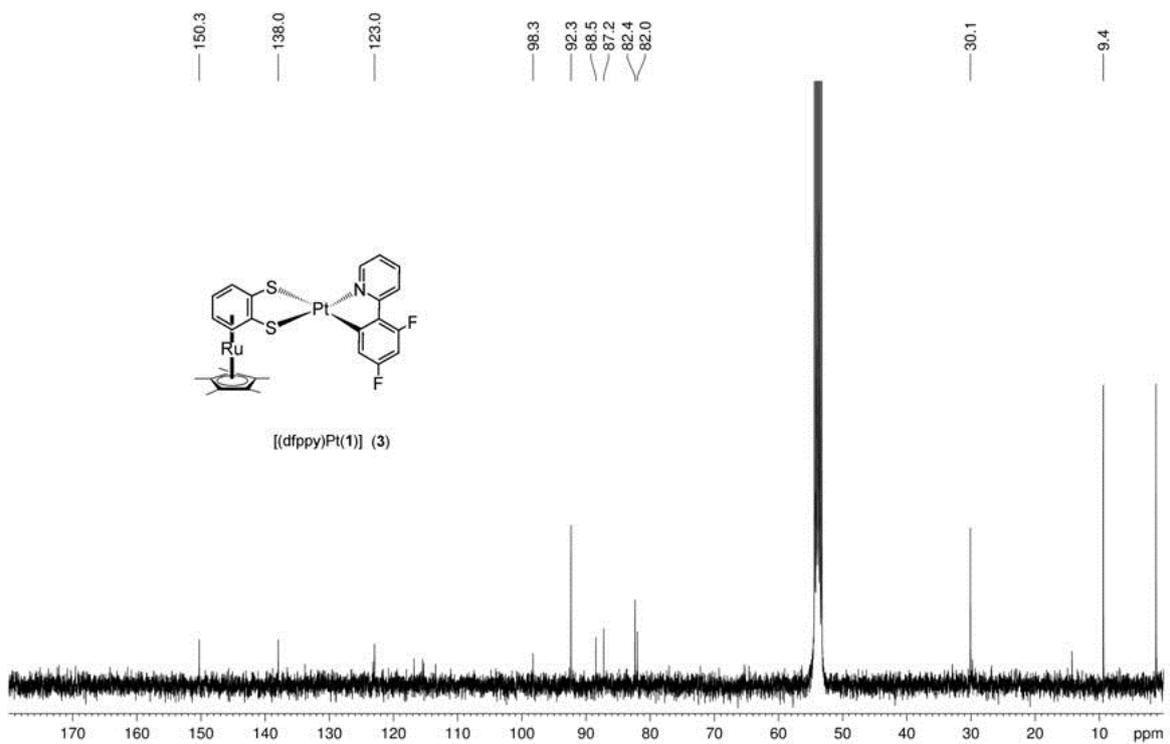
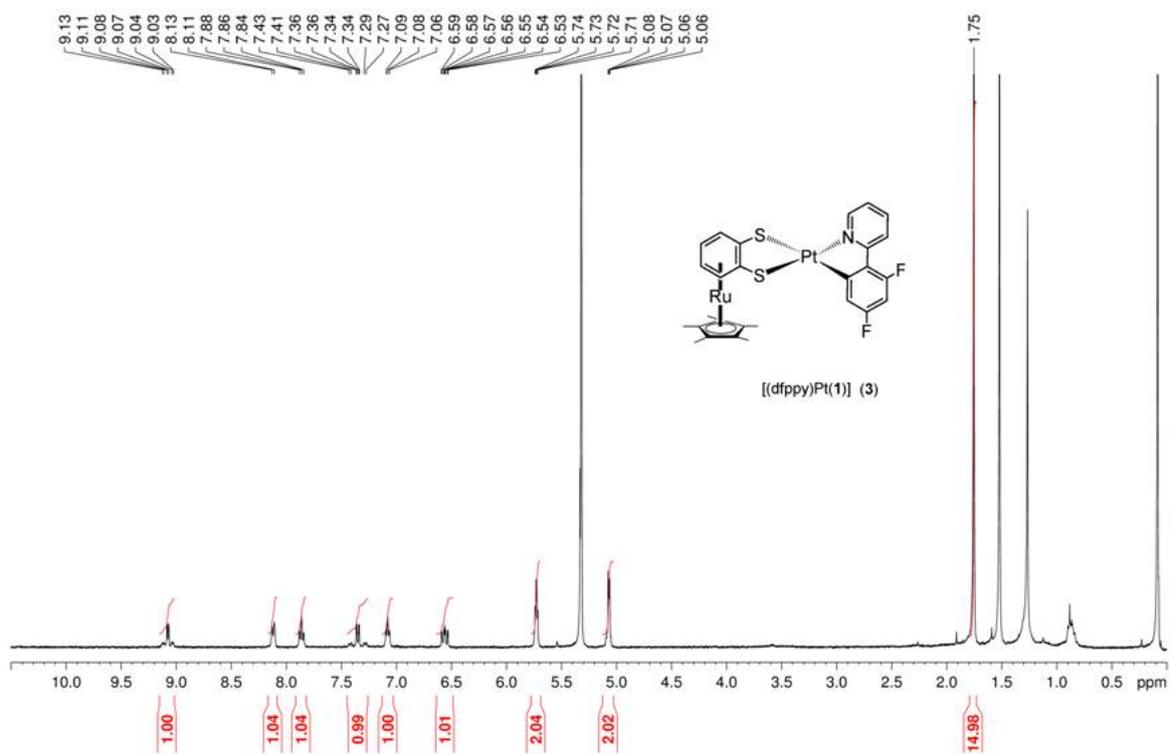
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3. Sheldrick, G.M. A short history of SHELX *Acta Cryst. A* **2008**, *64*, 112-122.

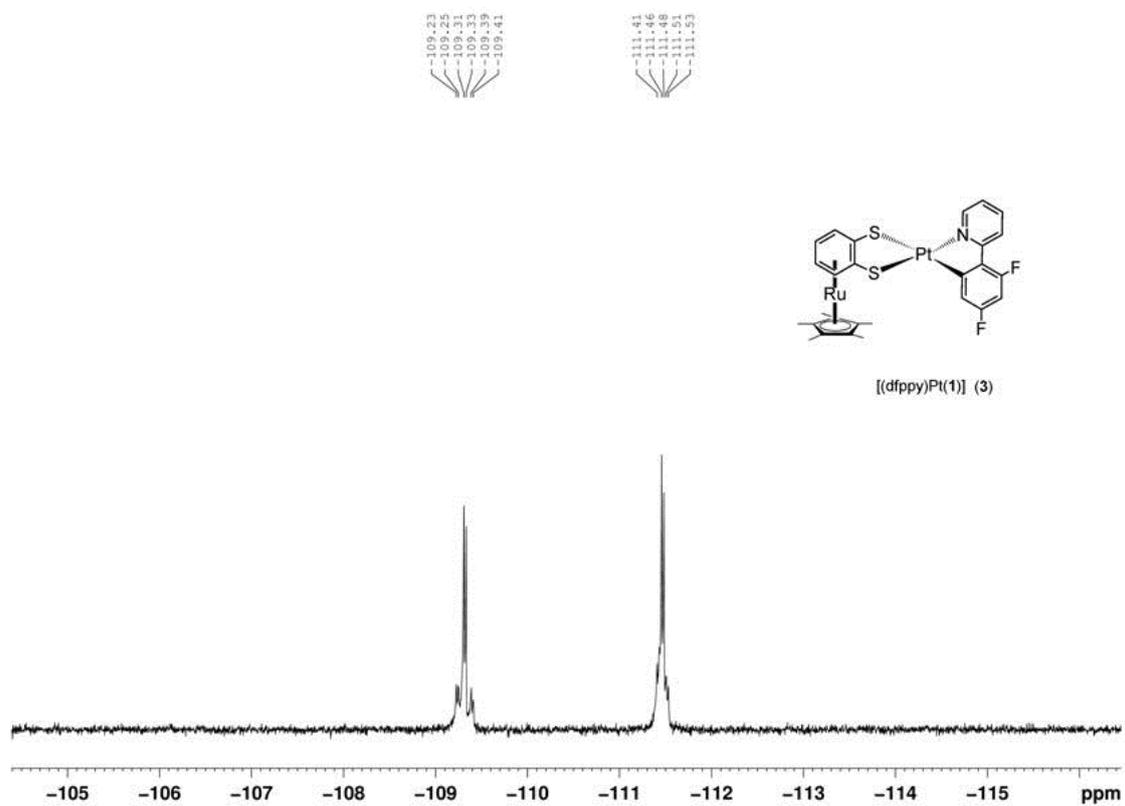
^1H NMR spectrum of Na-(1)



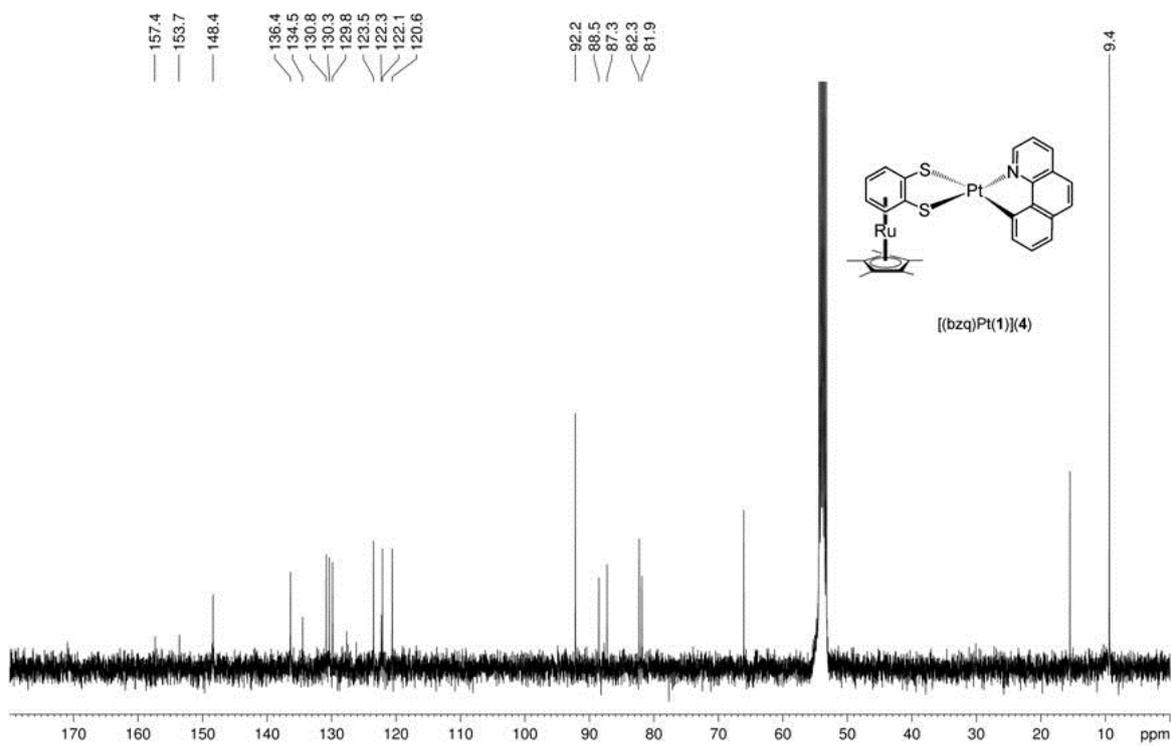
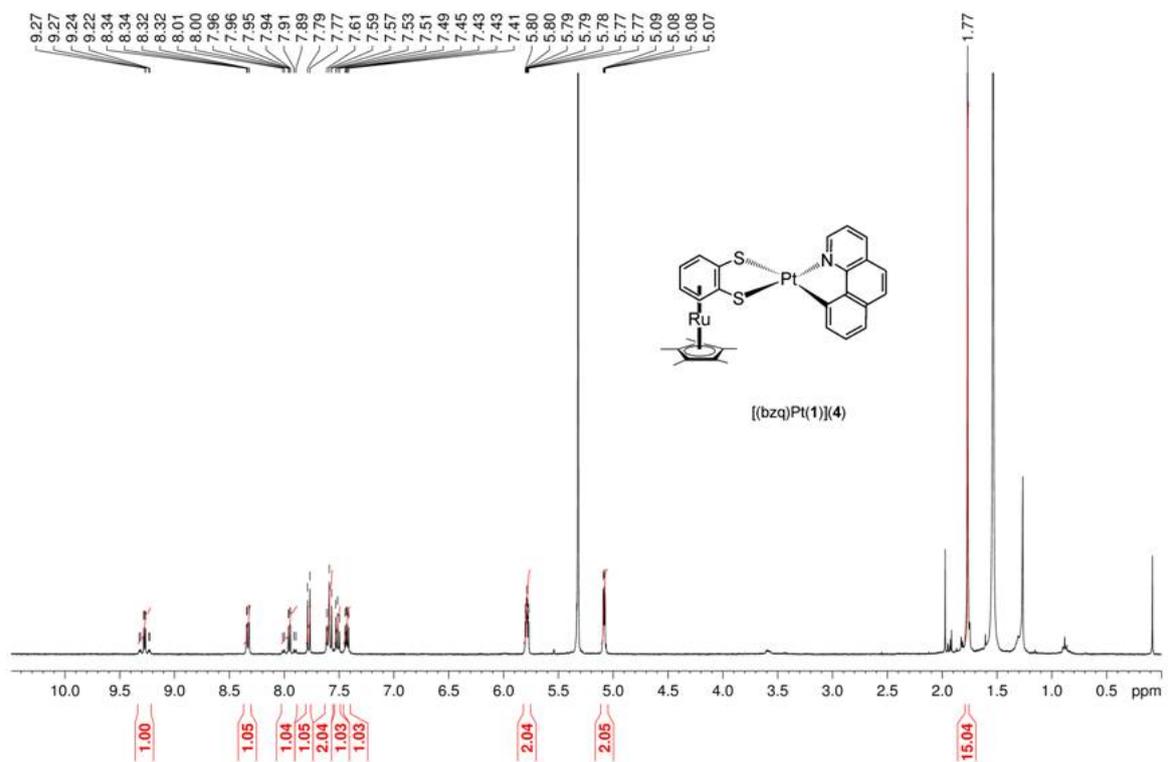
^1H and ^{13}C NMR spectra of (3)

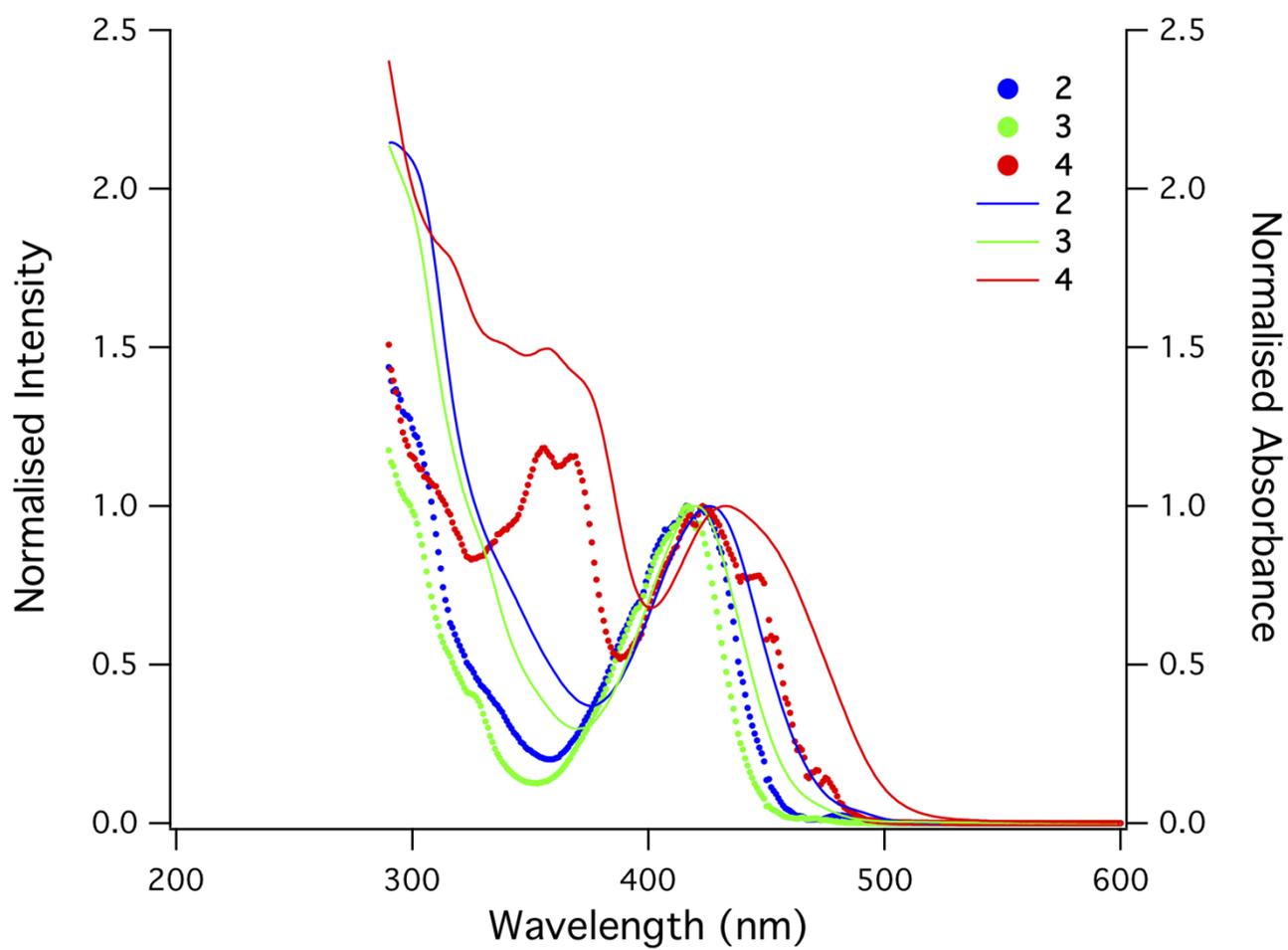


^{19}F NMR spectrum of **(3)**



^1H and ^{13}C NMR spectra of (4)





Normalised excitation spectra in $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$ (1:1) mixture at 77 K (dots) compared to the relevant normalised absorption spectra in CH_2Cl_2 at rt (lines) of complexes **2-4**.