

Introduction of a Triphenylamine Substituent on Pyridyl Rings as a Springboard for a New Appealing Brightly Luminescent 1,3-Di-(2-pyridyl)benzene Platinum(II) Complex Family

Alessia Colombo,^a Giulia De Soricellis,^a Francesco Fagnani,^a Claudia Dragonetti,^{*a} Massimo Cocchi^b, Bertrand Carboni,^c Véronique Guerschais,^c and Daniele Marinotto^d

a. Dipartimento di Chimica, Università degli Studi di Milano, Udr INSTM di Milano, via C. Golgi 19, 20133 Milan, Italy

b. Istituto per la Sintesi Organica e la Fotoreattività (ISOFA), Consiglio Nazionale delle Ricerche (CNR), via P. Gobetti 101, 40129 Bologna, Italy

c. Université de Rennes 1, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France.

d. Istituto di Scienze e Tecnologie Chimiche (SCITEC) "Giulio Natta", Consiglio Nazionale delle Ricerche (CNR), via C. Golgi 19, 20133 Milan, Italy

Contents

I. General Information	S2
II. Synthesis of platinum complexes	S4
III. ¹ H, ¹³ C, and ¹⁹ F NMR spectra	S11
IV. Photoluminescence investigations	S21
V. EQE vs Luminance and Current density vs Applied Voltage	S53

I. General Information

Solvents were freshly distilled under argon from sodium / benzophenone (tetrahydrofuran, toluene) or from phosphorus pentoxide (dichloromethane). Anhydrous dimethylformamide was used as received for the supplier. Column chromatography purifications were performed with silica gel (Merck Geduran 60, 0.063–0.200 mm). Flash chromatography purifications were performed on a Grace Reveleris™ with Puriflash™ 40µm flash cartridges (Buchi). NMR spectra were recorded on a Bruker AV III 300 MHz or AV III 400 MHz spectrometer. ¹H, ¹⁹F and ¹³C chemical shifts are reported in parts per million (ppm) whilst the coupling constants (J) are expressed in Hz. The abbreviations reported in brackets refer to the multiplicities: s, d, t, q, m indicate respectively singlet, doublet, triplet, quartet, multiplet. Mass spectrometry was performed by the Centre Regional de Mesures Physiques de l'Ouest, University of Rennes 1, on a LC-MS Agilent 6510, a Bruker MaXis 4G or a Thermo Fisher Q-Exactive using ESI and ASAP techniques. Elemental analyses were carried out in the Department of Chemistry of the University of Milan.

Electronic absorption spectra of the three complexes in solution and solid state were obtained with a UV-3600i Plus UV-VIS-NIR Spectrophotometer (Shimadzu Italia S.r.l., Milan, Italy).

Luminescence measurements at room temperature were carried out in CH₂Cl₂ solution after three freeze-pump-thaw cycles in order to remove dissolved oxygen; while low temperature measurements at 77 K were performed in CH₂Cl₂ solution after bubbling with argon for 5 minutes.

Absolute photoluminescence quantum yield, Φ, was measured using a C11347 Quantaaurus Hamamatsu Photonics K.K spectrometer. A description of the experimental setup and measurement method can be found in the article of K. Suzuki et al.¹ Φ was calculated through Equation:

$$\Phi = \frac{PN(Em)}{PN(Abs)} = \frac{\int \frac{\lambda}{hc} [I_{em}^{sample}(\lambda) - I_{em}^{reference}(\lambda)] d\lambda}{\int \frac{\lambda}{hc} [I_{exc}^{sample}(\lambda) - I_{exc}^{reference}(\lambda)] d\lambda}$$

where PN(Em) is the number of emitted photons, PN(Abs) the number of absorbed photons, λ the wavelength, h the Planck's constant, c the speed of light, I_{em}^{sample} and $I_{em}^{reference}$ the photoluminescence intensities of the sample solution and reference in CH₂Cl₂, I_{exc}^{sample} and $I_{exc}^{reference}$ the excitation light intensities of the sample solution and reference in CH₂Cl₂. PN(Em) is calculated in the wavelength interval [λ_i, λ_f], where λ_i is taken 10nm above the excitation wavelength, while λ_f is the upper end wavelength in the emission spectrum. The error made was estimated at around 5%.

Steady state and time-resolved fluorescence data were obtained using a FLS980 spectrofluorimeter (Edinburgh Instrument Ltd). For diluted solutions, quartz cuvettes with 1 cm optical path length were used in a right-angle configuration between the excitation beam and the detection system; while, for concentrated solutions, quartz cuvettes of 1 mm optical path length were used in a configuration front-face with an angle of 45° or less between the excitation beam and the detection system. Emission spectra were corrected for background intensity and quantum efficiency of the photomultiplier tube. Excitation spectra were corrected for the intensity fluctuation of a 450 W Xenon arc lamp. Moreover, in order to remove inner filter effects that appear in a concentrated solution, the luminescence signal was optimized by varying the angle between the excitation beam and the detection system, while the excitation and emission wavelength were fixed at the maximum absorption and maximum emission wavelength, respectively.

Time-resolved fluorescence measurements were performed by either the time-correlated single photon counting technique with an Edinburgh Picosecond Pulsed Diode Laser (emitted wavelength 404 nm and 445 nm) or Multi-Channel Scaling technique with a microsecond pulsed Xenon flashlamp.

In the case of excitation with a diode laser the full width at half maximum (FWHM) of the instrumental response function (IRF) is of about 0.23 ns, which is negligible compared to the intrinsic lifetime (of the order of μs) of the decay. Thus, the IRF is not required by the program for the fitting procedure analysis of phosphorescence decay measurements, as in Figures S24, S26, S27, S28, S32, and S42. For excitation with a microsecond pulsed Xenon flashlamp, the FWHM of the IRF is of about 2.4 μs ; therefore, also in this case the IRF is not necessary for intrinsic lifetime bigger than 100 μs , as in Figures S6 and S8. In Figures S10, S12, S14, and S16, the IRF measurements have been added and the relative lifetimes have been recalculated.

Time-resolved fluorescence curves were fitted using a multi-exponential function:

$$I(\lambda, t) = \sum_{i=1}^n \alpha_i(\lambda) \exp\left(-\frac{t}{\tau_i}\right)$$

where n is the number of exponentials, $\alpha_i(\lambda)$ is the amplitude at wavelength λ and τ_i is the lifetime of the component i . The quality of the fit was evaluated through the reduced χ^2 values.

In case of multi-exponential decay, it is possible define an average lifetime as:

$$\tau_{\text{av}} = \frac{\sum_{n=1}^m \alpha_n \tau_n^2}{\sum_{n=1}^m \alpha_n \tau_n}, \quad m = \text{multi-exponential decay number of the fit.}$$

Steady state and time-resolved fluorescence measurements on thin film were performed with a geometry in which the angle of incidence of the excitation beam on the sample was 45° or less.

Preparation and characterization of blended PMMA thin film

Thin film containing a 0.5 wt% of [PtL¹Cl] complex in polymethyl methacrylate (PMMA, $\bar{M}_w \approx 15000$ g/mol) on quartz plate (thickness 1 mm) was obtained by spin-coating (Cookson Electronic Company P-6708D). The parameters of spinning (RPM = revolutions per minute) were RPM 1: 800; Ramp 1: 1 s, Time 1: 5 s; RPM 2: 2000; Ramp 2: 1 s, Time 2: 60 s. The solution was prepared with 6.57 mg of complex, 1.33 g of PMMA in 10 ml of dichloromethane. The thickness, measured by an α -step stylus profilometer (DektaK XT, Bruker), was 1.97 ± 0.16 μm .

Preparation and characterization of neat thin film

Pure PtL¹Cl complex film was prepared by thermal evaporation under high vacuum (10^{-6} hPa).

The film thickness of 50 ± 5 nm was measured by Tencor α -step 200 profilometer.

II. Synthesis of platinum complexes

II-1. Synthesis of [PtL¹Cl]

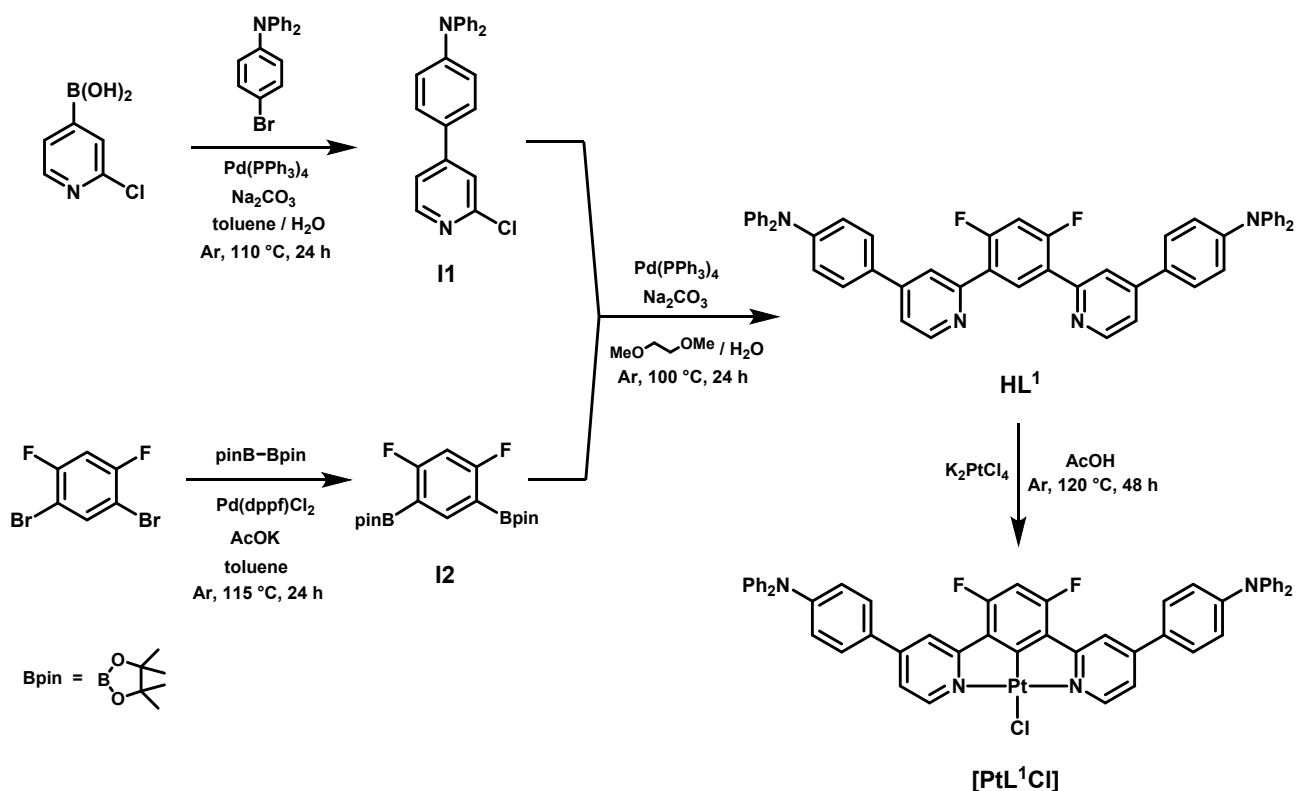


Figure S1. Synthetic pathway for the preparation of $[PtL^1Cl]$.

Synthesis of 4-(2-chloropyridin-4-yl)-*N,N*-diphenylaniline **I1.** 2-Chloro-pyridine-4-boronic acid (690 mg, 4.385 mmol), (4-bromophenyl)-diphenylamine (1.010 g, 3.115 mmol), 1,4-dioxane (18 mL) and 6 mL of an aqueous 1M Na_2CO_3 solution were placed in a Schlenk tube under argon atmosphere. The reaction mixture was degassed by bubbling argon under stirring for 30 min. Then, $Pd(PPh_3)_4$ (180 mg, 0.156 mmol) was added. The tube was sealed and heated at 110 °C overnight. Upon cooling to room temperature, the solution was neutralized with aqueous 1M HCl and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: cyclohexane/AcOEt, from 10:0 to 8:2) to obtain a clear oil (480 mg, 44%).

1H NMR (300 MHz, CD_2Cl_2 , δ): 8.39 (d, $J = 5.4$ Hz, 1H), 7.52-7.49 (m, 3H), 7.40 (dd, $J = 1.6$ Hz, $J = 5.3$ Hz, 1H), 7.35-7.28 (m, 4H), 7.19-7.09 (m, 8H).

^{13}C { 1H } NMR (75.48 MHz, $CDCl_3$, δ): 206.9, 152.2, 150.9, 149.9, 149.5, 147.0, 129.3, 127.7, 125.2, 123.9, 122.5, 121.1, 119.6.

HRMS (ESI+): $(M + H)^+$ calcd for $C_{23}H_{18}N_2^{35}Cl$, 357.1153; found: 357.1154.

Synthesis of 2,2'-(4,6-difluoro-1,3-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **I2.**

Anhydrous toluene (25.0 mL) was transferred under argon to a two neck round flask containing 1,3-dibromo-4,6-difluorobenzene (2.00 g, 7.356 mmol), bis(pinacolato)diboron (4.076 g, 16.053 mmol), AcOK (3.675 g, 37.446 mmol) and Pd(dppf)Cl₂ (342 mg, 0.467 mmol). The mixture was heated at 110 °C under argon atmosphere for 18h. Upon cooling to room temperature, a mixture of AcOEt and water were added and the phases were separated. The organic phase was then washed with water and brine, dried over MgSO₄, and the solvent removed under reduced pressure. The crude product was filtered on silica gel (eluent: cyclohexane/AcOEt 8:2). The obtained product was dissolved in pentane and placed in the freezer overnight. The precipitate was thus filtrated and dried (1.745 g, 65%). The spectroscopic data match with those reported in the literature.²

¹H NMR (300 MHz, CDCl₃, δ): 8.15 (t, ³J(¹⁹F) = 7.6 Hz, 1H), 6.74 (t, ³J(¹⁹F) = 9.7 Hz, 1H), 1.37 (s, 24H).

¹⁹F {1H} NMR (282.36 MHz, CDCl₃, δ): -94.15 (s, 2F).

Synthesis of 4,4'-((4,6-difluoro-1,3-phenylene)bis(pyridine-2,4-diyl))bis(N,N-diphenylaniline) **HL1.**

A two neck round bottom flask filled with argon was charged with **I1** (480 mg, 1.348 mmol), **I2** (220 mg, 0.601 mmol), 1,2-dimethoxyethane (8.0 mL) and a 1.2 M Na₂CO₃ solution in water (8.0 mL). The mixture was vigorously bubbled with argon for 30 min before adding Pd(PPh₃)₄ (110 mg, 0.095 mmol) and sealing the flask. The reaction mixture was heated at 100 °C for 24 h. The solution was cooled to room temperature. Dichloromethane and water were added, the two layers were separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with brine, dried over MgSO₄ and evaporated at reduced pressure. The oily residue was purified by silica gel chromatography (eluent: cyclohexane/AcOEt, from 9:1 to 8:2) and a clear yellow lacquer was obtained (190 mg, 42% yield).

¹H NMR (300 MHz, CDCl₃, δ): 8.74 (d, J = 5.2 Hz, 2H), 8.68 (t, ³J(¹⁹F) = 8.9 Hz, 1H), 7.98 (s, 2H), 7.62-7.58 (m, 4H), 7.47 (dd, J = 1.7 Hz, J = 3.4 Hz, 2H), 7.36-7.29 (m, 8H), 7.21-7.16 (m, 12H), 7.13-7.08 (m, 4H), 7.09 (t, ³J(¹⁹F) = 10.6 Hz, 1H).

¹⁹F {1H} NMR (282.36 MHz, CDCl₃, δ): -112.57 (s, 2F).

¹³C {1H} NMR (75.48 MHz, CDCl₃, δ): 153.1, 150.1, 149.0, 148.3, 147.3, 133.8, 131.9, 129.4, 127.8, 125.0, 123.6, 122.9, 121.6, 119.8, 105.0 (t, J = 27.0 Hz). Not all signals are seen (15 on 17 signals) because of the splitting of some carbons of the central benzene ring on two F atom to multiplets making them "invisible" due to low signals intensities.

HRMS (ESI⁺): (M + H)⁺ calcd for C₅₂H₃₇N₄F₂, 755.2981; found: 755.2978.

Synthesis of [PtL¹Cl]. HL¹ (190 mg, 0.252 mmol) was solubilized in acetonitrile (12 mL) and placed under argon in a Schlenk tube. In parallel, K₂PtCl₄ (210 mg, 0.506 mmol) was dissolved in water (1.3 mL) using an ultrasonic bath and then added to the reaction vessel. The mixture was degassed by directly bubbling argon for 30 min in the solvent under stirring. The flask was then sealed and heated at 110°C for three days. Upon cooling to room temperature, the suspension was filtered through a 0.45 μm Nylon membrane. The isolated yellow solid was washed with water and diethyl ether, and dried under vacuum (200 mg, 82% yield).

¹H NMR (300 MHz, CDCl₃, δ): 9.28 (d, J = 6.4 Hz, ³J(¹⁹⁵Pt) = 44 Hz, 2H), 8.10 (s, 2H), 7.64-7.61 (m, 4H), 7.45 (dd, J = 2.2, J = 4.2 Hz, 2H), 7.38-7.31 (m, 8H), 7.22-7.10 (m, 16H), 6.77 (t, ³J(¹⁹F) = 11.3 Hz, 1H).

¹⁹F {¹H} NMR (282.36 MHz, CDCl₃, δ): -108.99 (s, 2F).

It was not possible to record a ¹³C NMR spectrum due to the very low solubility both in chlorinated solvents and DMSO.

HRMS (ESI⁺): (M + H)⁺ calcd for C₅₂H₃₅N₄F₂³⁵Cl¹⁹⁵Pt, 983.2161; found: 983.219. Anal. Calcd. for C₅₂H₃₅N₄F₂ClPt: C, 63.45; H, 3.58; N, 5.69; found: C, 63.56; H, 3.60; N, 5.72

II-2. Synthesis of [PtL²Cl]

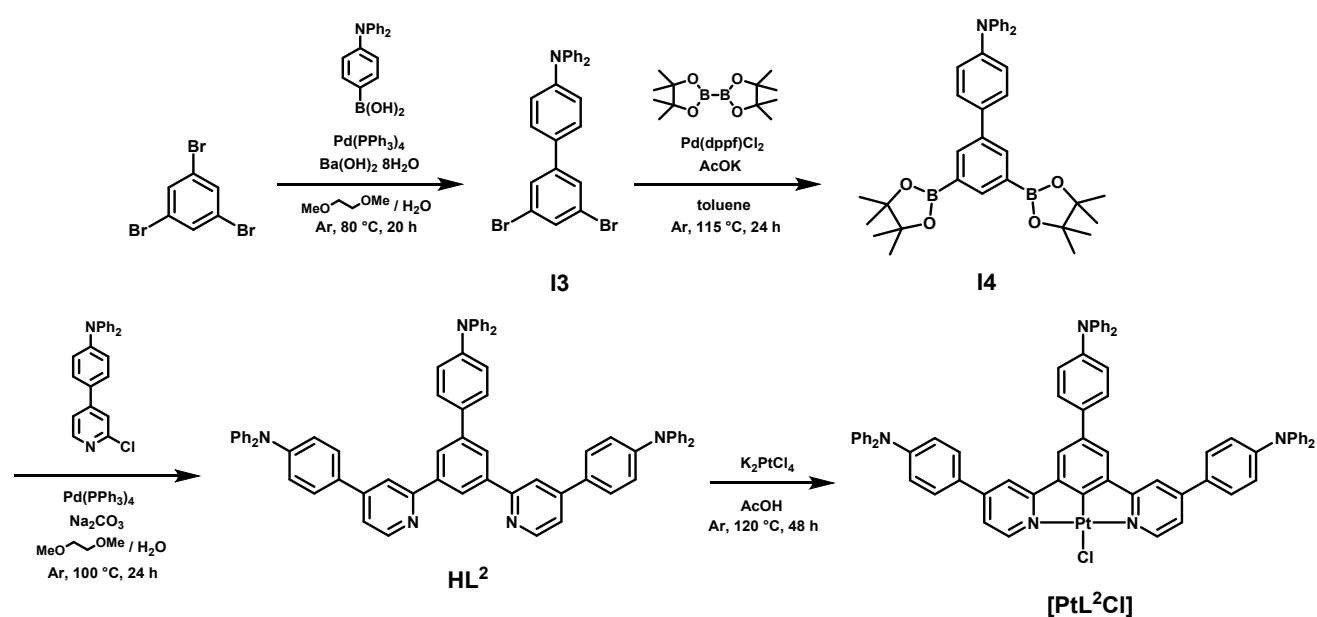


Figure S2. Synthetic pathway for the preparation of [PtL²Cl].

Synthesis of 3',5'-dibromo-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine I3. 1,3,5-tribromobenzene (500 mg, 1.588 mmol), 4-diphenylamino-phenylboronic acid (383 mg, 1.325 mmol), Ba(OH)₂ · 8H₂O (624 mg, 1.975 mmol) and Pd(PPh₃)₄ (50 mg, 0.043 mmol) were added to a mixture of 1,2-dimethoxyethane (3.0 mL) and water (0.5 mL) in a Schlenk tube. The reaction mixture was heated at reflux for 24 h under argon atmosphere. After cooling to room temperature, water and toluene were added and the phases were separated; the organic phase was washed with brine and water, dried over Na₂SO₄ and evaporated at reduced pressure. The product was purified by flash chromatography on silica gel (eluent: hexane), obtaining a white solid (435 mg, 69%). The spectroscopic data match with those reported in the literature.³

¹H-NMR (400 MHz, CDCl₃) δ (ppm): 7.64 (d, J = 1.7 Hz, 2H), 7.60 (t, J = 1.7 Hz, 1H), 7.40 (d, J = 8.7 Hz, 2H), 7.31 (t, J = 8.2 Hz, 4H), 7.18-7.06 (m, 8H).

Synthesis of *N,N*-diphenyl-3',5'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-amine I4. I3 (171 mg, 0.357 mmol), bis(pinacolato)diboron (200 mg, 0.785 mmol), AcOK (175 mg, 1.784 mmol) and Pd(dppf)Cl₂ (19 mg, 0.025 mmol) were added to toluene (1.25 mL) in a Schlenk tube. The reaction mixture was heated at reflux for 24 h under argon atmosphere. After cooling to room temperature, water and AcOEt were added and the phases were separated; the aqueous phase was extracted with AcOEt, the organic phases were washed with brine and water, dried over Na₂SO₄ and evaporated at reduced pressure. The product was purified by flash chromatography on silica gel (eluent: hexane/AcOEt 9:1), obtaining a white solid (117 mg, 57%).

¹H-NMR (400 MHz, CD₂Cl₂) δ (ppm): 8.12 (bs, 1H), 8.09 (d, J = 0.9 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.32 (t, J = 8.4 Hz, 4H), 7.18-7.12 (m, 6H), 7.07 (t, J = 7.3 Hz, 2H), 1.39 (s, 24H).

Synthesis of 4,4'-((4'-(diphenylamino)-[1,1'-biphenyl]-3,5-diyl)bis(pyridine-2,4-diyl))bis(*N,N*-diphenylaniline) HL². I1 (217 mg, 0.612 mmol), I4 (117 mg, 0.204 mmol), Na₂CO₃ (150 mg, 1.428 mmol) and Pd(PPh₃)₄ (17 mg, 0.015 mmol) were added to a mixture of 1,2-dimethoxyethane (3.0 mL) and water (3.0 mL) in a Schlenk tube. The reaction mixture was heated at reflux for 24 h under argon atmosphere. After cooling to room temperature, water and AcOEt were added and the phases were separated; the organic phase was washed with water, dried over Na₂SO₄ and evaporated at

reduced pressure. The product was purified by flash chromatography on silica gel (eluent: hexane/AcOEt 75:25), obtaining a white solid (108 mg, 55%).

$^1\text{H-NMR}$ (300 MHz, CD_2Cl_2) δ (ppm): 8.79-8.74 (m, 3H), 8.40 (d, $J = 1.4$ Hz, 2H), 8.15 (s, 2H), 6.76-6.67 (m, 6H), 7.53 (dd, $J = 1.4$ Hz, $J = 5.4$ Hz, 2H), 7.39-7.29 (m, 12H), 7.24-7.06 (m, 24H).
Anal. Calcd. for $\text{C}_{70}\text{H}_{51}\text{N}_5$: C, 87.38; H, 5.35; N, 7.28; found: C, 87.52; H, 5.37; N, 7.25

Synthesis of $[\text{PtL}^2\text{Cl}]$. HL^2 (100 mg, 0.104 mmol) and K_2PtCl_4 (52 mg, 0.125 mmol) were added to glacial acetic acid (6.0 mL) in a Schlenk tube. The reaction mixture was heated at reflux under argon atmosphere. After 48 h a precipitate had appeared and, once cooled to room temperature, water was added to complete the precipitation. The solid, which was filtered on a Buchner funnel and washed with water, methanol and diethyl ether, was obtained as an orange powder (116 mg, 93%).

$^1\text{H-NMR}$ (400 MHz, CD_2Cl_2) δ (ppm): 9.15 (d, $J = 6.1$ Hz, $^3J(^{195}\text{Pt}) = 38$ Hz, 2H), 8.02 (d, $J = 1.9$ Hz, 2H), 7.82 (s, 2H), 7.72 (d, $J = 8.8$ Hz, 4H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.55 (dd, $J = 1.9$ Hz, $J = 6.1$ Hz, 2H), 7.40-7.30 (m, 12H), 7.23-7.15 (m, 22H), 7.09 (t, $J = 7.3$ Hz, 2H).

It was not possible to record a good ^{13}C NMR spectrum due to the very low solubility both in chlorinated solvents and DMSO. In any case we report the best obtained spectrum in CD_2Cl_2

^{13}C { ^1H } NMR (100 MHz, CD_2Cl_2 , δ): 147.01, 141.45, 129.59, 129.51, 129.27, 127.93, 127.61, 125.42, 124.35, 122.11, 122.97, 122.75, 121.96

Anal. Calcd. for $\text{C}_{70}\text{H}_{50}\text{ClN}_5\text{Pt}$: C, 70.55; H, 4.23; N, 5.88; found: C, 70.87; H, 4.25; N, 5.86

II-3. Synthesis of $[\text{PtL}^3\text{Cl}]$

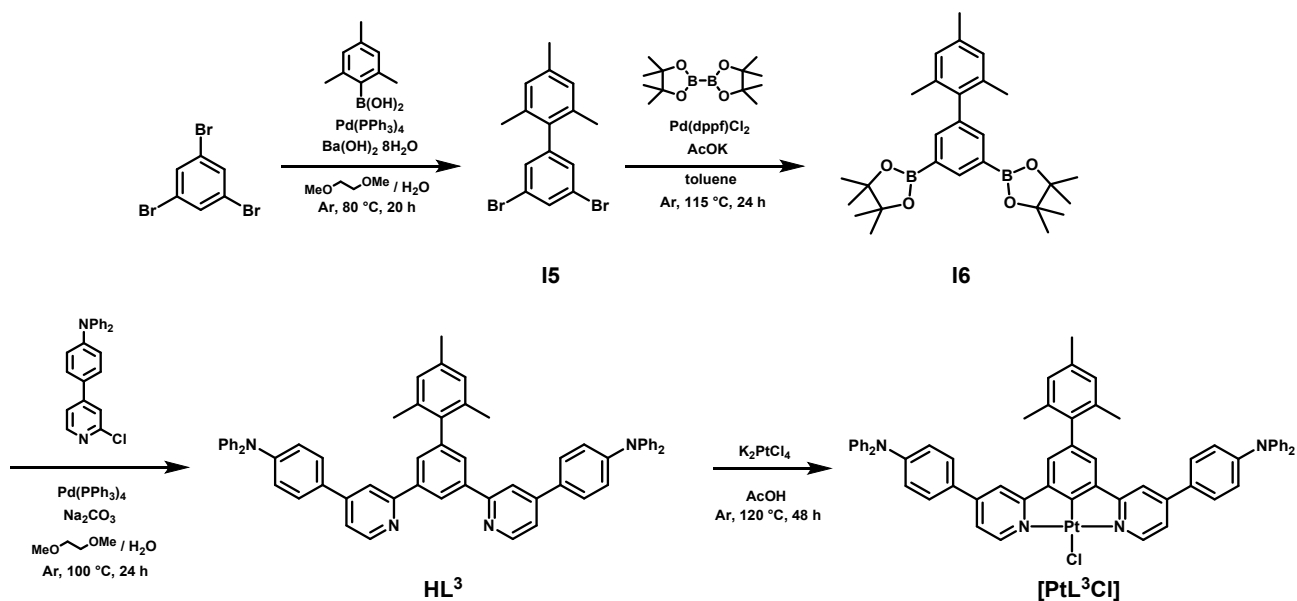


Figure S3. Synthetic pathway for the preparation of $[\text{PtL}^3\text{Cl}]$.

Synthesis of 3',5'-dibromo-2,4,6-trimethyl-1,1'-biphenyl **I5.** 1,3,5-tribromobenzene (962 mg, 3.056 mmol), 2,4,6-trimethylphenylboronic acid (500 mg, 3.048 mmol), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (1.445 g, 4.575 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (104 mg, 0.091 mmol) were added to a mixture of 1,2-dimethoxyethane (6.0 mL) and water (1.0 mL) in a Schlenk tube. The reaction mixture was heated at reflux for 24 h under argon atmosphere. After cooling to room temperature, water and toluene were added and the phases were separated; the organic phase was washed with brine and water, dried over Na_2SO_4 and evaporated at reduced pressure. The product was purified by flash chromatography on silica gel (eluent: hexane), obtaining a white solid (534 mg, 77%). The spectroscopic data match with those reported in the literature.⁴

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ (ppm): 7.66 (t, $J = 1.6$ Hz, 1H), 7.26 (d, $J = 1.6$ Hz, 2H), 6.94 (s, 2H), 2.34 (s, 3H), 2.02 (s, 6H).

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}$: C, 50.82; H, 3.99; found: C, 50.90; H, 4.0

Synthesis of 2,2'-(2',4',6'-trimethyl-[1,1'-biphenyl]-3,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **I6.** **I5** (303 mg, 0.860 mmol), bis(pinacolato)diboron (477 mg, 1.878 mmol), AcOK (419 mg, 4.269 mmol) and $\text{Pd}(\text{dppf})\text{Cl}_2$ (44 mg, 0.060 mmol) were added to toluene (3.0 mL) in a Schlenk tube. The reaction mixture was heated at reflux for 24 h under argon atmosphere. After

cooling to room temperature, water and AcOEt were added and the phases were separated; the aqueous phase was extracted with AcOEt, the organic phases were washed with water, dried over Na₂SO₄ and evaporated at reduced pressure. The product was purified by flash chromatography on silica gel (eluent: hexane/AcOEt 9:1), obtaining a white solid (217 mg, 54%)

¹H-NMR (400 MHz, CD₂Cl₂) δ (ppm): 8.25 (t, J = 1.0 Hz, 1H), 7.70 (d, J = 1.0 Hz, 2H), 6.90 (s, 2H), 2.32 (s, 3H), 1.99 (s, 6H), 1.36 (s, 24H).

Synthesis of 4,4'-((2',4',6'-trimethyl-[1,1'-biphenyl]-3,5-diyl)bis(pyridine-2,4-diyl))bis(*N,N*-diphenylaniline) HL³. **I1** (91 mg, 0.255 mmol), **I6** (39 mg, 0.085 mmol), Na₂CO₃ (63 mg, 0.595 mmol) and Pd(PPh₃)₄ (7 mg, 0.006 mmol) were added to a mixture of 1,2-dimethoxyethane (1.0 mL) and water (1.0 mL) in a Schlenk tube. The reaction mixture was heated at reflux for 24 h under argon atmosphere. After cooling to room temperature, water and AcOEt were added and the phases were separated; the organic phase was washed with water, dried over Na₂SO₄ and evaporated at reduced pressure. The product was purified by flash chromatography on silica gel (eluent: hexane/AcOEt 9:1), obtaining a white solid (40 mg, 57%).

¹H-NMR (400 MHz, CD₂Cl₂) δ (ppm): 9.15 (2H, d, J = 6.1 Hz, J(¹⁹⁵Pt) = 40 Hz), 7.92 (2H, d, J = 1.8 Hz), 7.67 (4H, d, J = 8.8 Hz), 7.54 (2H, dd, J = 2.1 Hz, J = 6.1 Hz), 7.40-7.32 (10H, m), 7.21-7.12 (16H, m), 7.01 (2H, s), 2.36 (3H, s), 2.13 (6H, s).

Anal. Calcd. for C₆₁H₄₆N₄: C, 87.53; H, 5.78; N, 6.69; found: C, 87.48; H, 5.80; N, 6.71

Synthesis of [PtL³Cl]. HL³ (14 mg, 0.017 mmol) and K₂PtCl₄ (9 mg, 0.022 mmol) were added to glacial acetic acid (1.0 mL) in a Schlenk tube. The reaction mixture was heated at reflux under argon atmosphere. After 48 h a precipitate had appeared and, once cooled to room temperature, water was added to complete the precipitation. The solid was filtered on a Buchner funnel and washed with water, methanol and diethyl ether, to give an orange powder (16 mg, 88%).

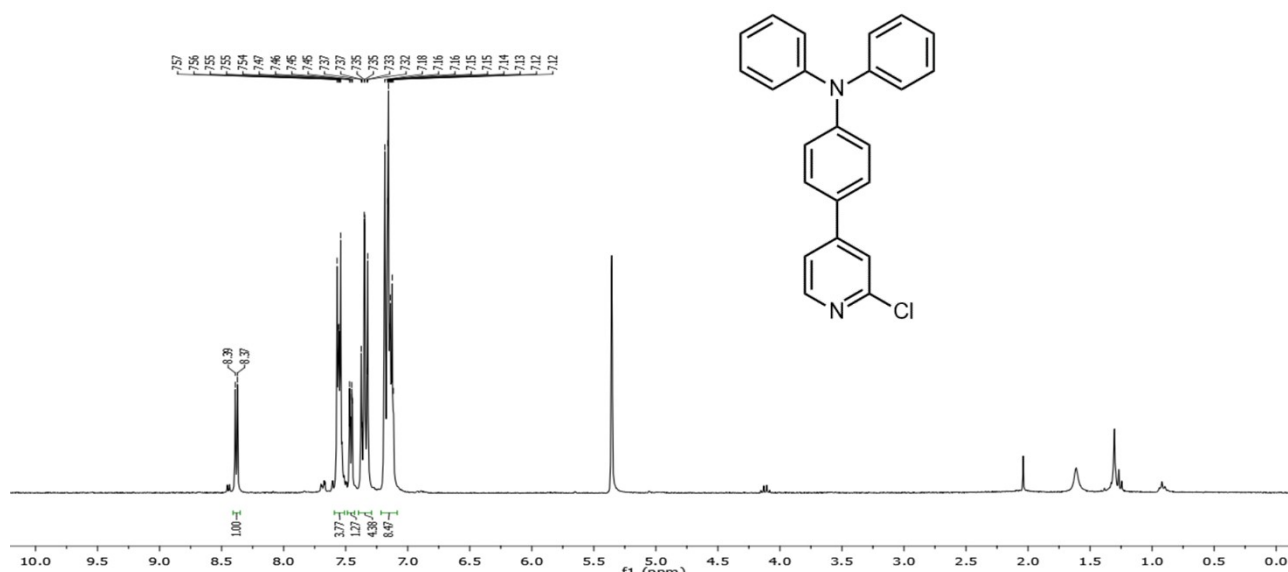
¹H-NMR (400 MHz, CD₂Cl₂) δ (ppm): 9.15 (d, J = 6.1 Hz, ³J(¹⁹⁵Pt) = 40 Hz, 2H), 7.92 (d, J = 1.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 4H), 7.54 (dd, J = 2.1 Hz, J = 6.1 Hz, 2H), 7.40-7.32 (m, 10H), 7.21-7.12 (m, 16H), 7.01 (s, 2H), 2.36 (s, 3H), 2.13 (s, 6H).

It was not possible to record a good ¹³C NMR spectrum due to the very low solubility both in chlorinated solvents and DMSO. In any case we report the best obtained spectrum in CD₂Cl₂

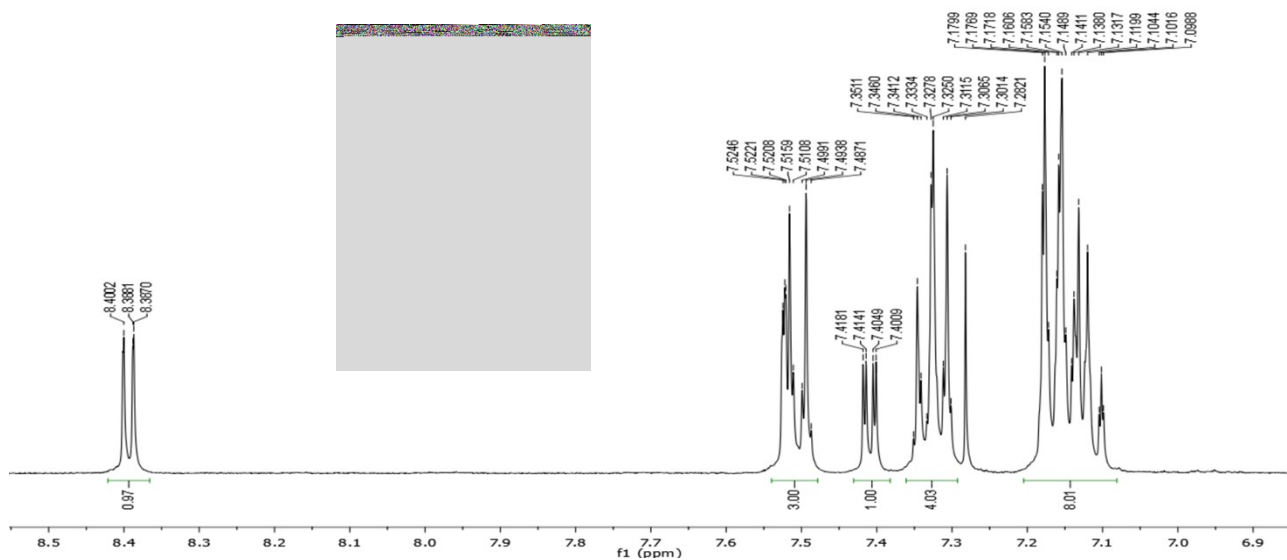
^{13}C { ^1H } NMR (100 MHz, CD_2Cl_2 , δ): 129.59, 129.50, 127.83, 125.81, 125.42, 124.09, 121.94.

Anal. Calcd. for $\text{C}_{61}\text{H}_{47}\text{ClN}_4\text{Pt}$: C, 68.69; H, 4.44; N, 5.25; found: C, 68.73; H, 4.42; N, 5.27

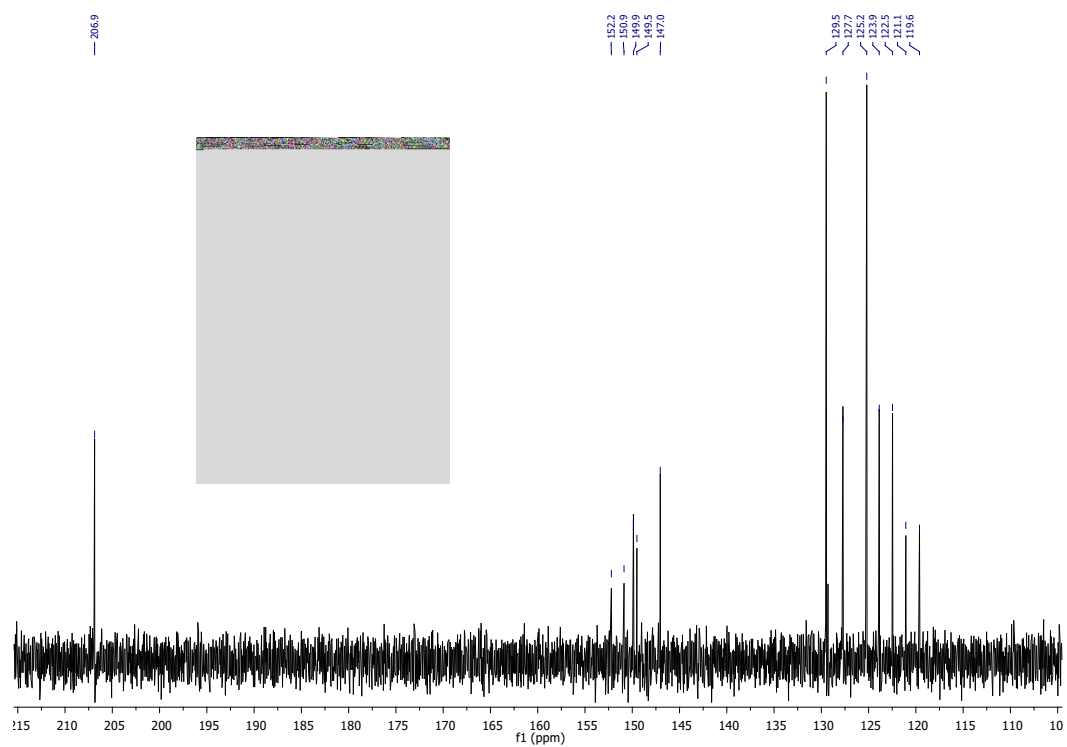
III. ^1H , ^{13}C , and ^{19}F NMR Spectra



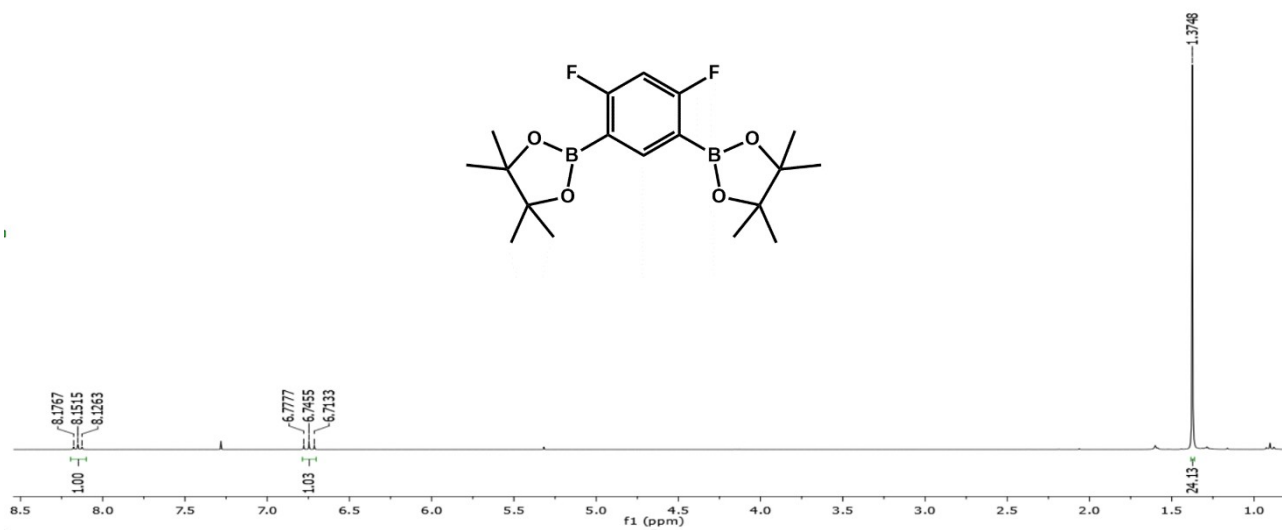
^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of compound II.



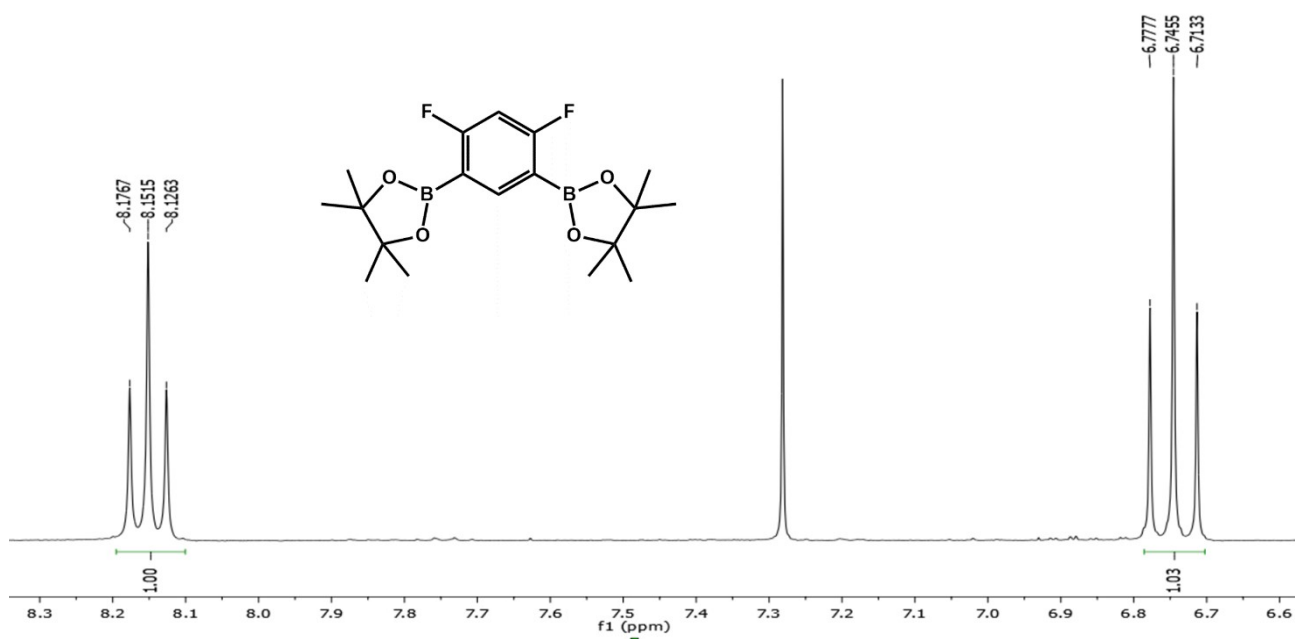
^1H NMR spectrum (CD_2Cl_2 , 300 MHz) of compound **II**, aromatic region.



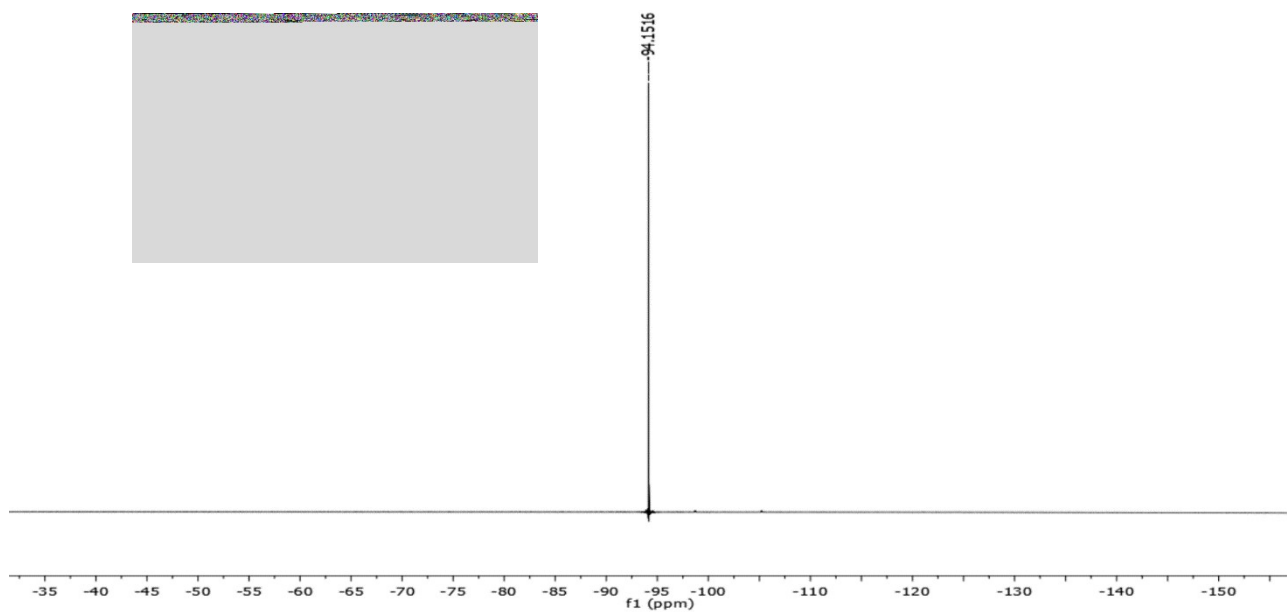
^{13}C $\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 75.48 MHz) of compound **II**.



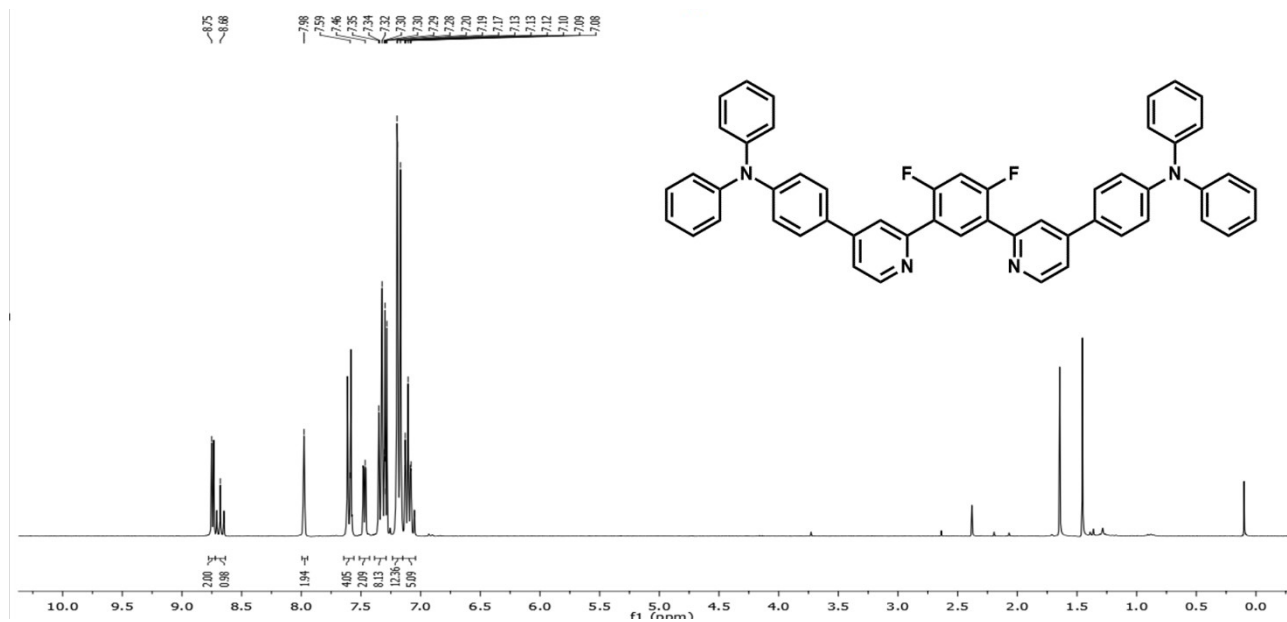
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **12**.



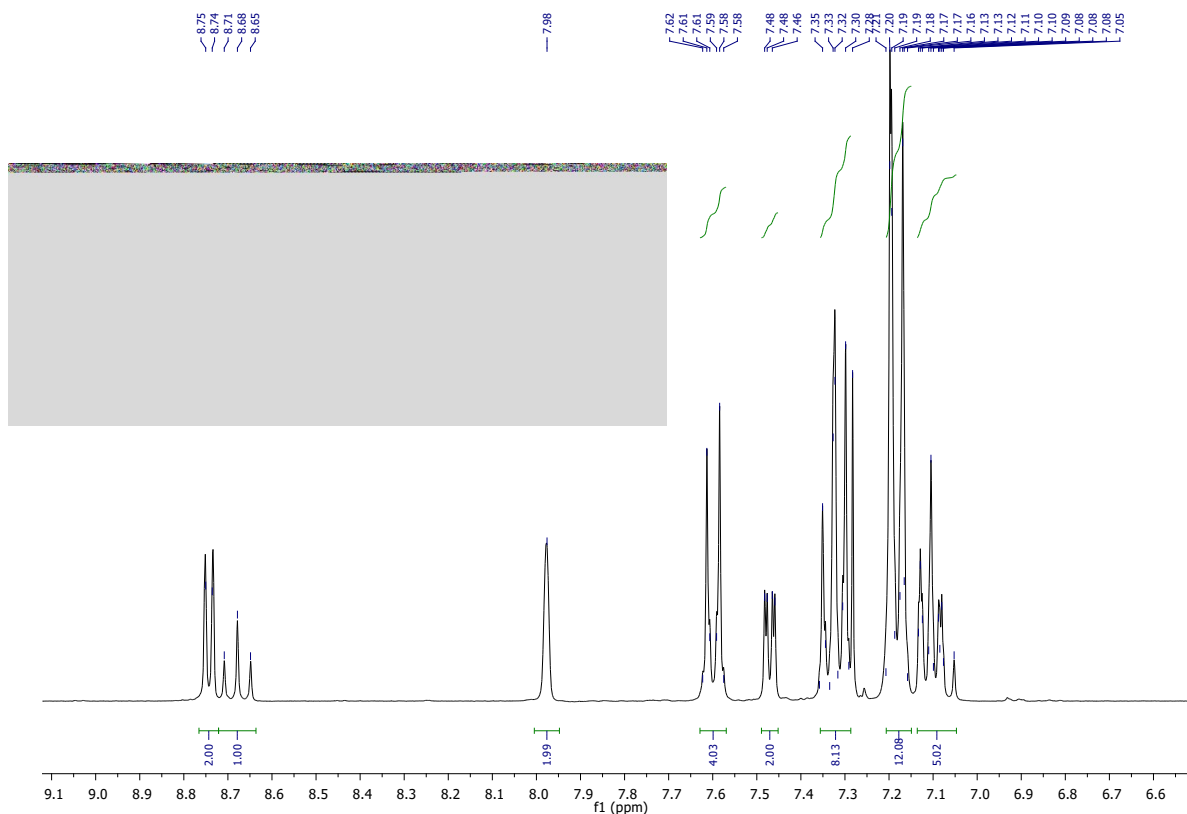
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **12**, aromatic region.



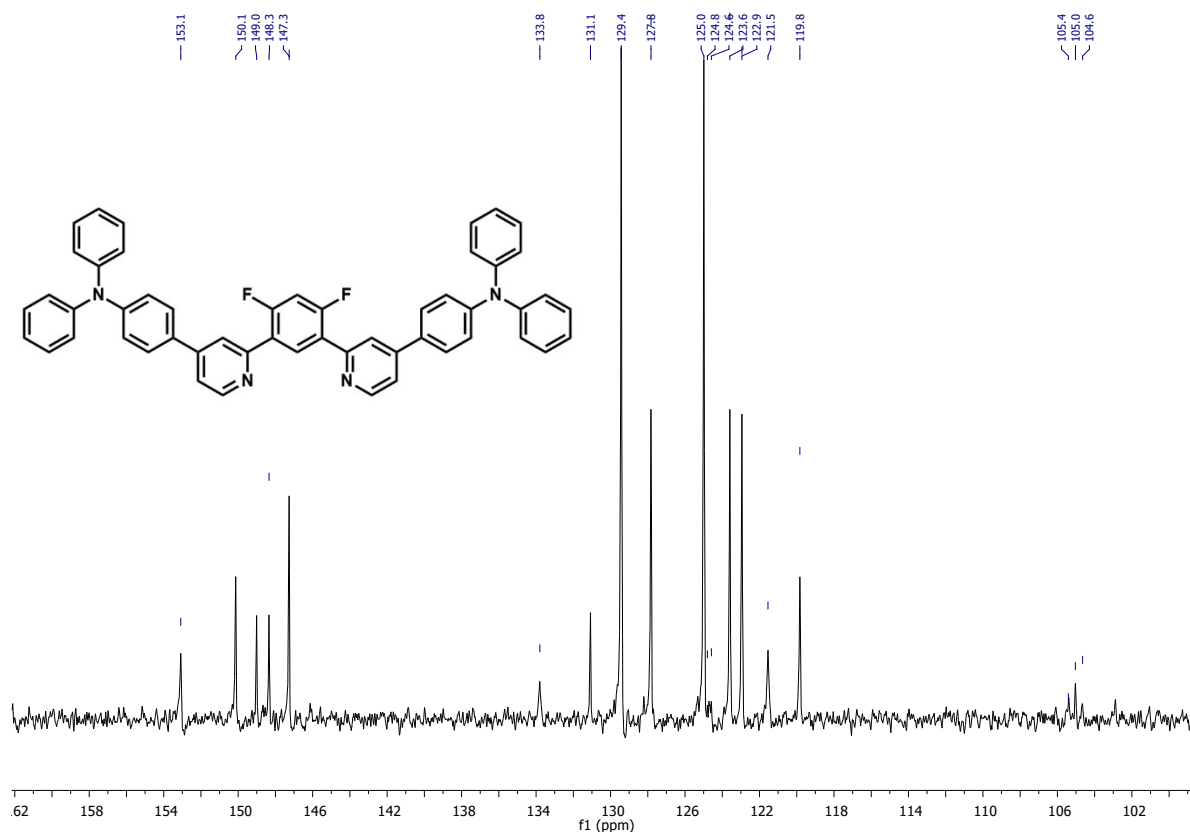
^{19}F $\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 282.36 MHz) of compound **12**.



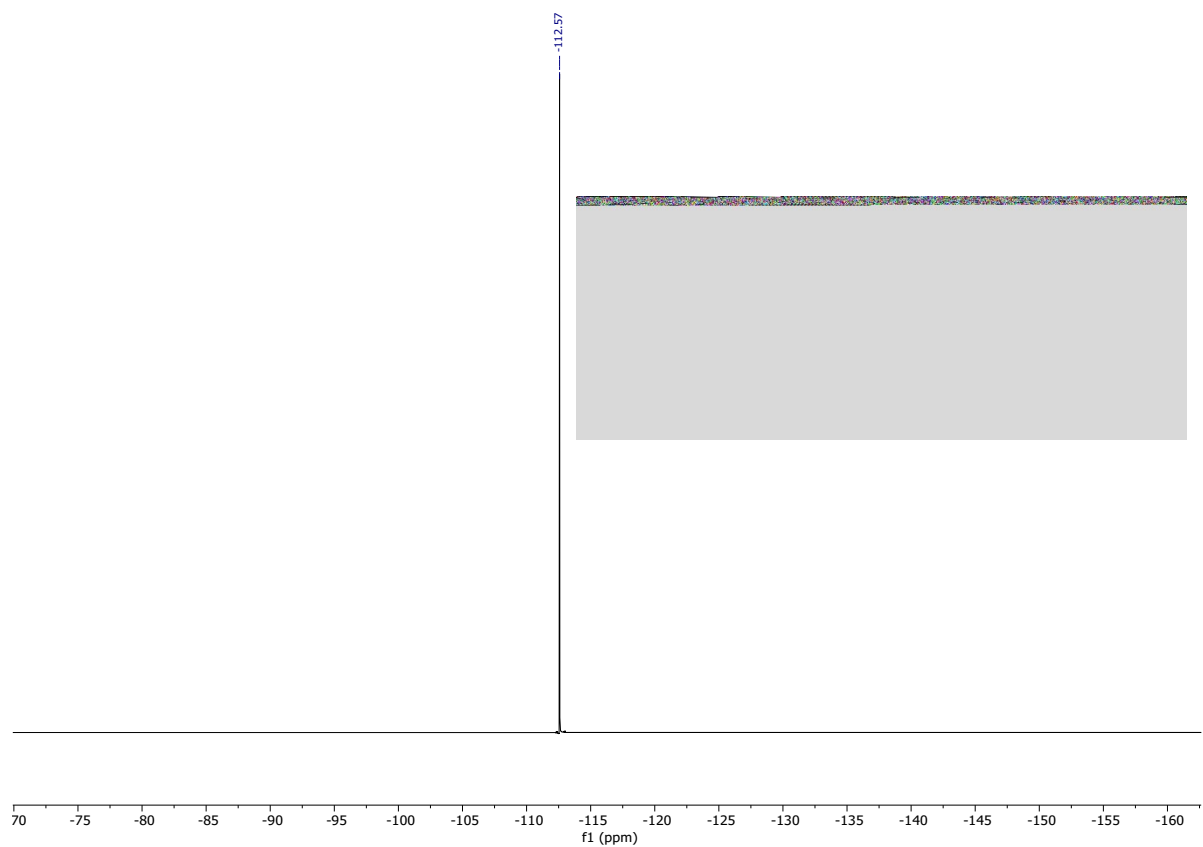
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **HL¹**.



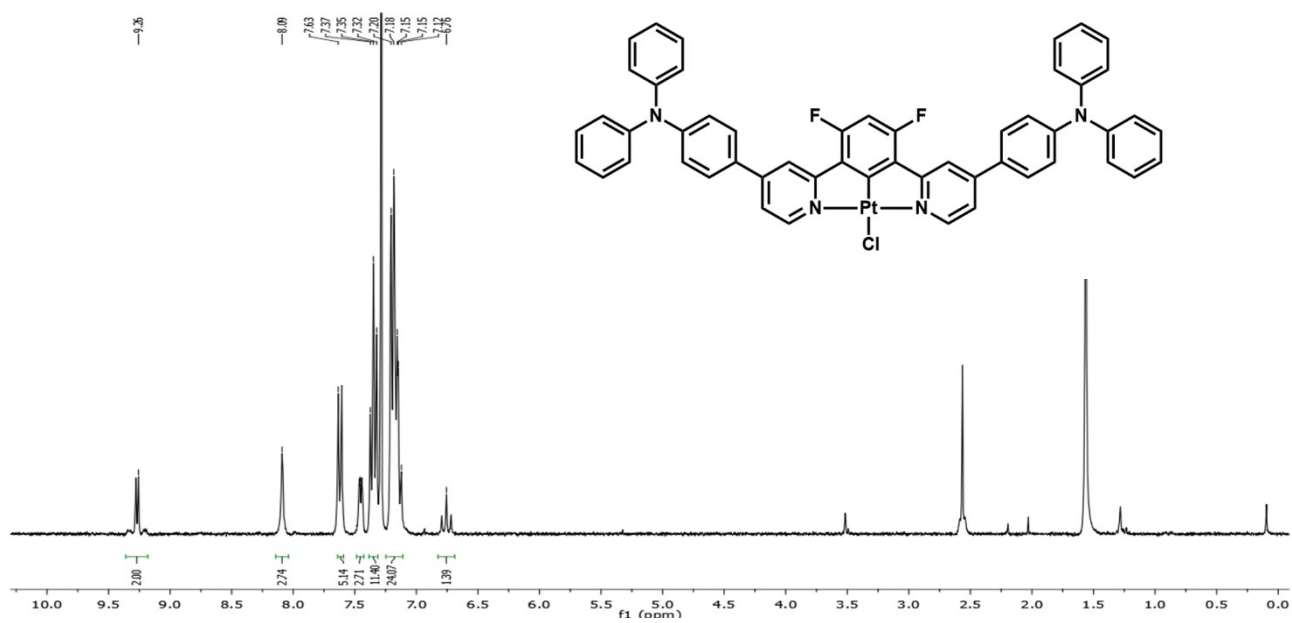
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **HL¹**, aromatic region.



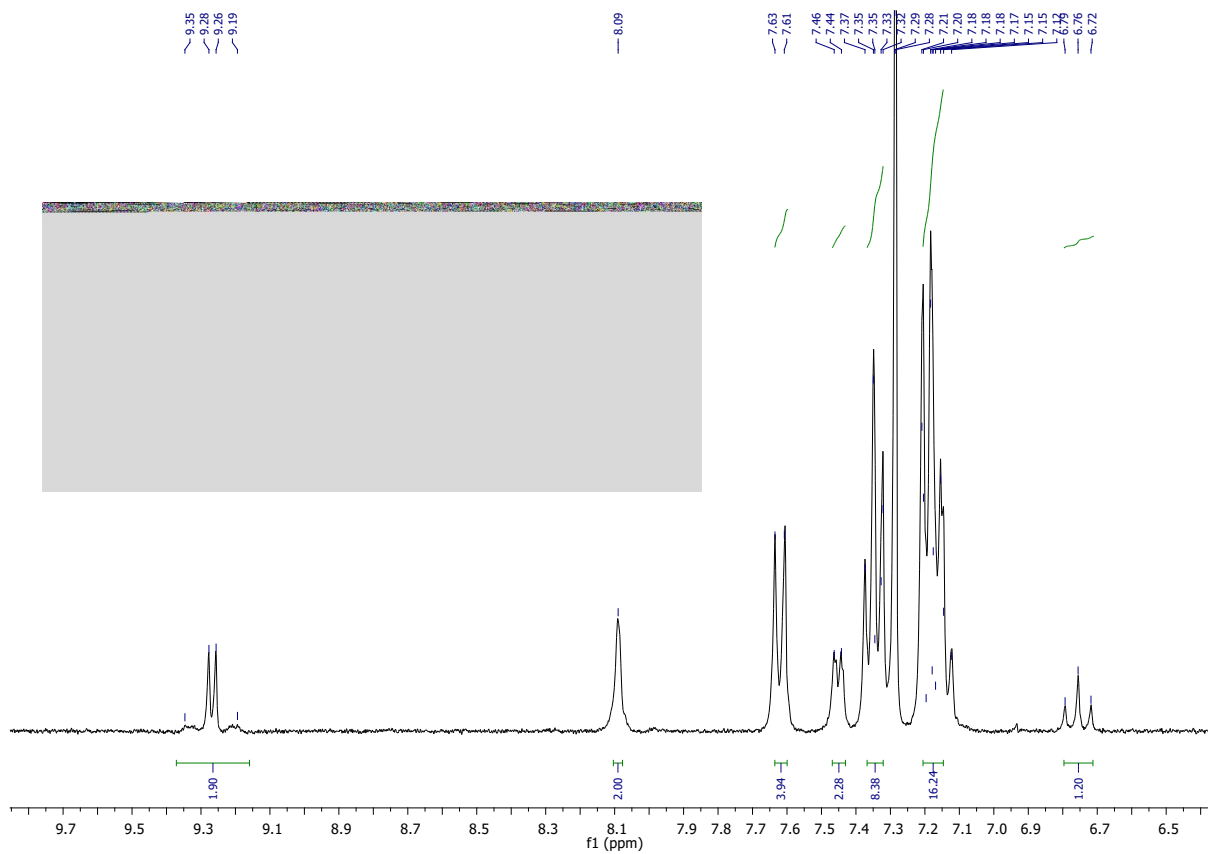
^{13}C $\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 75.48 MHz) of compound **HL¹**.



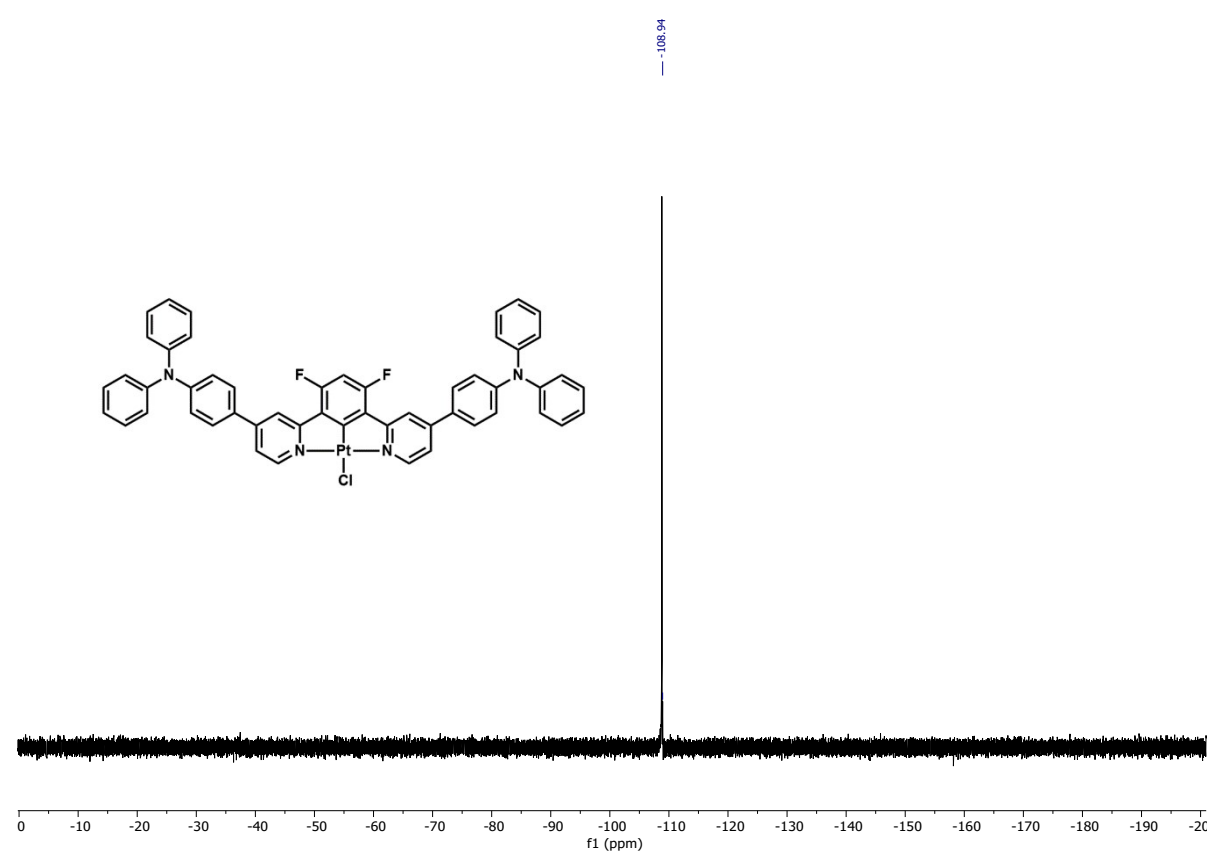
^{19}F { ^1H } NMR spectrum (CDCl₃, 282.36 MHz) of compound HL¹.



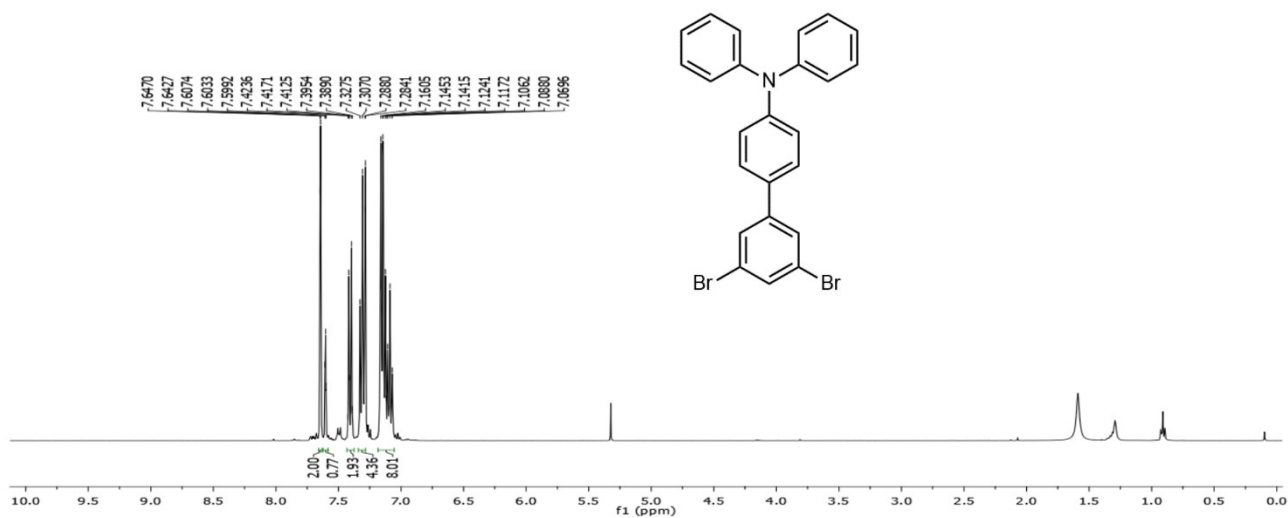
^1H NMR spectrum (CDCl₃, 300 MHz) of compound [PtL¹Cl].



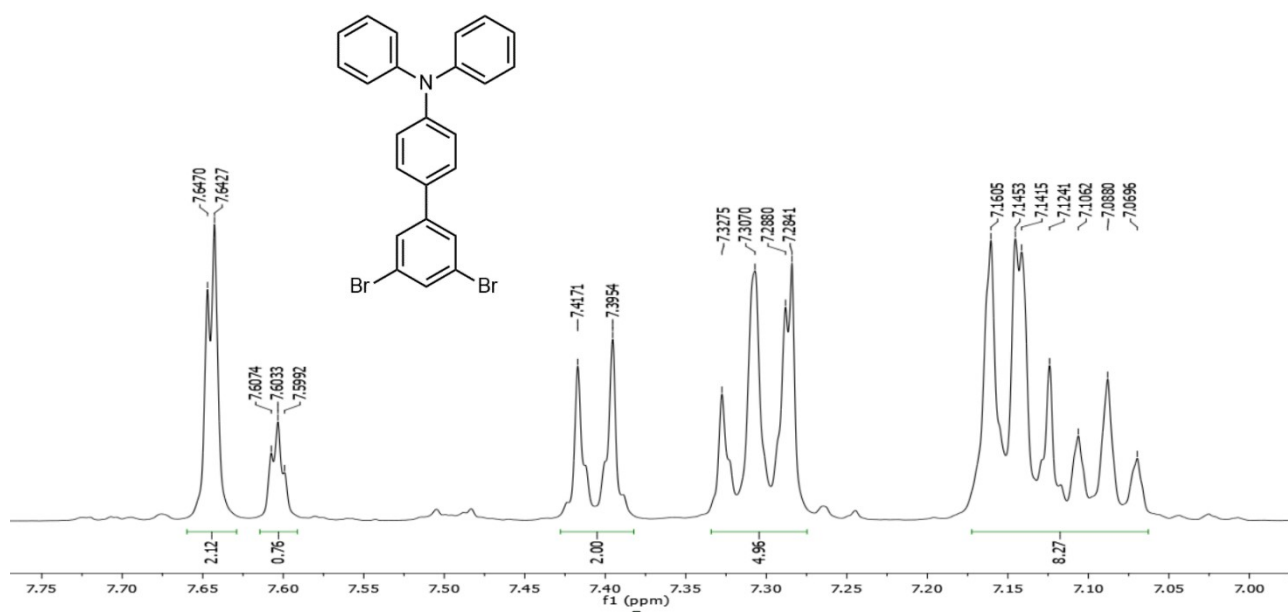
¹H NMR spectrum (CDCl₃, 300 MHz) of compound [PtL¹Cl], aromatic region.



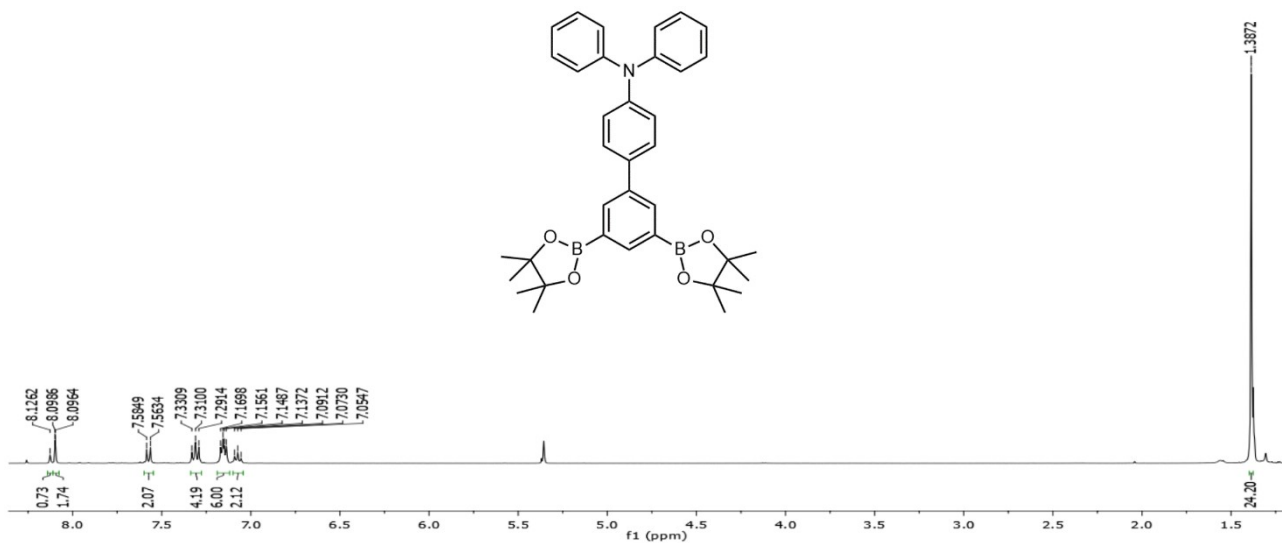
¹⁹F {¹H} NMR spectrum (CDCl₃, 282.36 MHz) of compound [PtL¹Cl].



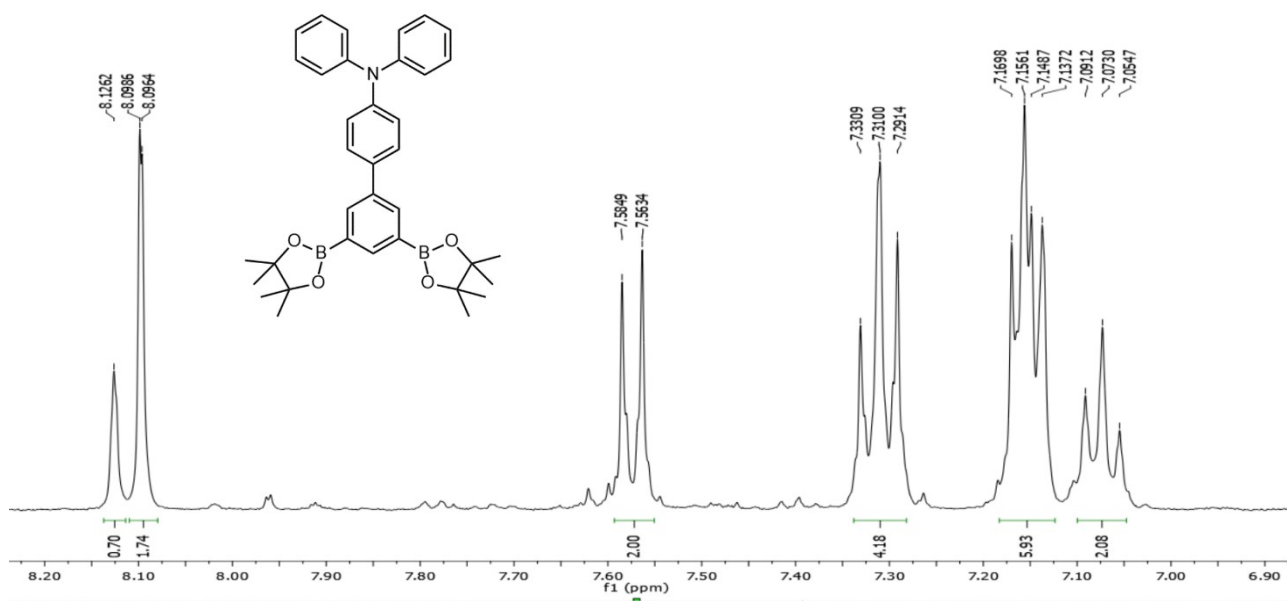
¹H NMR spectrum (CDCl₃, 400 MHz) of compound **13**.



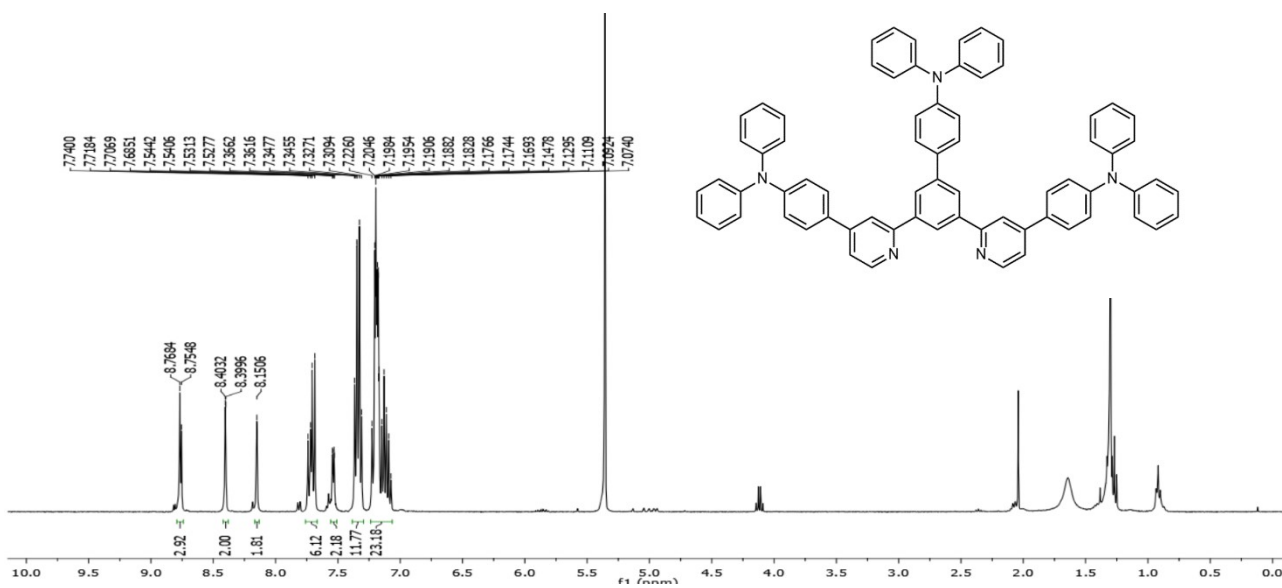
¹H NMR spectrum (CDCl₃, 400 MHz) of compound **13**, aromatic region.



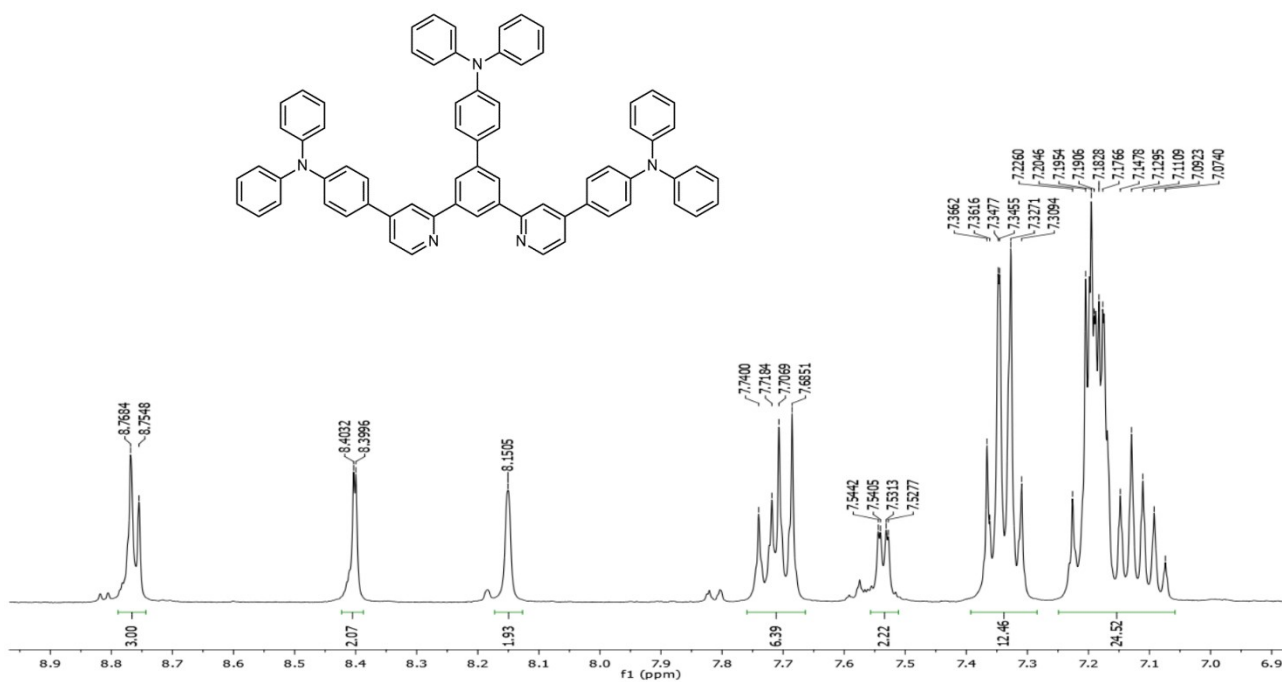
^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of compound **14**.



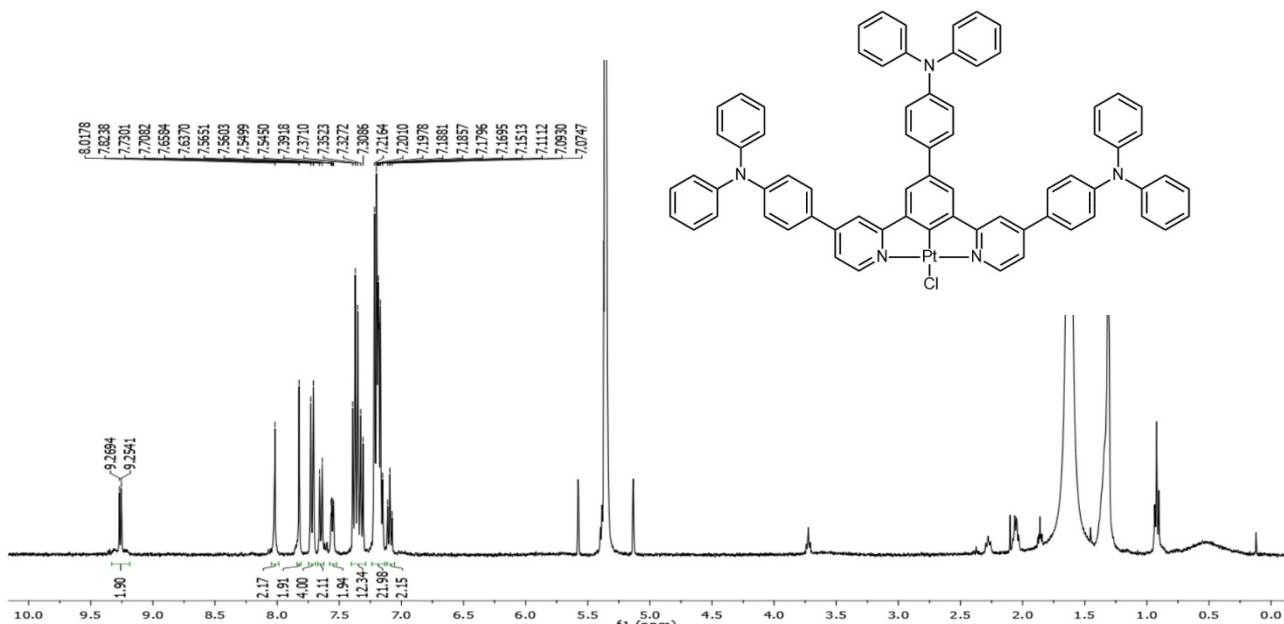
^1H NMR spectrum (CD_2Cl_2 , 400 MHz) of compound **14**, aromatic region.



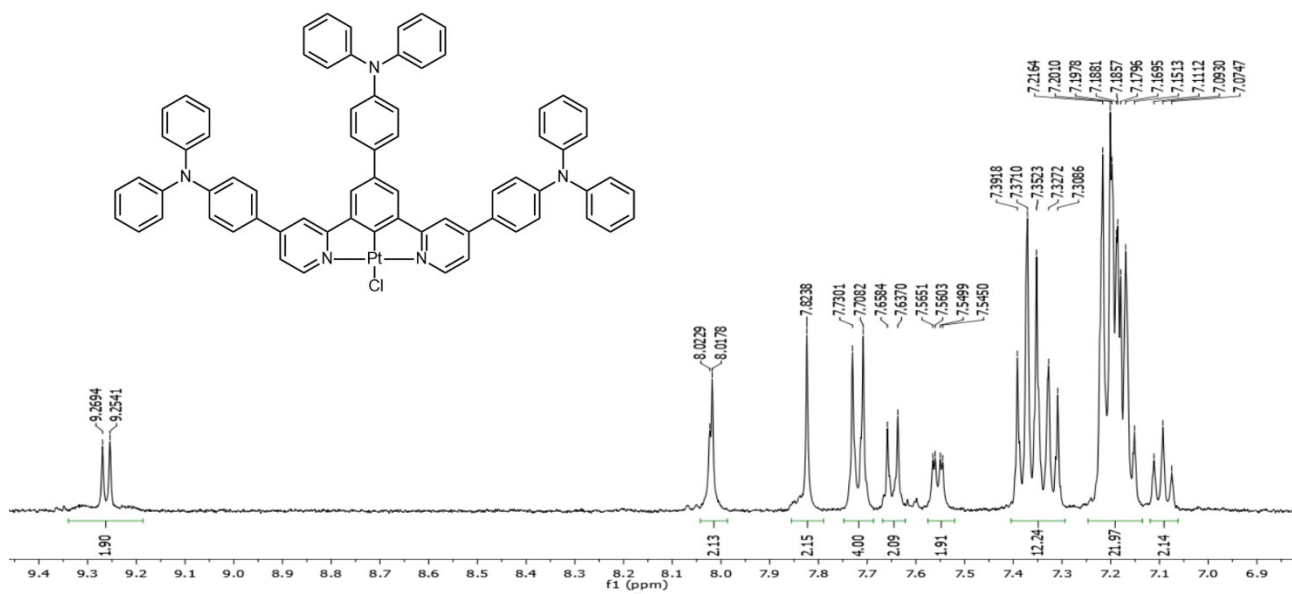
¹H NMR spectrum (CD₂Cl₂, 400 MHz) of compound **HL**².



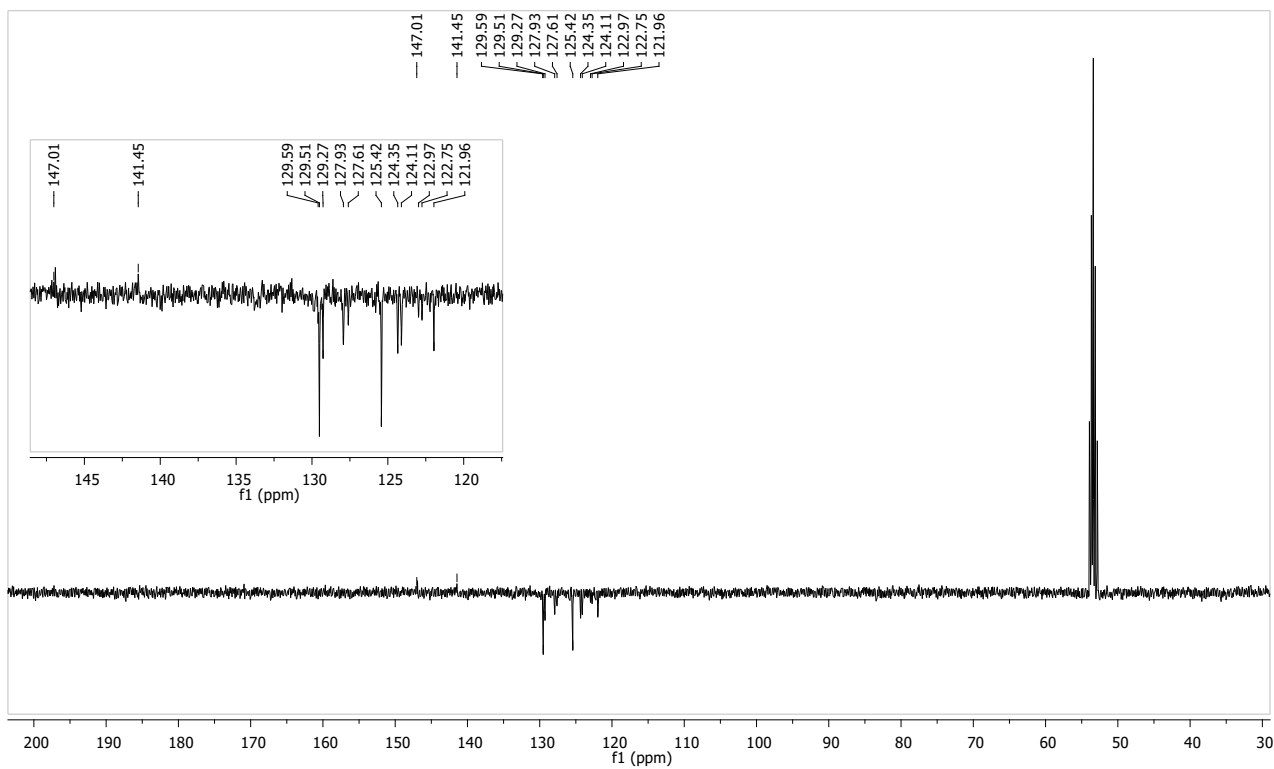
¹H NMR spectrum (CD₂Cl₂, 300 MHz) of compound **HL**², aromatic region.



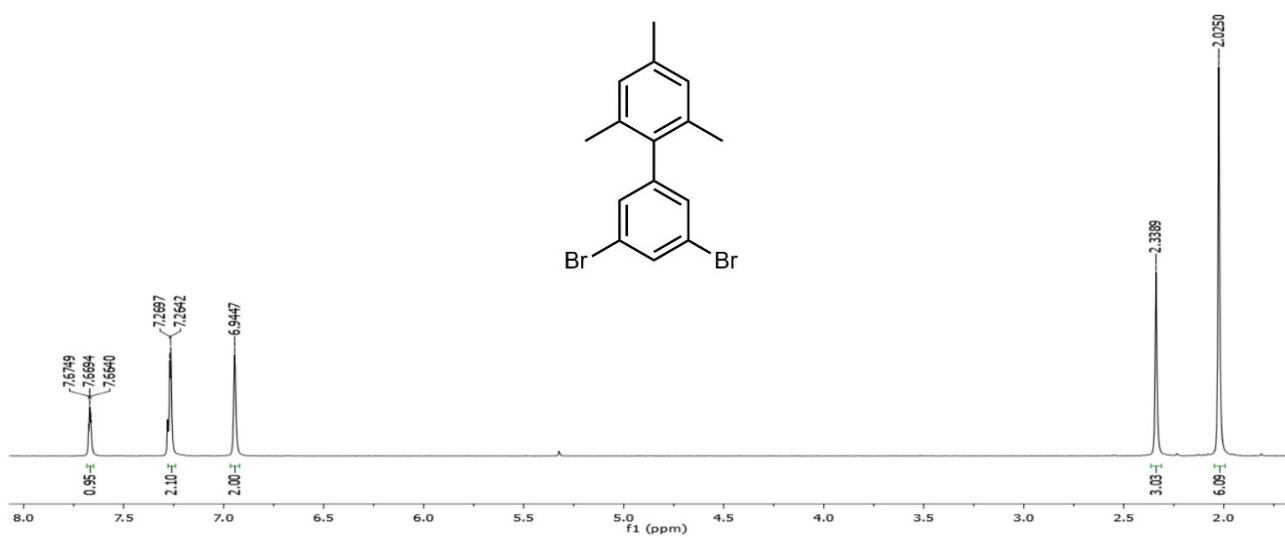
1H NMR spectrum (CD_2Cl_2 , 400 MHz) of compound $[PtL^2Cl]$.



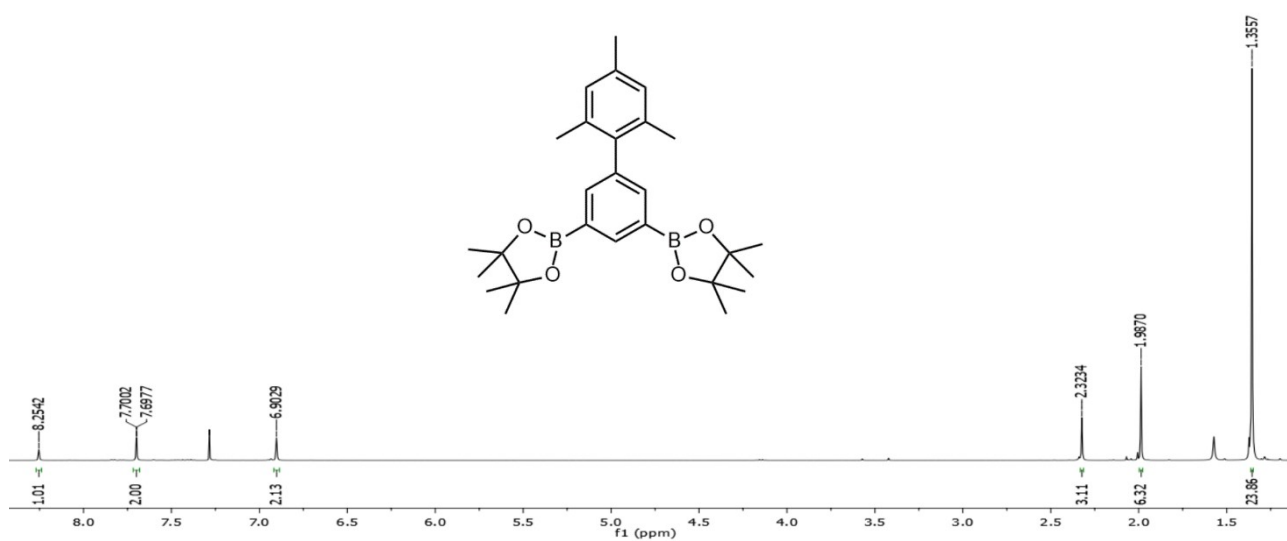
1H NMR spectrum (CD_2Cl_2 , 400 MHz) of compound $[PtL^2Cl]$, aromatic region.



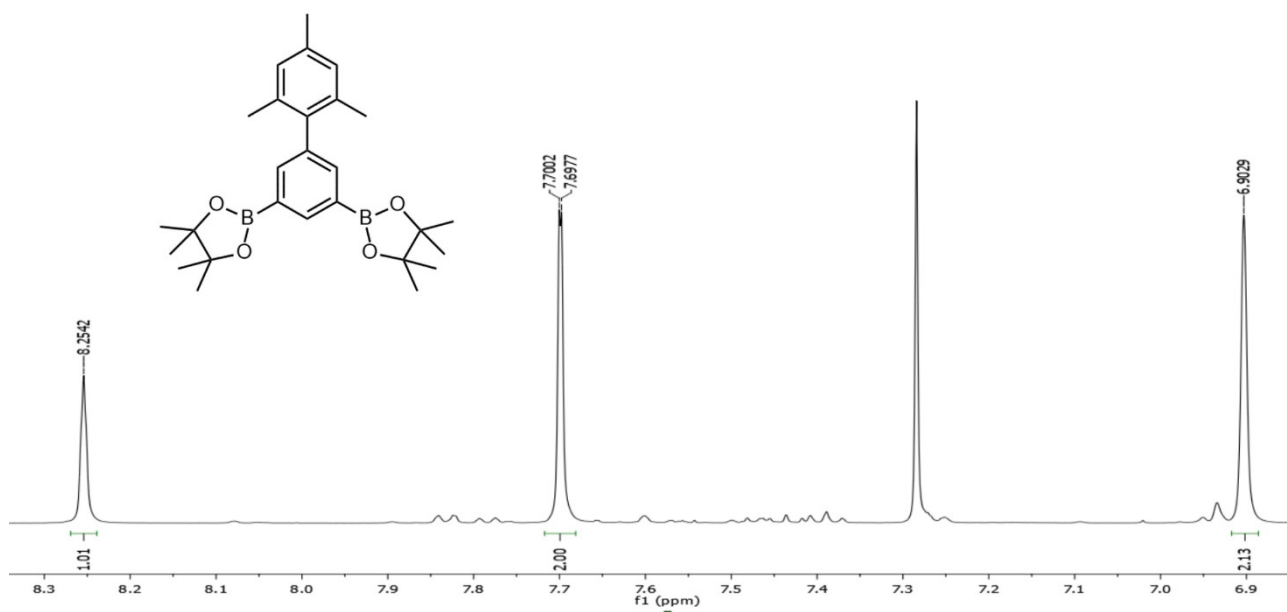
^{13}C NMR-DEPT spectrum (CD_2Cl_2 , 100 MHz) of compound $[\text{PtL}_2\text{Cl}]$.



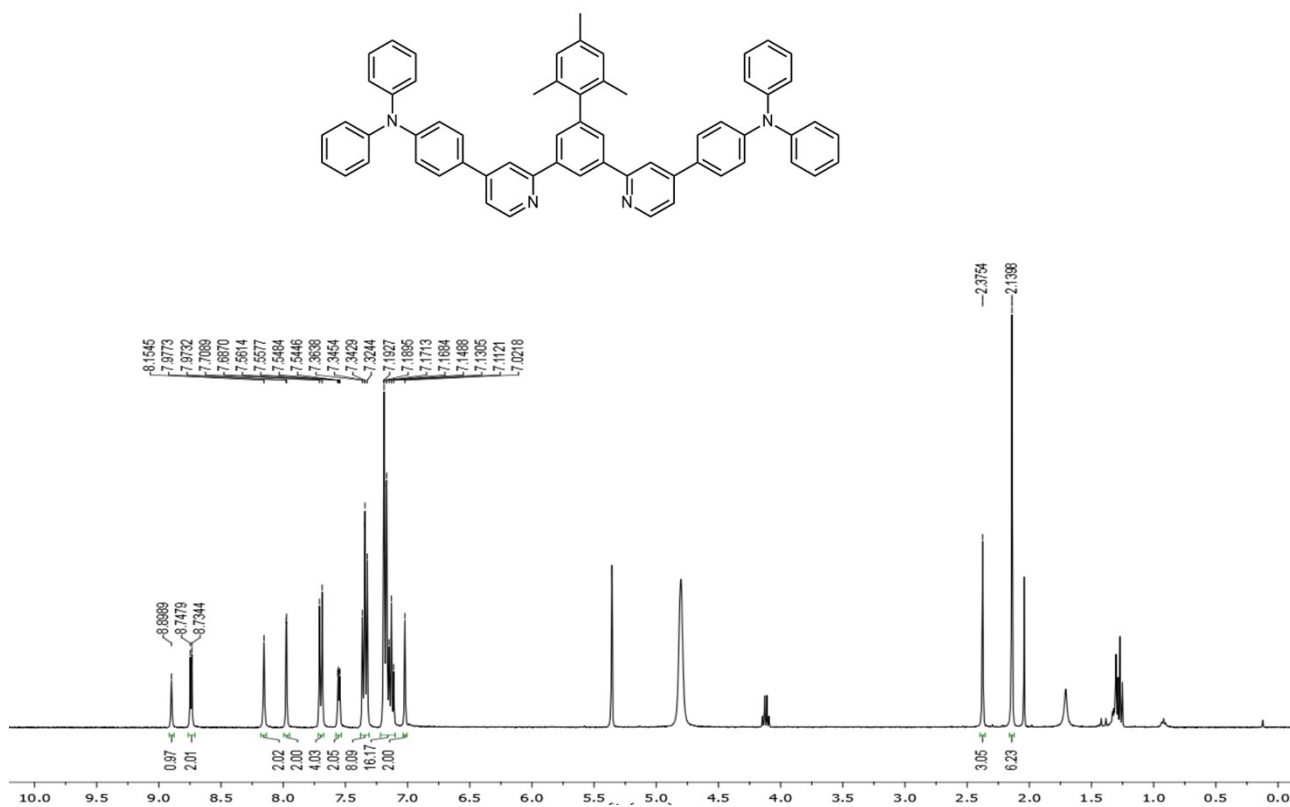
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **15**.



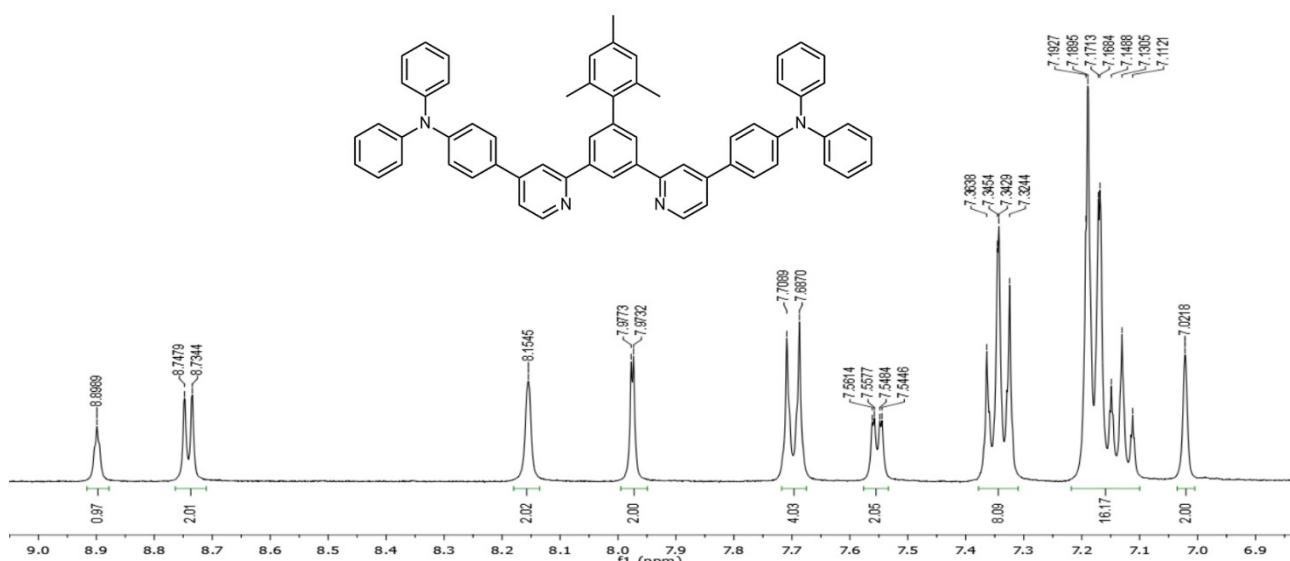
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **16**.



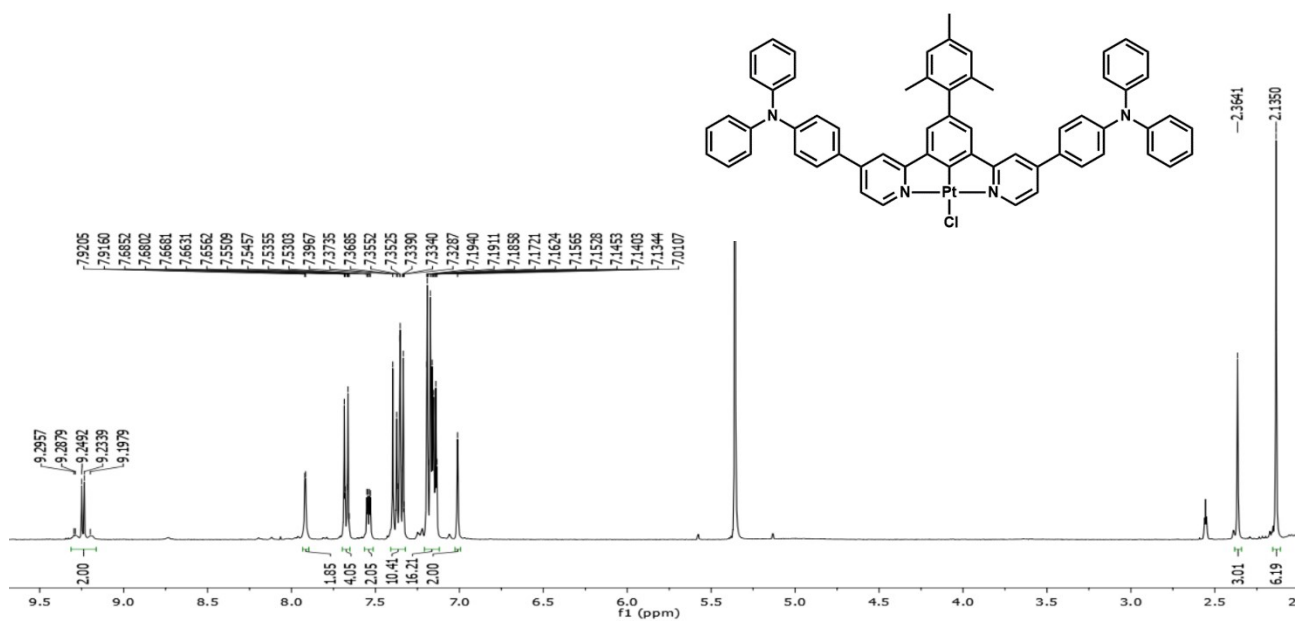
^1H NMR spectrum (CDCl_3 , 300 MHz) of compound **16**, aromatic region.



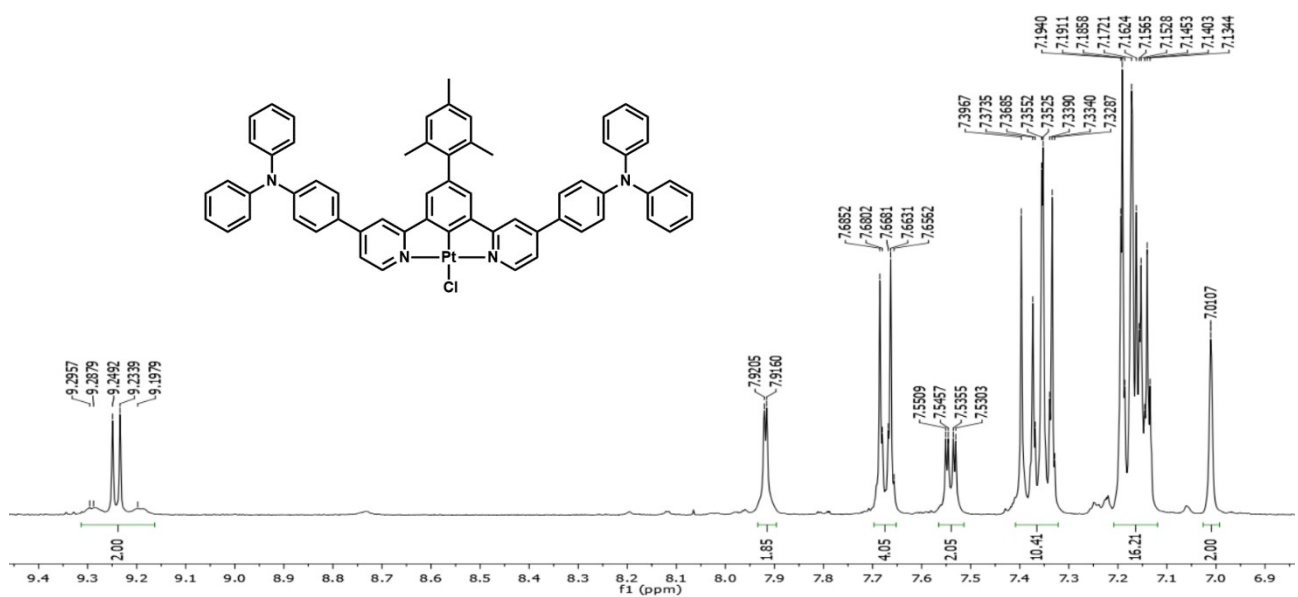
¹H NMR spectrum (CD₂Cl₂, 400 MHz) of compound **HL³**.



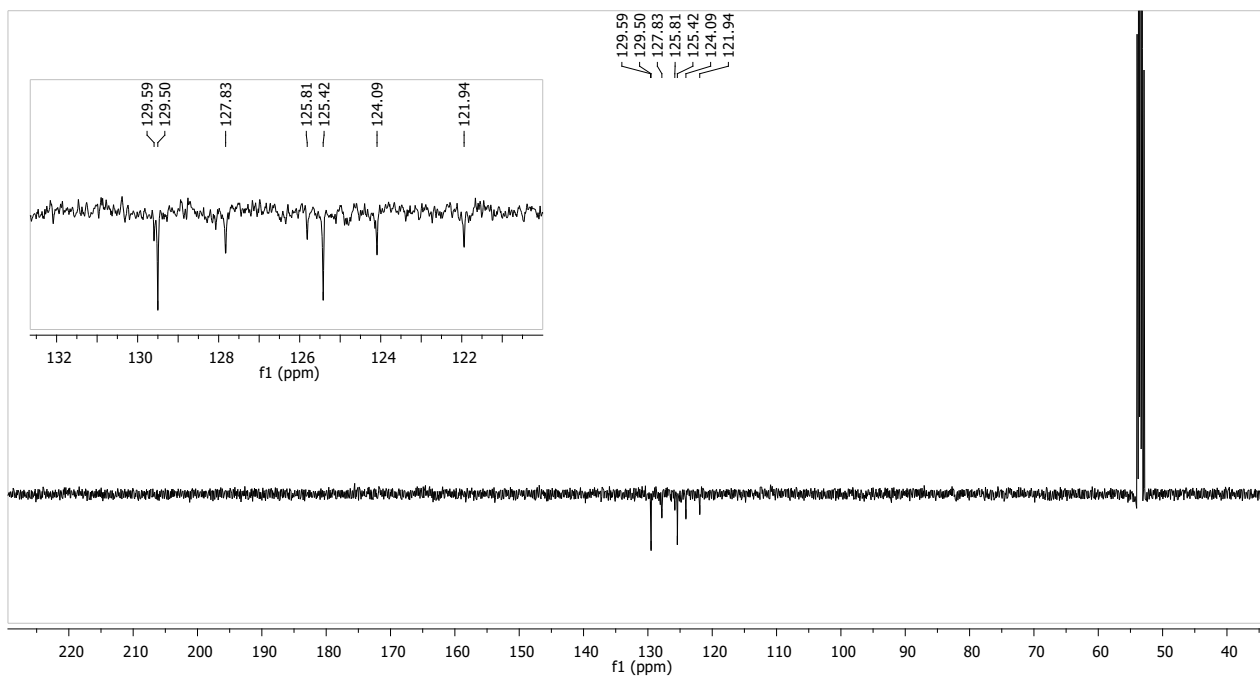
¹H NMR spectrum (CD₂Cl₂, 400 MHz) of compound **HL³**, aromatic region.



¹H NMR spectrum (CD₂Cl₂, 400 MHz) of compound [PtL³Cl].



¹H NMR spectrum (CD₂Cl₂, 400 MHz) of compound [PtL³Cl], aromatic region.



^{13}C NMR-DEPT spectrum (CD_2Cl_2 , 100 MHz) of compound $[\text{PtL}^3\text{Cl}]$.

IV. Photoluminescence investigations of the complexes

$[\text{PtL}^1\text{Cl}]$: Solution

Concentration (M)	Before FPT (%)	After FPT (%)
$2.5 \cdot 10^{-6}$	5.9	89.9
$5 \cdot 10^{-6}$	4.2	84.6
$1 \cdot 10^{-5}$	3.6	74.5
$2.4 \cdot 10^{-4}$	2.6	66.3

Table S1. Absolute Quantum Yield (%) of $[\text{PtL}^1\text{Cl}]$ in dichloromethane at different concentrations, before and after the Freeze-Pump-Thaw (FPT) cycles.

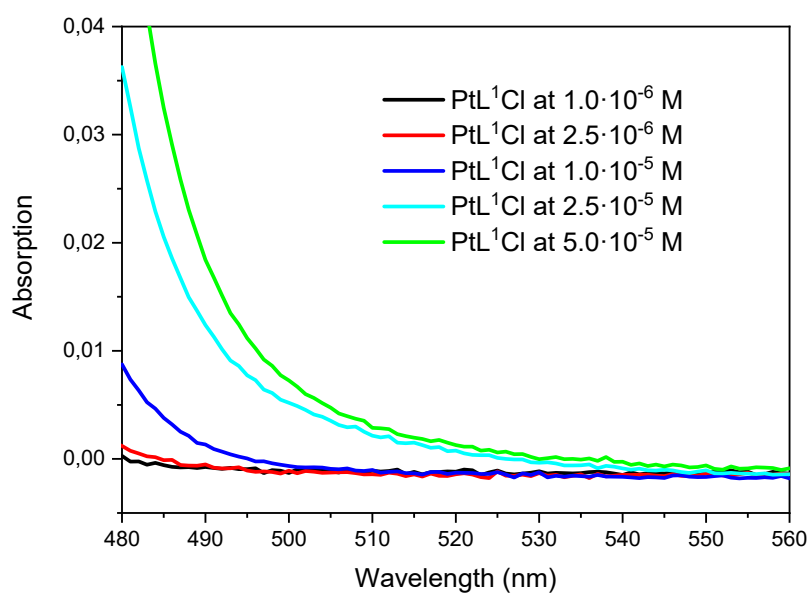


Figure S4. Absorption spectra of [PtL¹Cl] in dichloromethane, expanded scale.

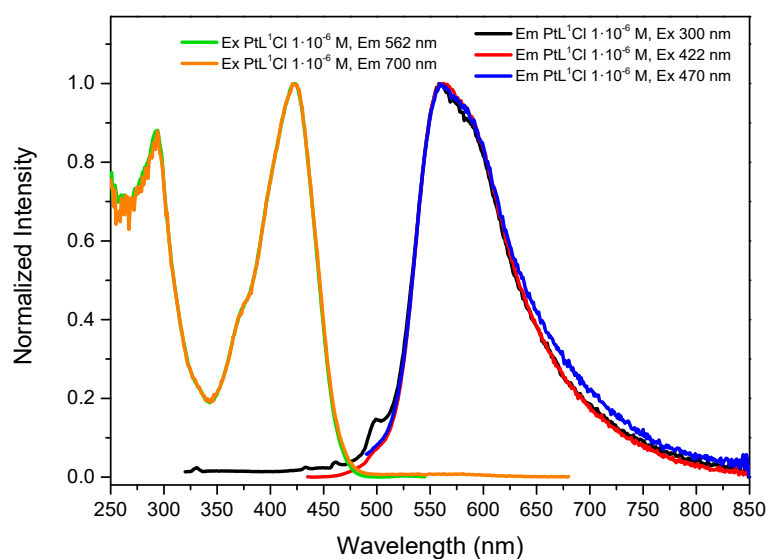


Figure S5. Normalized excitation and emission spectra of a diluted solution (1 · 10⁻⁶ M) of [PtL¹Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

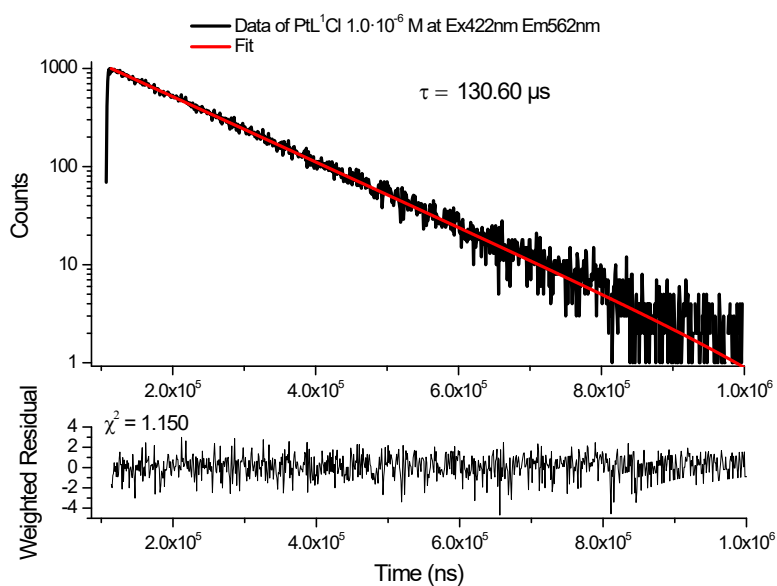


Figure S6. Lifetime measurement of a diluted solution ($1 \cdot 10^{-6}$ M) of $[\text{PtL}^1\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 562 nm, Excitation 422 nm.

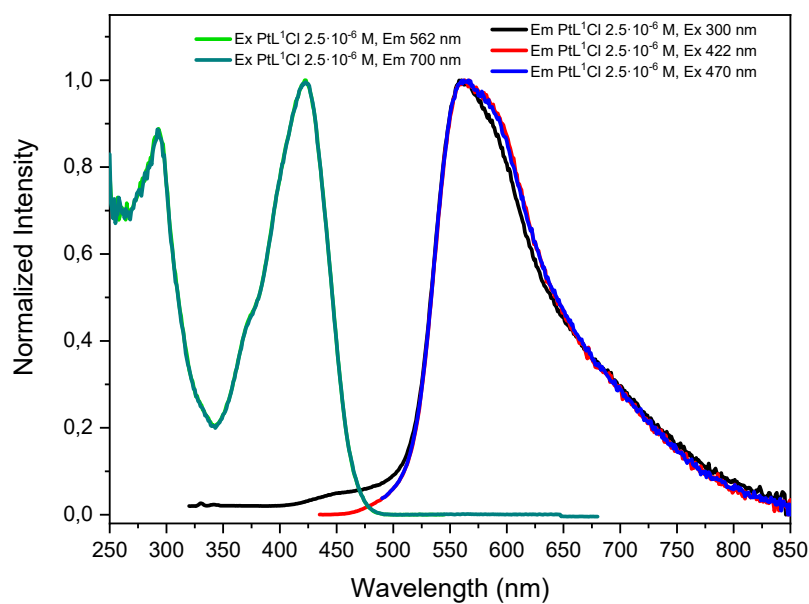


Figure S7. Normalized excitation and emission spectra of a $2.5 \cdot 10^{-6}$ M solution of $[\text{PtL}^1\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

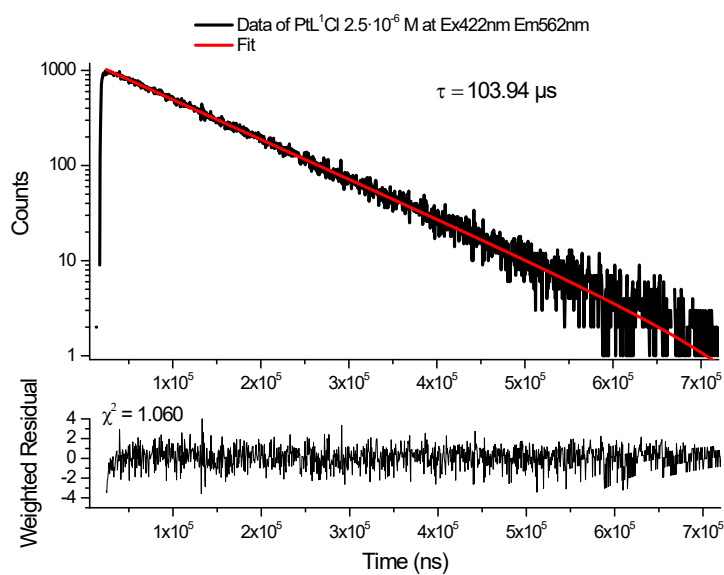


Figure S8. Lifetime measurement of a $2.5 \cdot 10^{-6}$ M solution of $[\text{PtL}^1\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 562 nm, Excitation 422 nm.

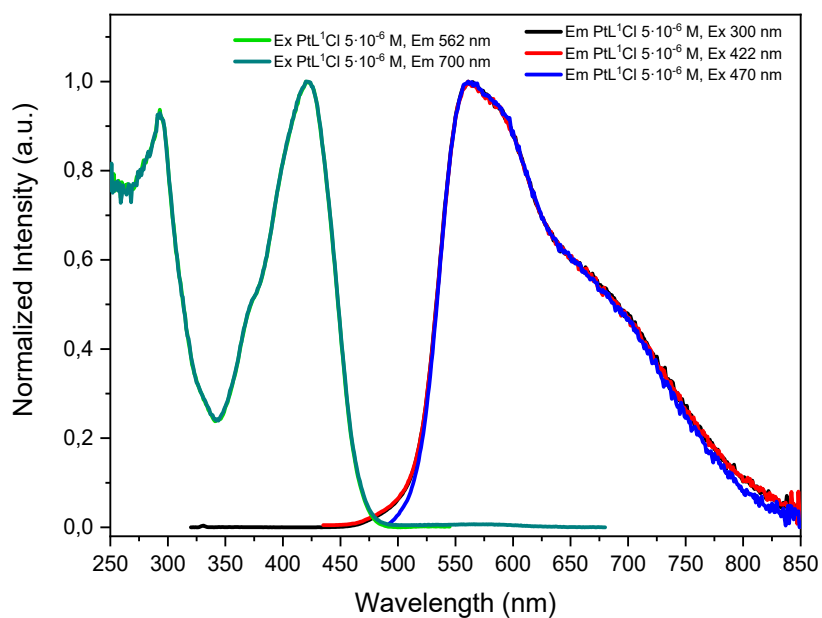


Figure S9. Normalized excitation and emission spectra of a $5 \cdot 10^{-6}$ M solution of $[\text{PtL}^1\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

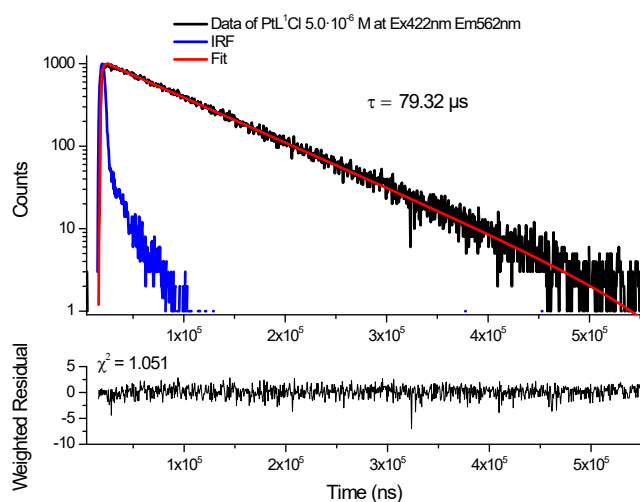


Figure S10. Lifetime measurement of a $5 \cdot 10^{-6}$ M solution of [PtL¹Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 562 nm, Excitation 422 nm.

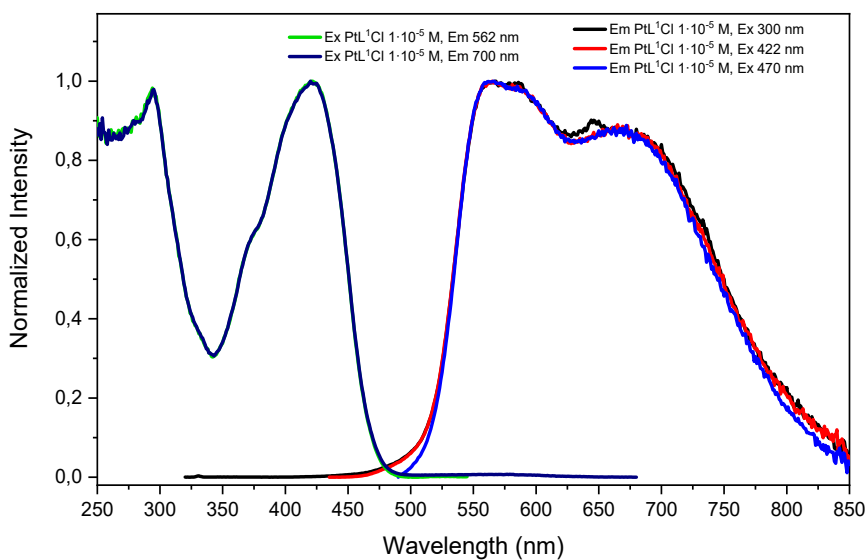


Figure S11. Normalized excitation and emission spectra of a $1 \cdot 10^{-5}$ M solution of [PtL¹Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

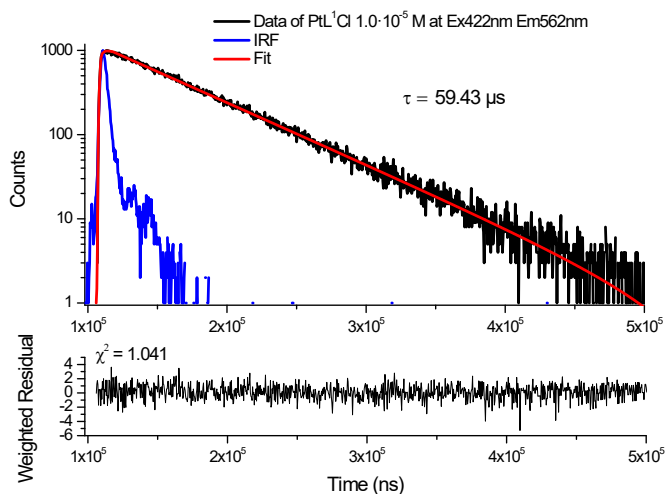


Figure S12. Lifetime measurement of a $1 \cdot 10^{-5}$ M solution of [PtL¹Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 562 nm, Excitation 422 nm.

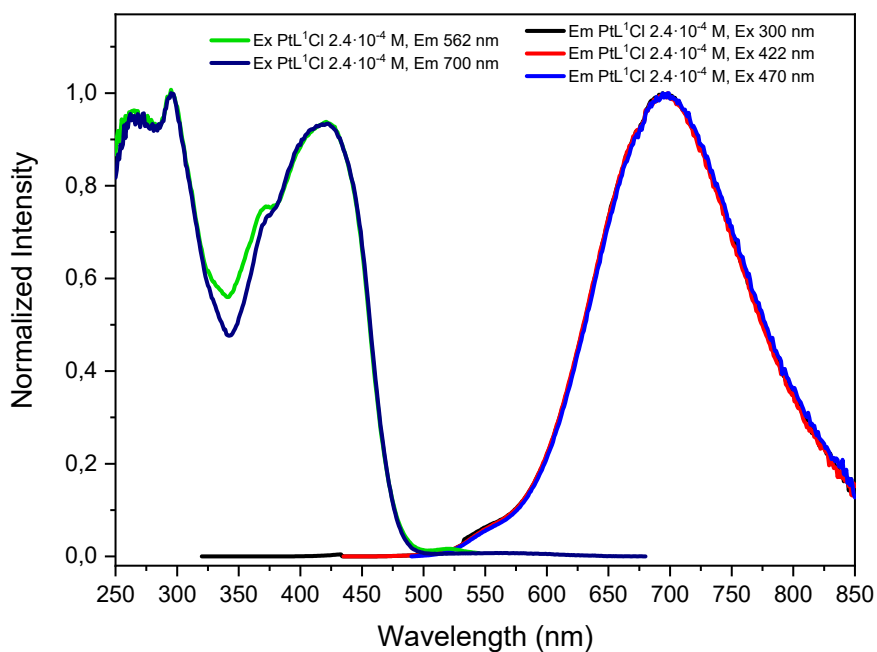


Figure S13. Normalized excitation and emission spectra of concentrated ($2.4 \cdot 10^{-4}$ M) solution of [PtL¹Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

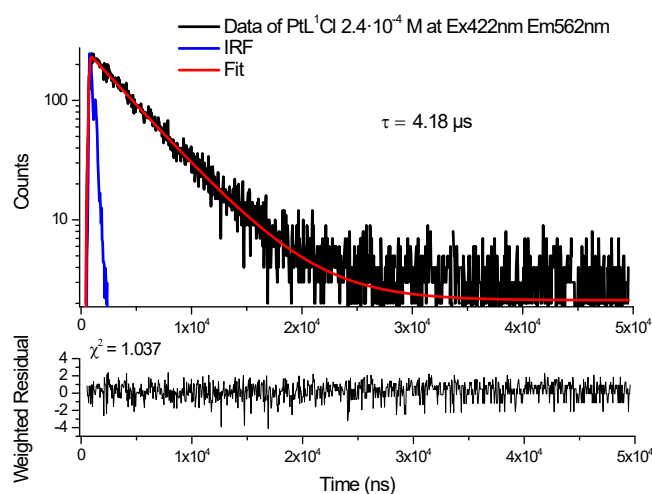


Figure S14. Lifetime measurement of a concentrated solution ($2.4 \cdot 10^{-4}$ M) of [PtL¹Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 562 nm, Excitation 422 nm.

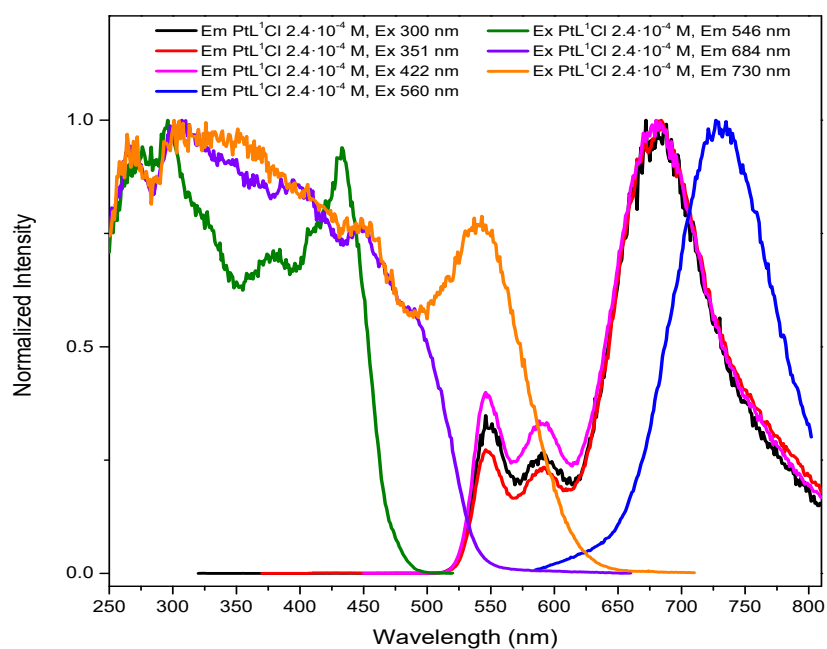


Figure S15. Normalized excitation and emission spectra of concentrated ($2.4 \cdot 10^{-4}$ M) solution of [PtL¹Cl] at low temperature in dichloromethane, after bubbling for 5 minutes.

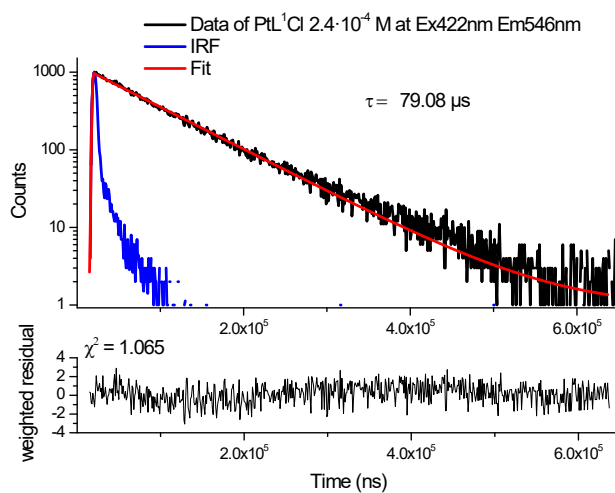


Figure S16. Lifetime measurement of a concentrated solution ($2.4 \cdot 10^{-4}$ M) of [PtL¹Cl] at low temperature in dichloromethane, after bubbling for 5 minutes. Emission 546 nm, Excitation 422 nm.

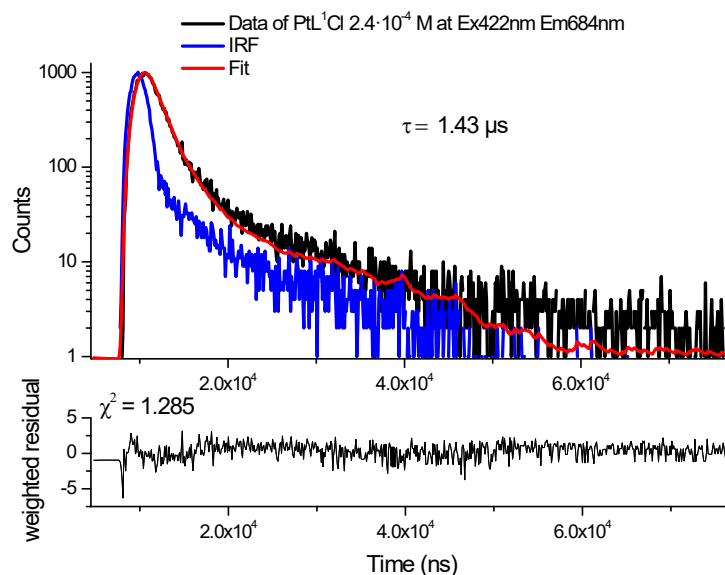


Figure S17. Lifetime measurement of a concentrated solution ($2.4 \cdot 10^{-4}$ M) of [PtL¹Cl] at low temperature in dichloromethane, after bubbling for 5 minutes. Emission 684 nm, Excitation 422 nm.

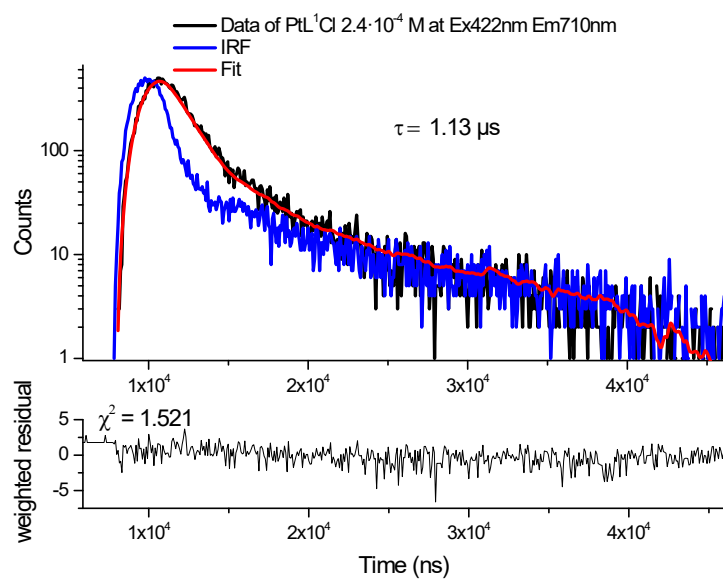


Figure S18. Lifetime measurement of a concentrated solution ($2.4 \cdot 10^{-4} \text{ M}$) of $[\text{PtL}^1\text{Cl}]$ at low temperature in dichloromethane, after bubbling for 5 minutes. Emission 710 nm, Excitation 422 nm.

$[\text{PtL}^1\text{Cl}]$: Solid state

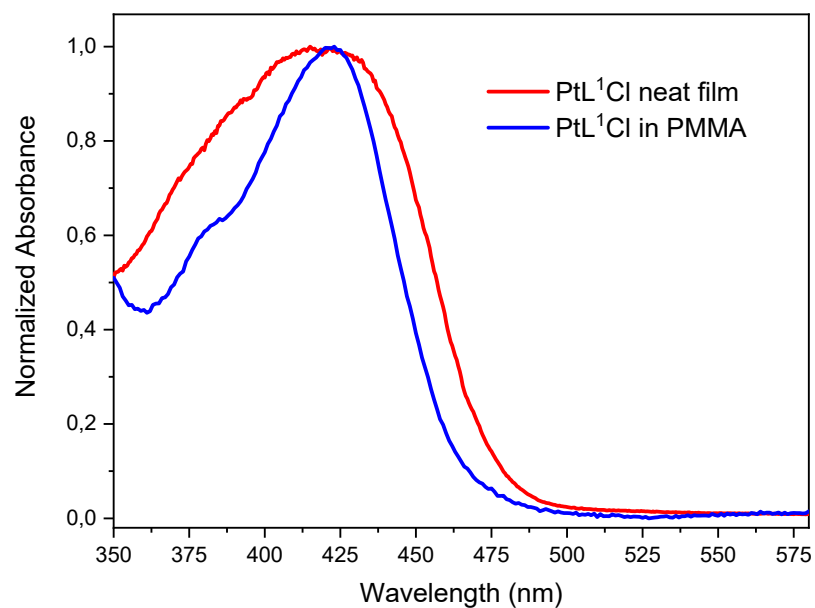


Figure S19. Normalized absorption spectra of [PtL¹Cl] as neat film and in PMMA film.

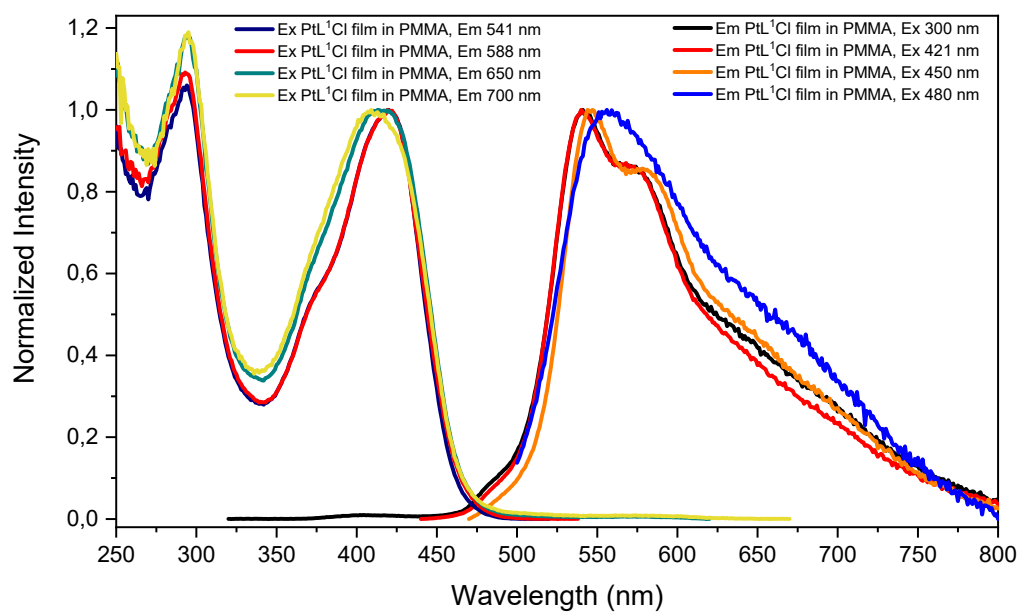


Figure S20. Normalized excitation and emission spectra of [PtL¹Cl] as film in PMMA.

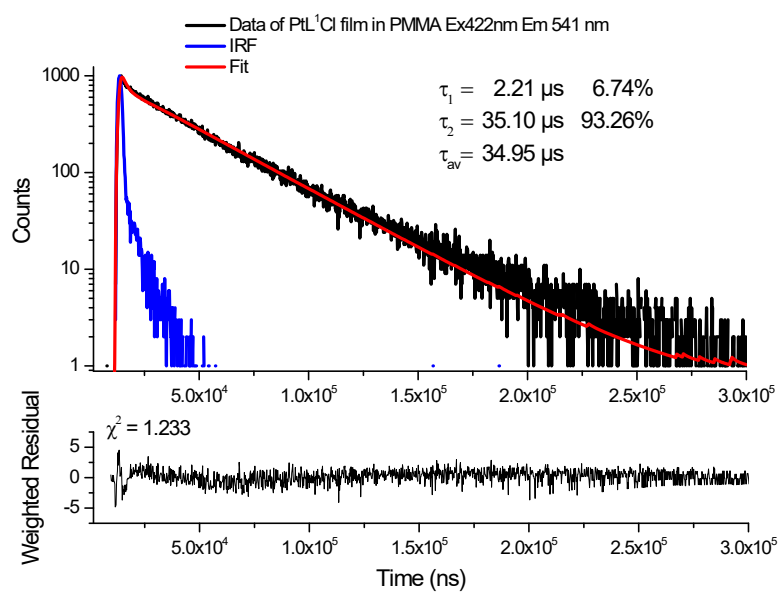


Figure S21. Lifetime measurement of $[\text{PtL}^1\text{Cl}]$ as films in PMMA. Emission 541 nm, Excitation 422 nm.

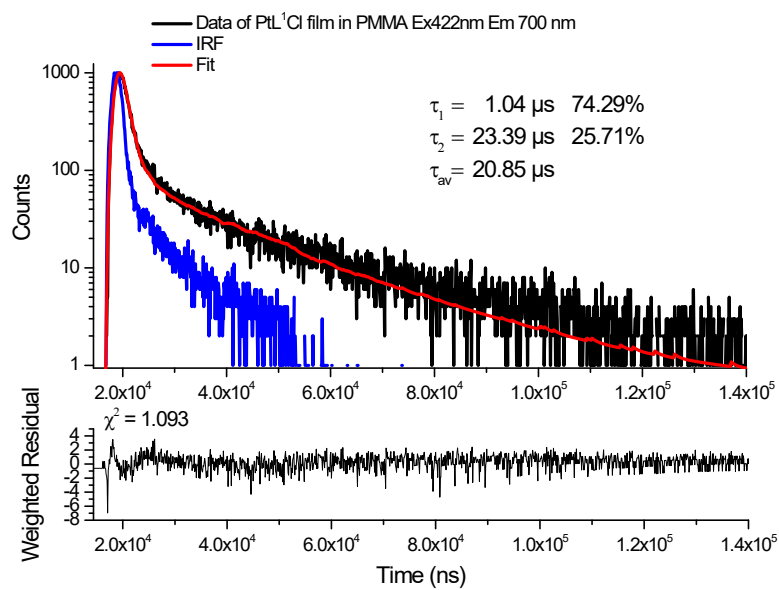


Figure S22. Lifetime measurement of $[\text{PtL}^1\text{Cl}]$ as films in PMMA. Emission 700 nm, Excitation 422 nm.

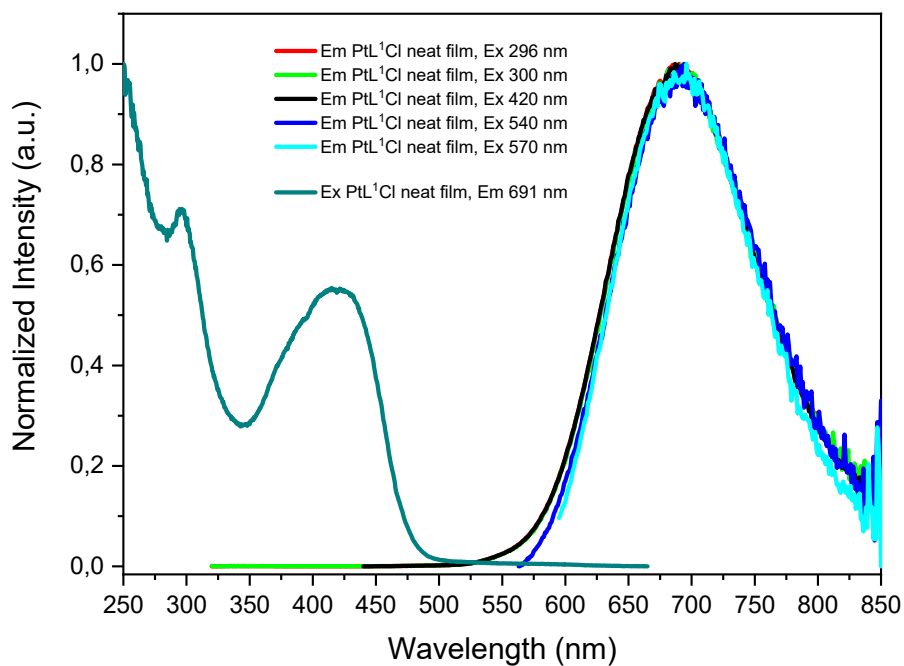


Figure S23. Normalized excitation and emission spectra of $[\text{PtL}^1\text{Cl}]$ as neat film.

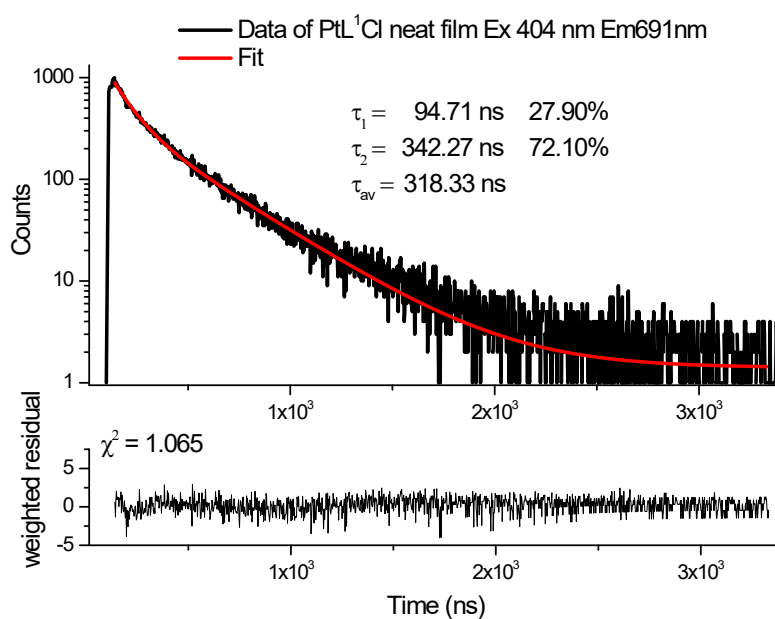


Figure S24. Lifetime measurement of $[\text{PtL}^1\text{Cl}]$ as films in PMMA. Emission 691 nm, Excitation 404 nm.

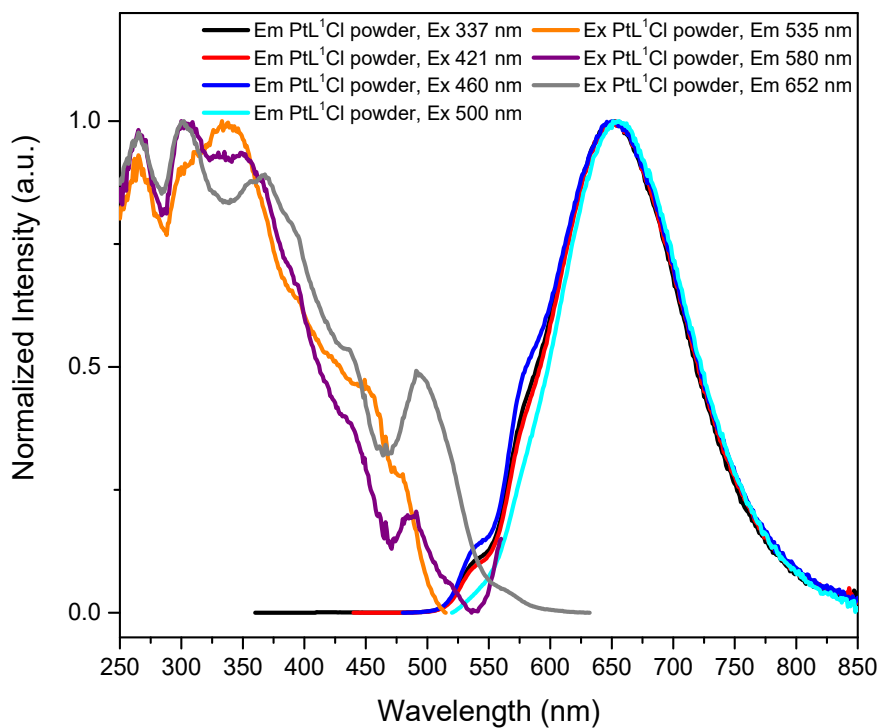


Figure S25. Normalized excitation and emission spectra of $[\text{PtL}^1\text{Cl}]$ powder at room temperature.

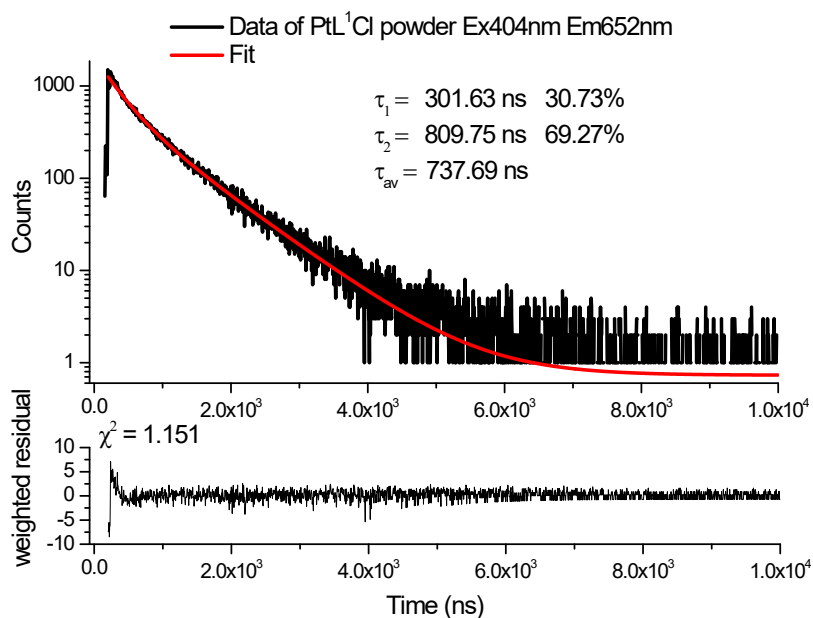


Figure S26. Lifetime measurement of $[\text{PtL}^1\text{Cl}]$ powder at room temperature. Emission 652 nm, Excitation 404 nm.

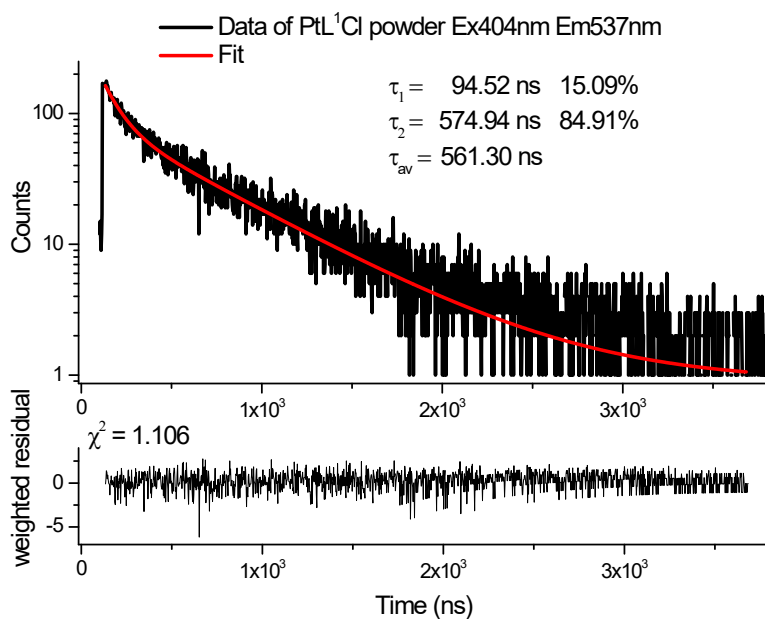


Figure S27. Lifetime measurement of [PtL¹Cl] powder at room temperature. Emission 537 nm, Excitation 404 nm.

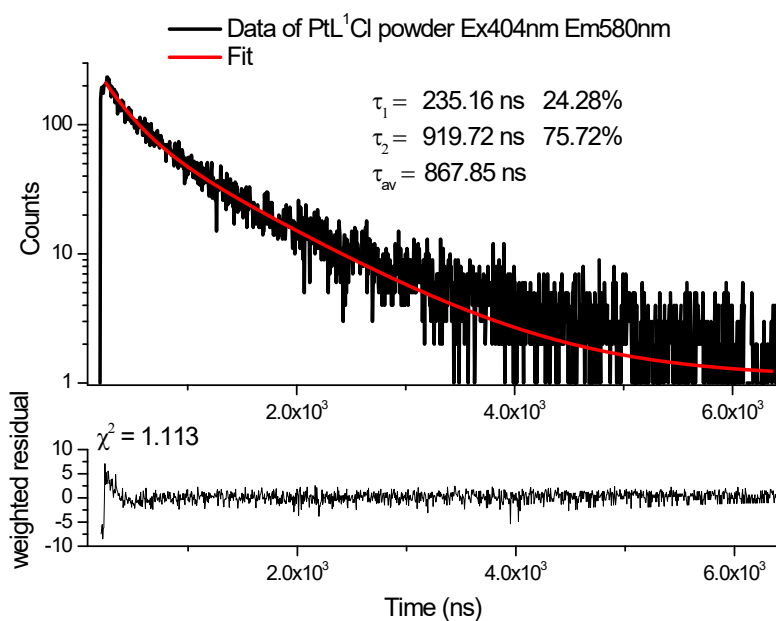


Figure S28. Lifetime measurement of [PtL¹Cl] powder at room temperature. Emission 580 nm, Excitation 404 nm.

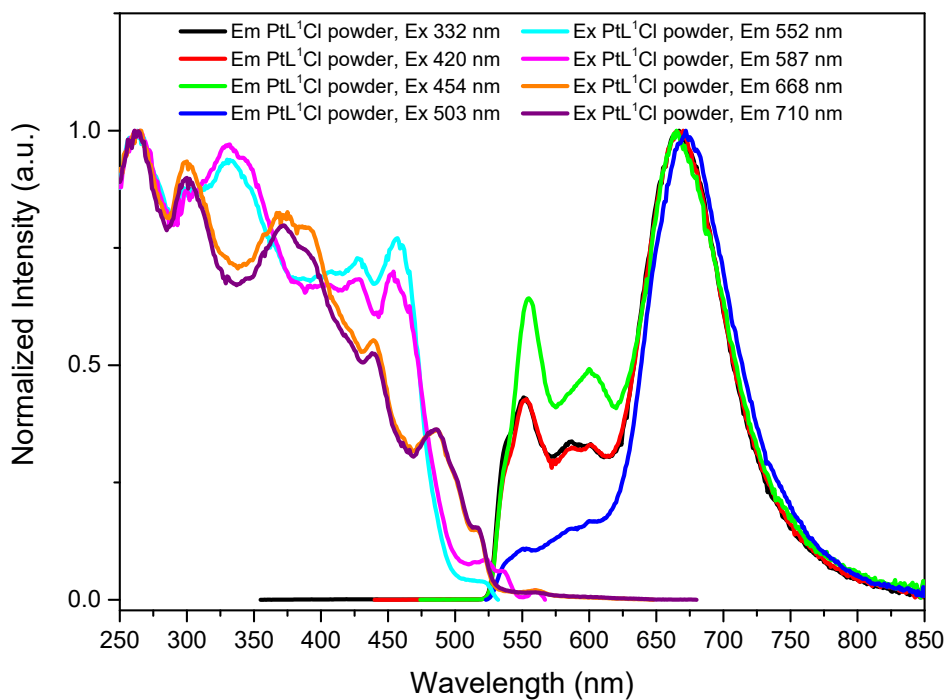


Figure S29. Normalized excitation and emission spectra of $[\text{PtL}^1\text{Cl}]$ powder at 77 K.

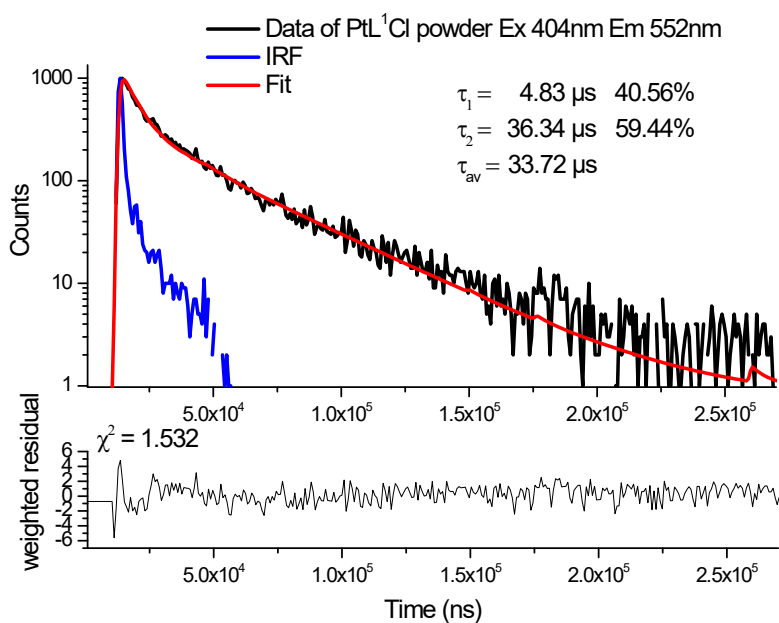


Figure S30. Lifetime measurement of $[\text{PtL}^1\text{Cl}]$ powder at 77 K. Emission 552 nm, Excitation 404 nm.

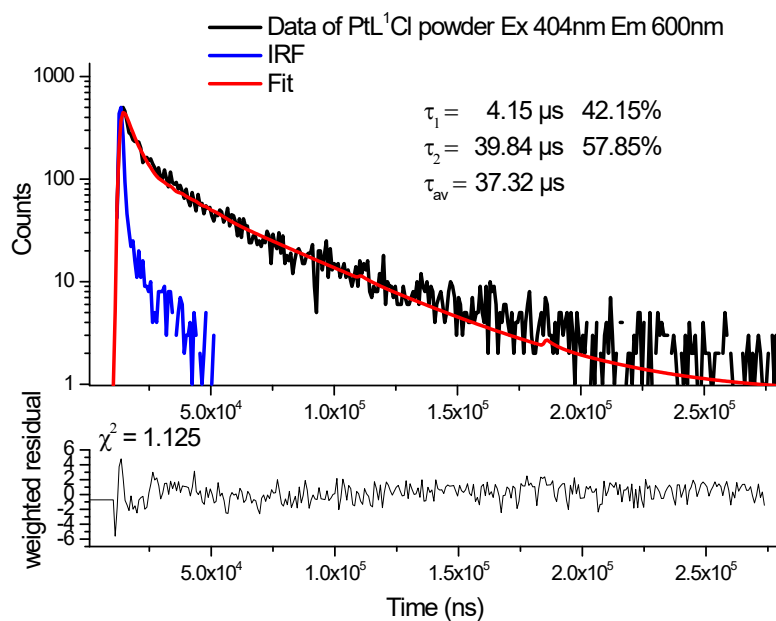


Figure S31. Lifetime measurement of [PtL¹Cl] powder at 77 K. Emission 600 nm, Excitation 404 nm.

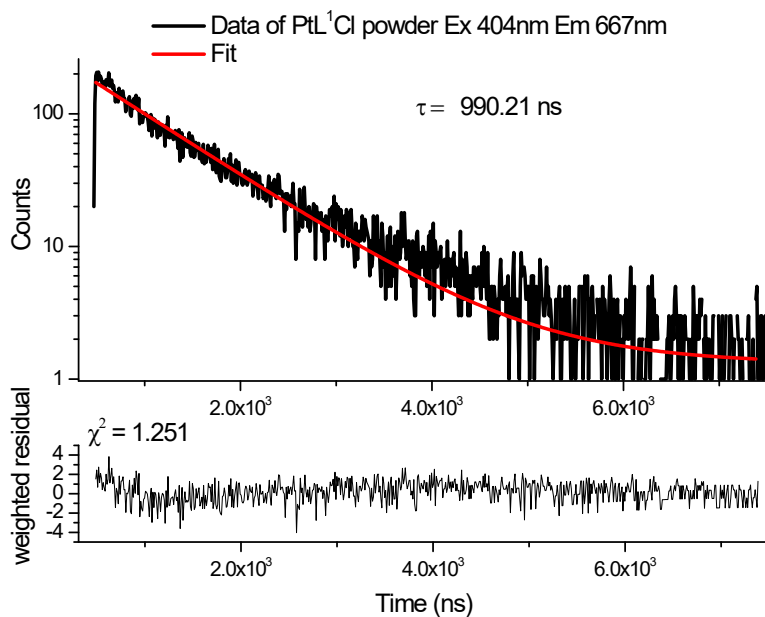


Figure S32. Lifetime measurement of [PtL¹Cl] powder at 77 K. Emission 667 nm, Excitation 404 nm.

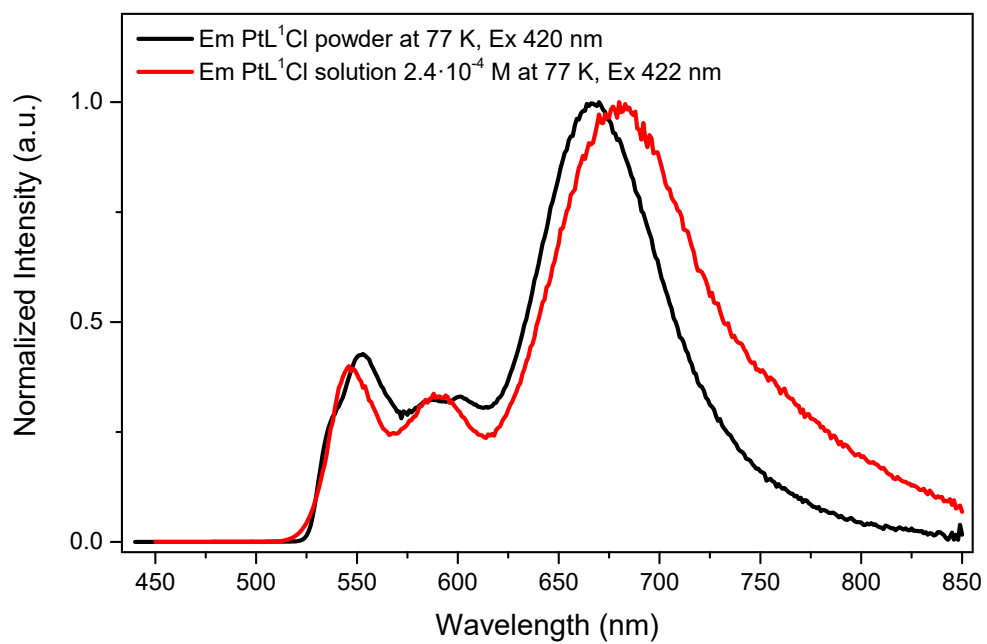


Figure S33. Normalized emission spectra of concentrated solution ($2.4 \cdot 10^{-4}$ M) and powder of the [PtL¹Cl] complex at 77 K.

[PtL²Cl]: Solution

Concentration (M)	Before FPT (%)	After FPT (%)
$2 \cdot 10^{-6}$	5.1	87.9
$1 \cdot 10^{-5}$	4.5	81.7
$2 \cdot 10^{-4}$	3.2	70.1

Table S2. Absolute Quantum Yield (%) of [PtL²Cl] in dichloromethane at different concentrations, before and after the Freeze-Pump-Thaw (FPT) cycles.

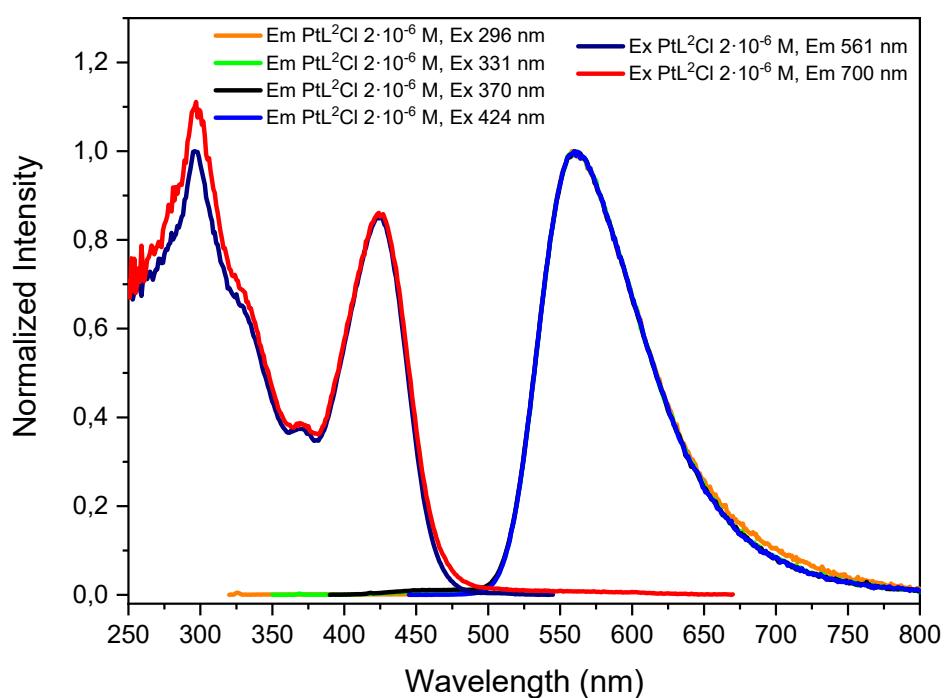


Figure S34. Normalized excitation and emission spectra of a diluted solution ($2 \cdot 10^{-6}$ M) of [PtL²Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

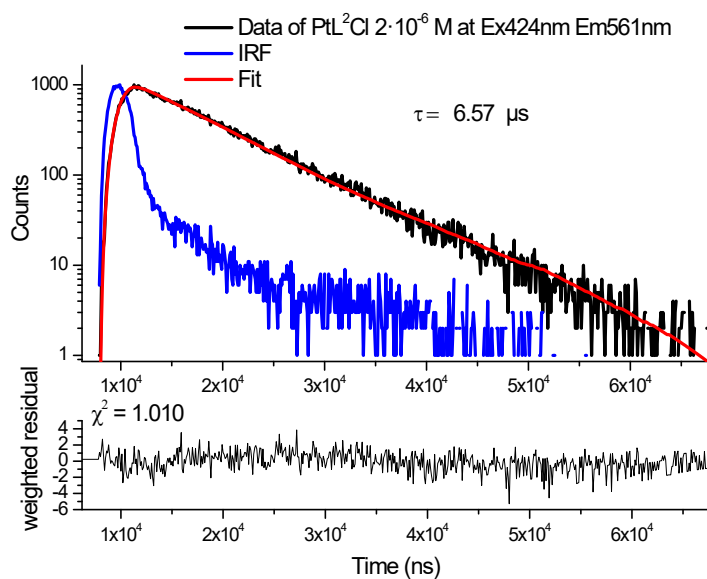


Figure S35. Lifetime measurement of a diluted solution ($2 \cdot 10^{-6} \text{ M}$) of $[\text{PtL}^2\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 561 nm, Excitation 424 nm.

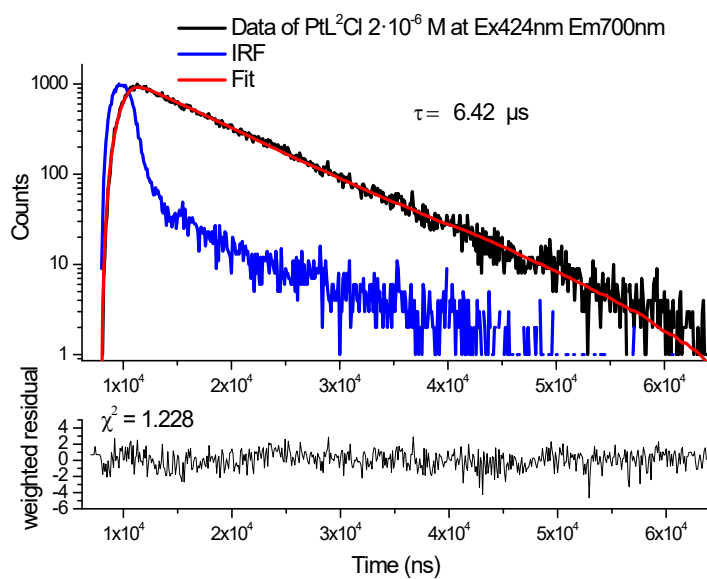


Figure S36. Lifetime measurement of a diluted solution ($2 \cdot 10^{-6} \text{ M}$) of $[\text{PtL}^2\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 700 nm, Excitation 424 nm.

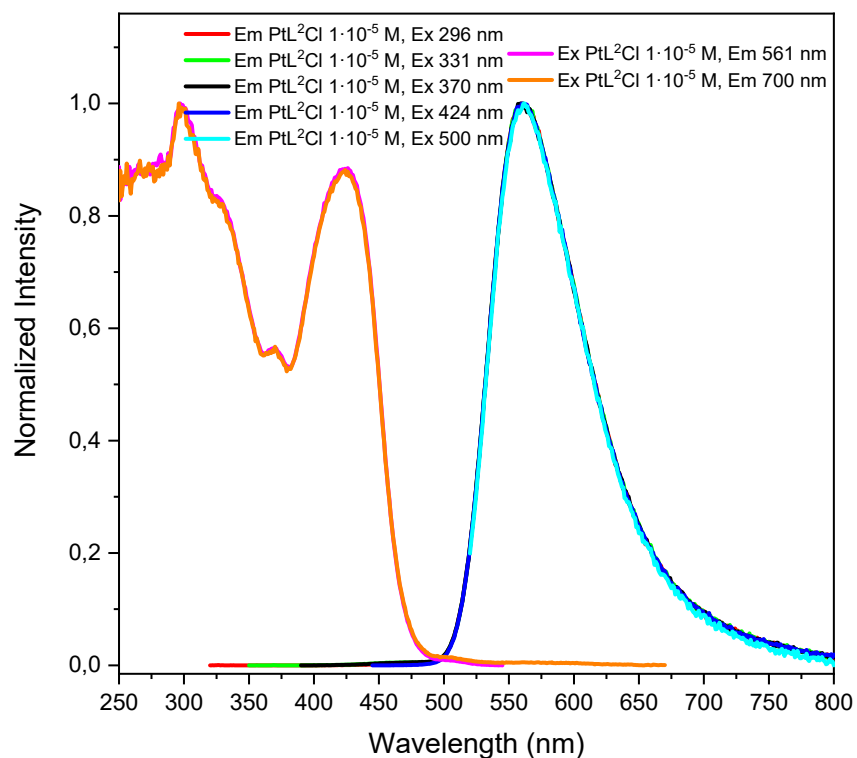


Figure S37. Normalized excitation and emission spectra of a $1 \cdot 10^{-5}$ M solution of $[\text{PtL}^2\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

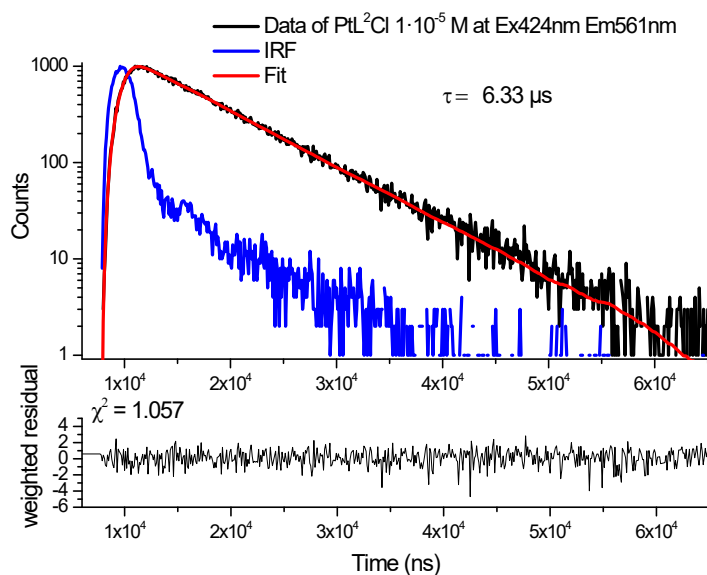


Figure S38. Lifetime measurement of a $1 \cdot 10^{-5}$ M solution of $[\text{PtL}^2\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 561 nm, Excitation 424 nm.

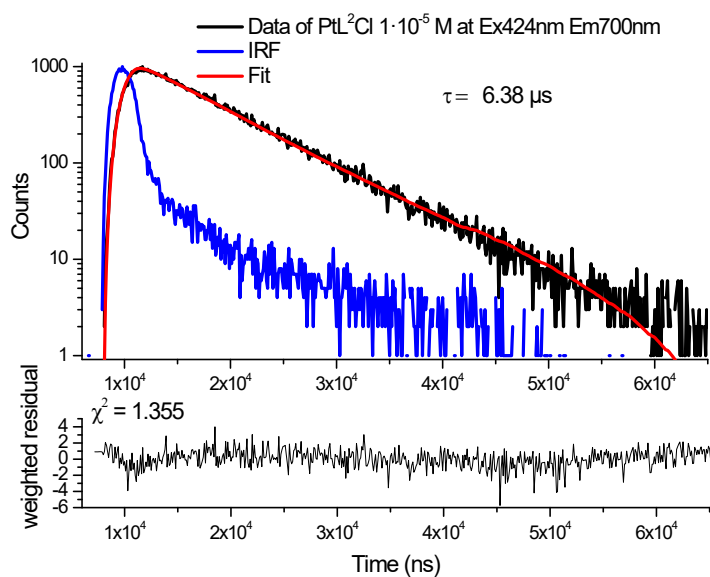


Figure S39. Lifetime measurement of a $1 \cdot 10^{-5} \text{ M}$ solution of $[\text{PtL}^2\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 700 nm, Excitation 424 nm.

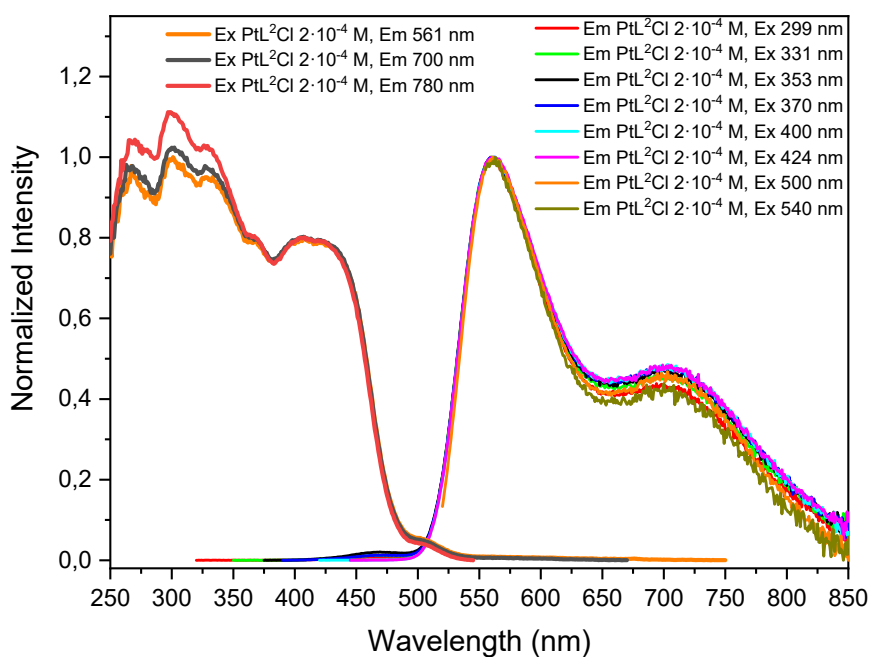


Figure S40. Normalized excitation and emission spectra of concentrated solution ($2 \cdot 10^{-4} \text{ M}$) solution of $[\text{PtL}^2\text{Cl}]$ at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

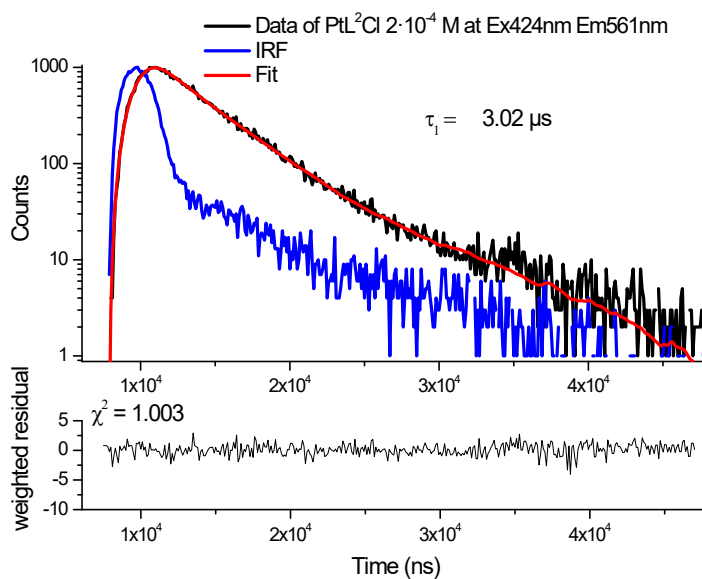


Figure S41. Lifetime measurement of a concentrated solution ($2 \cdot 10^{-4}$ M) of [PtL²Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 561 nm, Excitation 424 nm.

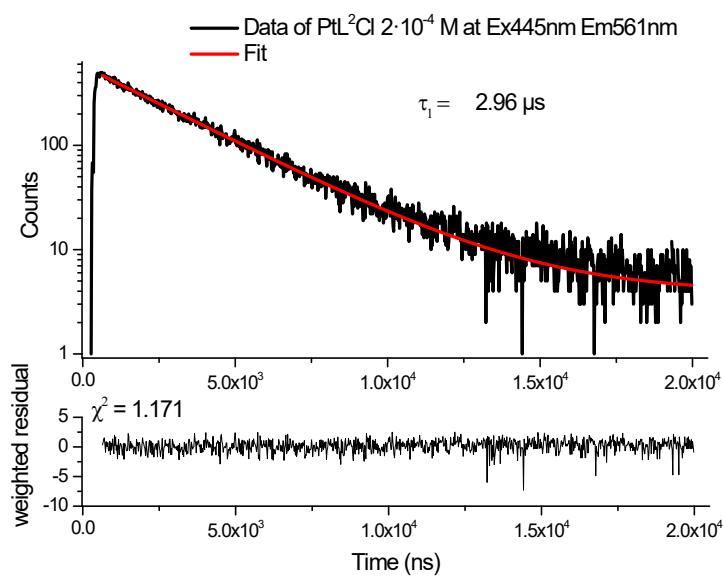


Figure S42. Lifetime measurement of a concentrated solution ($2 \cdot 10^{-4}$ M) of [PtL²Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 561 nm, Excitation 445 nm.

[PtL³Cl]: Solution

Concentration (M)	Before FPT (%)	After FPT (%)
$2 \cdot 10^{-6}$	<1	89.4
$1 \cdot 10^{-5}$	<1	57.2
$1 \cdot 10^{-4}$	<1	43.7

Table S3. Absolute Quantum Yield (%) of [PtL³Cl] in dichloromethane at different concentrations, before and after the Freeze-Pump-Thaw (FPT) cycles.

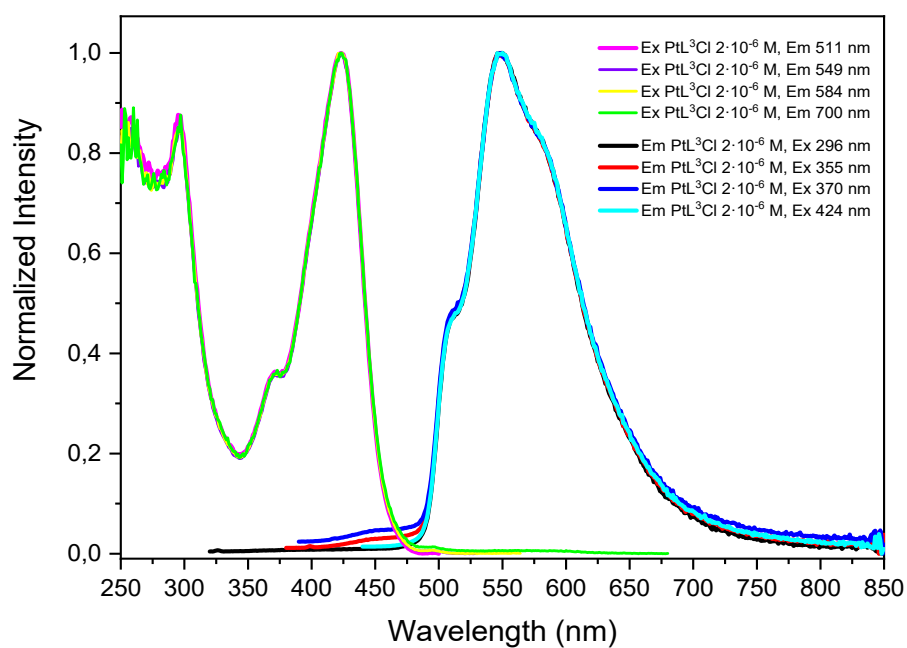


Figure S43. Normalized excitation and emission spectra of a diluted solution ($2 \cdot 10^{-6}$ M) of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

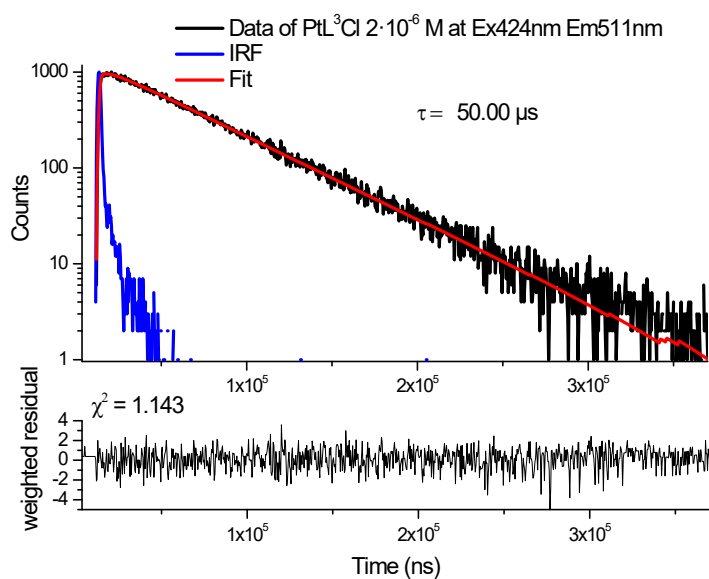


Figure S44. Lifetime measurement of a diluted solution ($2 \cdot 10^{-6}$ M) of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 511 nm, Excitation 424 nm.

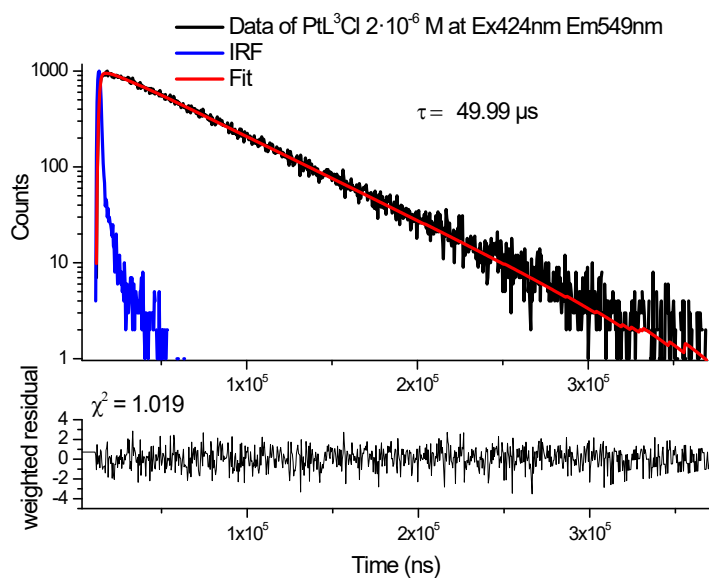


Figure S45. Lifetime measurement of a diluted solution ($2 \cdot 10^{-6}$ M) of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 549 nm, Excitation 424 nm.

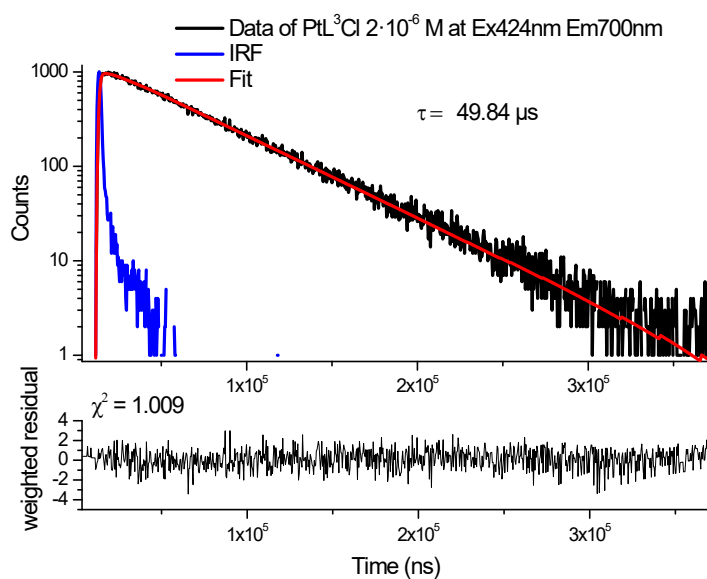


Figure S46. Lifetime measurement of a diluted solution (2·10⁻⁶ M) of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 700 nm, Excitation 424 nm.

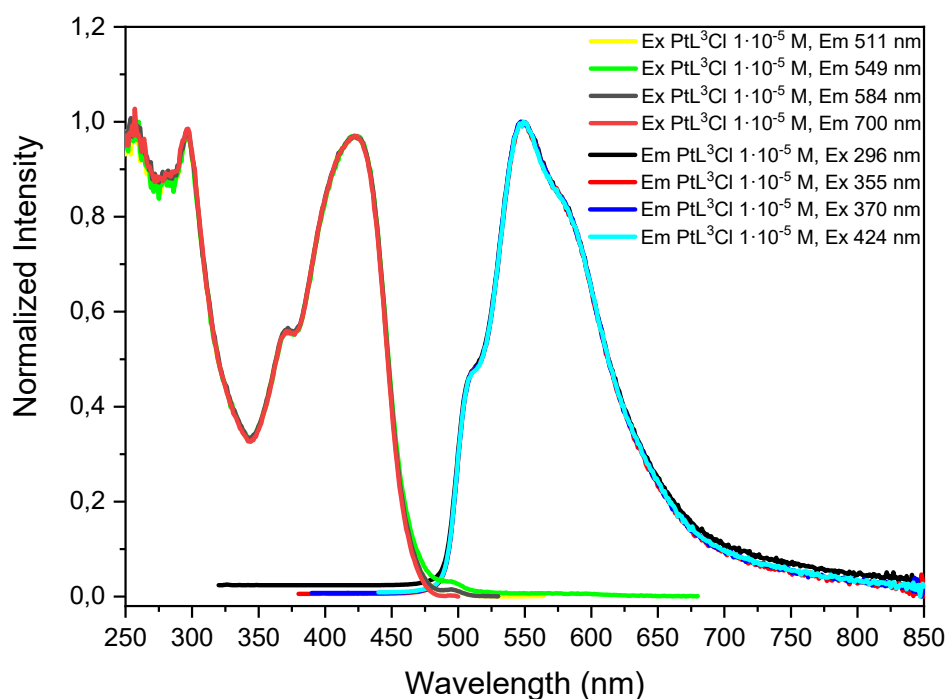


Figure S47. Normalized excitation and emission spectra of a 1·10⁻⁵ M solution of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

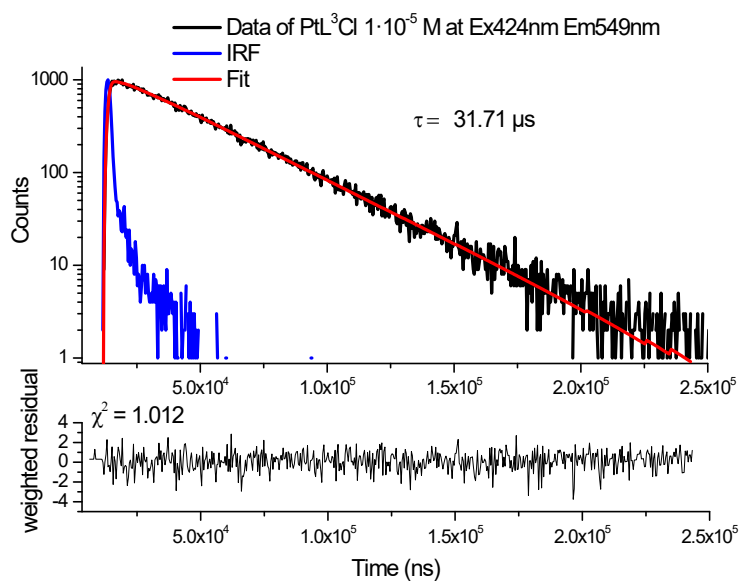


Figure S48. Lifetime measurement of a 1·10⁻⁵ M solution of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 549 nm, Excitation 424 nm.

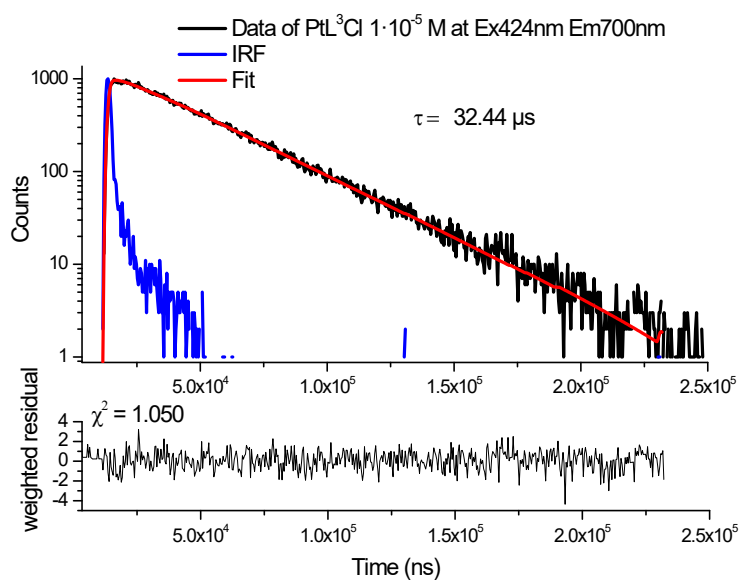


Figure S49. Lifetime measurement of a 1·10⁻⁵ M solution of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 700 nm, Excitation 424 nm.

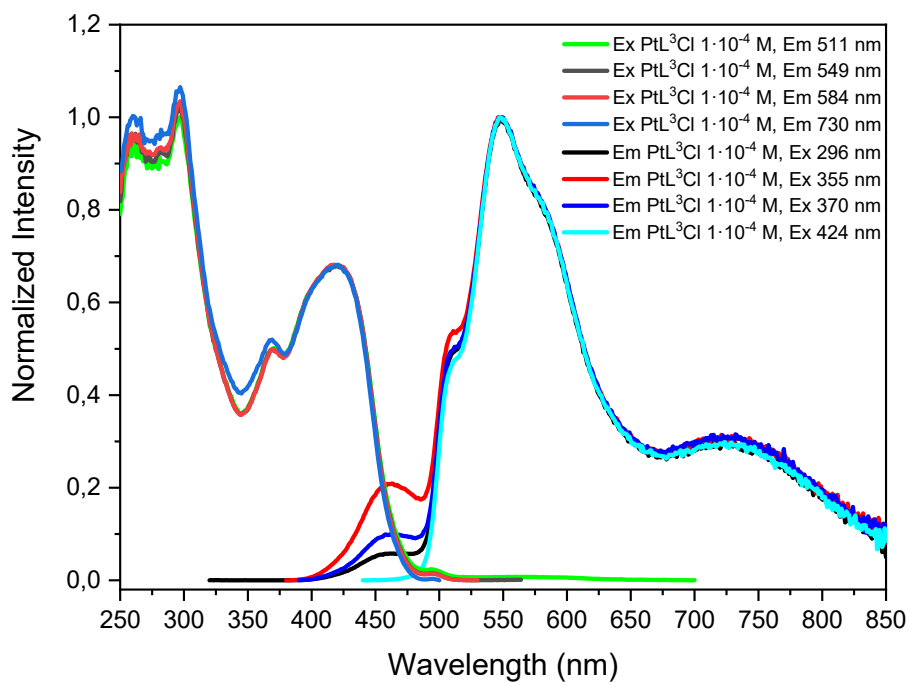


Figure S50. Normalized excitation and emission spectra of concentrated solution ($1 \cdot 10^{-4}$ M) solution of **[PtL³Cl]** at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles.

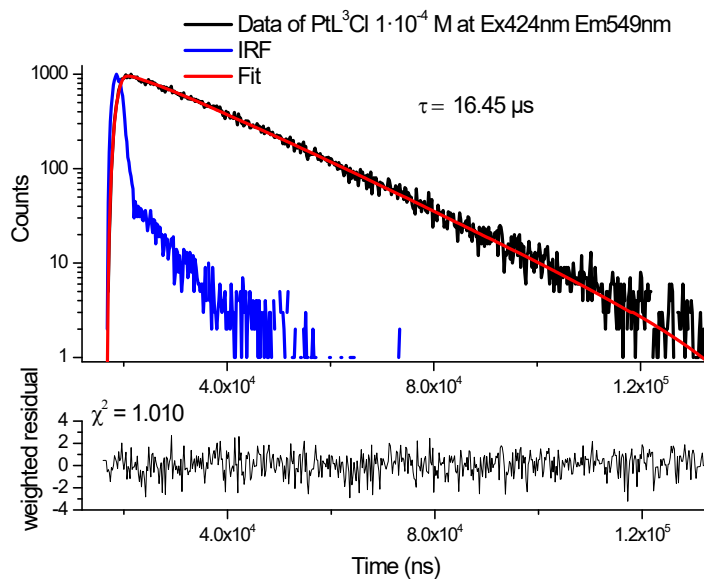


Figure S51. Lifetime measurement of a concentrated solution ($1 \cdot 10^{-4}$ M) of **[PtL³Cl]** at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 549 nm, Excitation 424 nm.

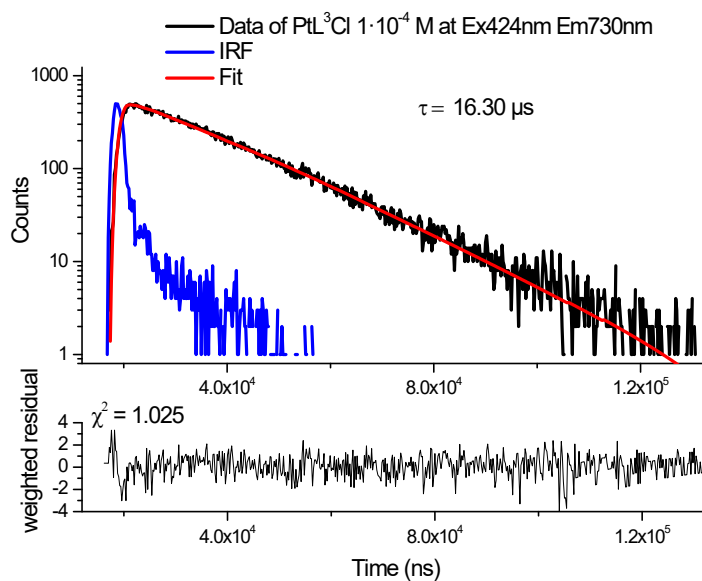


Figure S52. Lifetime measurement of a concentrated solution ($1 \cdot 10^{-4}$ M) of [PtL³Cl] at room temperature in dichloromethane, after the freeze-pump-thaw (FPT) cycles. Emission 730 nm, Excitation 424 nm.

V. EQE vs Luminance and Current density vs Applied Voltage

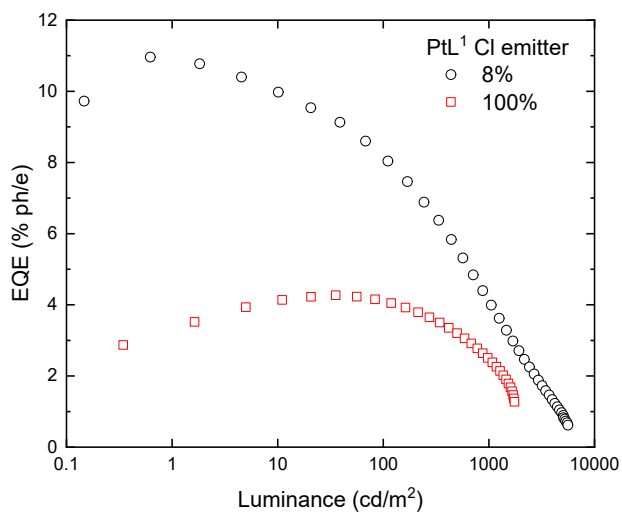


Figure S53. External Quantum Efficiency (EQE) vs Luminance of PtL¹Cl

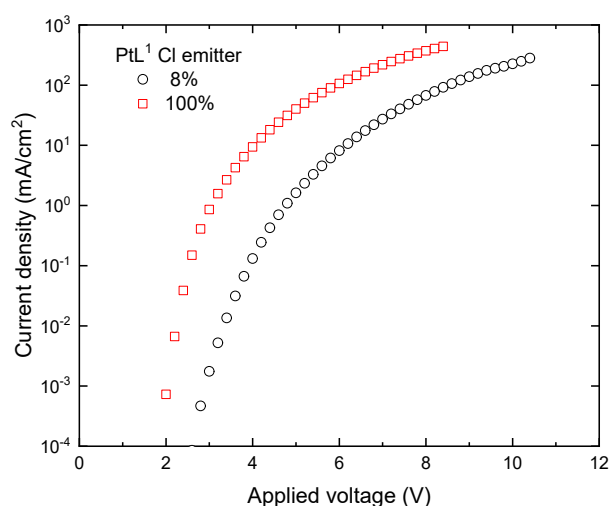


Figure S54. Current density vs Applied Voltage of of PtL¹Cl

References

1. K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishic, S. Tobita, “Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector”, *Phys. Chem. Chem. Phys.*, **2009**, 11, 9850–9860. DOI: 10.1039/b912178a
- 2 V. N. Kozhevnikov, B. Donnio, B. Heinrich, J. A. G. Williams, D. W. Bruce, Green-blue light-emitting platinum(ii) complexes of cyclometallated 4,6-difluoro-1,3-dipyridylbenzenes showing mesophase organisation, *J. Mat. Chem. C*: **2015**, 3, 10177-10187.
- 3 J. Wang, C.-J. Yang, H.-N. Peng, Y.-S. Deng, X.-C. Gao, Synthesis of triphenylamine-modified arylates and ketones via Suzuki coupling reactions. *Synth. Comm.* **2011**, 41, 832–840.
- 4 M. Cocchi, D. Virgili, V. Fattori, D. L. Rochester, J. A. G. Williams, NACAN-Coordinated platinum(II) complexes as phosphorescent emitters in high-performance organic light-emitting devices, *Adv. Funct. Mat.* **2007**, 17, 285–289.