Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Molecular tectonics: heterometallic (Ir,Cu) grid-type coordination networks based on cyclometallated Ir(III) chiral metallatectons

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General:

All air sensitive and anhydrous reactions were carried out under argon. Light sensitive reactions were protected from light by covering with aluminium foil. The glassware was oven dried at 100°C and cooled under argon flow. Commercially available chemicals were used without further purification. Anhydrous diisopropylamine, toluene, chloroform, dichloromethane and THF were used as supplied by commercial sources without further purification. Methanol was dried and distilled with magnesium methoxide under argon.

NMR (Nuclear magnetic resonance):

Nuclear magnetic resonance spectra were recorded on Bruker Avance AV300 (300 MHz for ^{1}H, 75 MHz for ^{13}C), Bruker Avance AV400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) or Bruker Avance AV500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) spectrometers at 20°C.

Chemicals shifts (in ppm) were determined relative to residual undeuterated solvent as internal reference ($CDCl_3$: 7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C; CD_3CN: 1.94 ppm for ^{1}H and 118.3 ppm and 1.3 ppm for ^{13}C). Spin multiplicities are given with the following abbreviations: s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quadruplet), m (multiplet) and coupling constants (*J*) quoted in Hz.

^{1}H NMR spectra were assigned by standard methods combined with COSY and NOESY/ROESY experiments. ^{13}C spectra were assigned by standard methods combined with DEPT, HMQC and HMBC experiments.

MS (Mass spectra):

Mass spectrometry was performed at the Service Commun d'Analyses, Université de Strasbourg. Low and high-resolution mass spectra (positive and negative mode ESI: Electro Spray Ionization) were recorded on Thermoquest AQA Navigator® with time of flight detector.

Elemental analyses

Elemental analyses were performed on a Thermo Scientific Flash 2000 by the "Service Commun de Microanalyses" of the University of Strasbourg.

X-Ray diffraction

X-ray crystal structure data were collected on a Bruker SMART CCD diffractometer with Mo-Kα radiation. The structures were solved using SHELXS-97 and refined by full matrix least squares on F2 using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model). CCDC 1413248-1413251 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 AV diffractometer using Cu-Kα radiation (λ = 1.5406 Å) operating at 40 kV and 40 mA with a scanning rang between 3.8 and 50° by a scan step size of 2°/min. For comparison, simulated patterns were calculated using the Mercury software.

Photophysical measurements:

UV/Vis spectra in solution and in the solid state were recorded on a Perkin-Elmer Lambda 650S spectrophotometer (spectra in the solid state recorded in the reflection mode, using a 150 mm integrating sphere and spectralon© as light spectral reference for the reflection corrections). Wavelengths are given in nm and molar absorption coefficients (ε) are given in $L.mol^{-1}.cm^{-1}$.

Steady-state emission spectra in solution were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm mm^{-1} dispersion; 1200 grooves mm^{-1}) and a Hamamatsu R928 photomultiplier tube. Steady-state emission spectra in the solid state were recorded on a Perkin Elmer LS55 spectrometer equipped with a Hamamatsu R928 photomultiplier tube. Due to the relative instability of the coordination network *rac*-$Ir(ppy)_2$(**1**)·$Cu(BF_4)_2$, single crystals were embedded in a few drops of a perfluorinated-ether oil (Fomblin® Y) and deposited between two quartz coverslips adapted on the sample holder directly after their removal from the mother solution in order to prevent collapsing of the architecture. The integrity of the crystals was checked before and after the luminescence measurement by visual inspection with a microscope. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Luminescence quantum yields in the solid state were performed by using an absolute photo-luminescence quantum yield spectrometer Quantaurus C11347-11 (Hamamatsu, Japan) exciting the samples from 300 nm to 500 nm. All solvents were spectrometric grade. Measurements in solution were performed on optically dilute solutions ($A_{\lambda exc} < 0.20$). Deaerated samples were prepared by the freeze-pump-thaw technique.

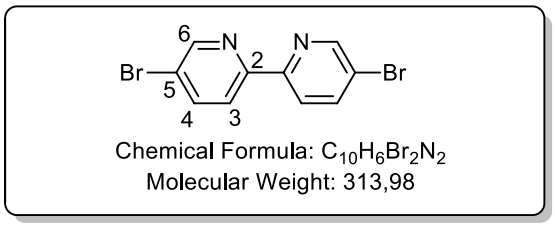
CD (Circular Dichroism)

Circular dichroism was performed on a JASCO J-810 spectropolarimeter. Data was collected over a wavelength range of 200-600 nm, at a scan speed of 100 nm/min, bandwidth of 1 nm and data pitch of 0.1 nm. Samples were measured at RT (23°C) and at given concentrations using a 10 mm path length cuvette (Starna Ltd.).

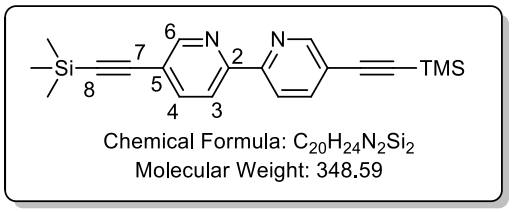
Optical rotation (α_D)

Polarimetric measurements were performed on a Perkin Elmer (model 341) instrument at a wavelength of 589 nm (Na). The $[\alpha]_D$ values are given in 10^{-1} $deg.cm^2.g^{-1}$ and concentrations are given in g/100mL.

Synthesis

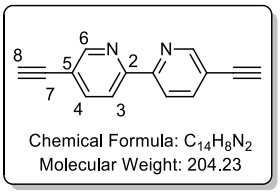


5,5'-dibromo-2,2'-bipyridine **2** was prepared in 67 % yield according to the literature procedure.[1] **δ_H/ppm ($CDCl_3$, 500 MHz)** 8.70 (2H, d, ^4J = 2.4, H_6), 8.29 (2H, d, ^3J = 8.6, H_3), 7.93 (2H, dd, ^3J = 8.6, ^4J = 2.4, H_4). **δ_C/ppm ($CDCl_3$, 125 MHz)** 153.8 (C_2), 150.4 (C_6), 139.7 (C_3), 122.3 (C_4), 121.5 (C_5). NMR assignment according to D Leigh *et al*.[1] **IR** ν_{max}/cm^{-1} 1544, 1455 (C=N), 1357, 1261, 1233, 1124, 1087, 1007, 827, 801, 726, 702, 638 (C-Br). **Elem. Anal.** Calcd for $C_{10}H_6Br_2N_2$: C, 38.25; H, 1.93; N, 8.92. Found: C, 38.16; H, 2.12; N, 8.57.



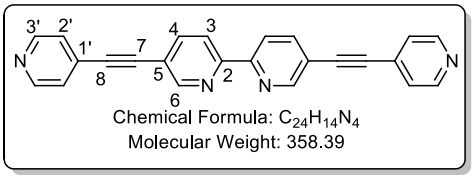
5,5'-bis((trimethylsilyl)ethynyl)-2,2'-bipyridine was prepared in 83% yield by a slightly modified literature procedure.[1] Trimethylsilylacetylene (0.25 mL, 1.84 mmol) was added to a degassed solution of 5,5'-dibromo-2,2'-bipyridine (0.20 g, 0.64 mmol) in a mixture of toluene (14 mL) and distilled NEt_3 (4 mL). The resulting mixture was degassed several times with argon. Then $Pd(PPh_3)_4$ (0.02 g, 0.017 mmol) and CuI (0.01 g, 0.52 mmol) were added. The mixture was stirred at 60 °C overnight. The solution was filtered through a celite pad then concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL), washed with an aqueous saturated NH_4Cl solution (30 mL) and brine (30 mL), dried over $MgSO_4$ and evaporated. The solid was then purified by chromatography (silica gel, CH_2Cl_2/Cyclohexane 50% to 100%) to afford the desired product as a white solid (0.19 g, 83%).

δ_H/ppm ($CDCl_3$, 300 MHz) 8.71 (2H, d, ^4J = 1.8, H_6), 8.35 (2H, d, ^3J = 8.4, H_3), 7.85 (2H, dd, ^3J = 8.3, ^4J = 1.9, H_4), 0.28 (18H, s, Si(CH_3)$_3$). **δ_C/ppm ($CDCl_3$, 100MHz)** 154.2 (C_2), 152.1 (C_6), 139.8 (C_4), 120.5 (C_3), 120.4 (C_5), 101.8 ($C_{7/8}$), 99.5 ($C_{7/8}$), -0.1 (Si(CH_3)$_3$) NMR assignment in agreement with D. Leigh *et al*. [1] **IR** ν_{max}/cm^{-1} 2161, 1457, 1363, 1249, 1220, 1024, 866, 834, 760, 738, 661, 646. **Elem. Anal.** Calcd for $C_{20}H_{24}N_2Si_2 \cdot 0.25\ H_2O$: C, 68.03; H, 6.99; N, 7.93. Found: C, 67.95; H, 6.96; N, 7.93.



5,5'-diethynyl-2,2'-bipyridine was prepared according to a modified literature procedure in 87 % yield. [1] 5,5'-bis((trimethylsilyl)ethynyl)-2,2'-bipyridine (0.26 g, 0.75 mmol) was dissolved in methanol: THF (1:1, 12 mL) and powdered K_2CO_3 (0.10 g, 0.72 mmol) was added. The mixture was stirred overnight at room temperature and the solvent was evaporated to dryness. CH_2Cl_2 (15 mL) was added and the mixture was washed with a saturated NH_4Cl solution (15 mL) and brine (15 mL). The organic layer was dried over $MgSO_4$ and concentrated to dryness. Chromatography (Al_2O_3, CH_2Cl_2/cyclohexane 0% to 70%) afforded the pure product as a beige solid (0.13 g, 87 %).

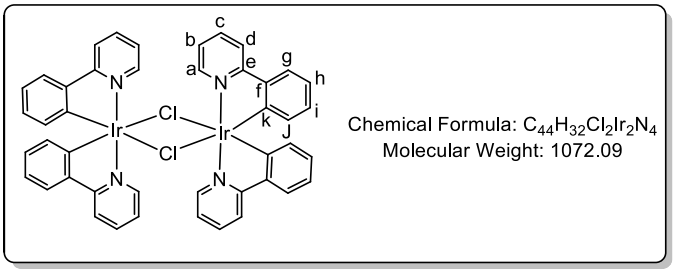
δ_H/ppm ($CDCl_3$, 300 MHz) 8.76 (2H, d, ^4J = 2.1, H_6), 8.39 (2H, d, ^3J = 8.2, H_3), 7.90 (2H, dd, ^3J = 8.2, ^4J = 1.4, H_4), 3.31 (2H, s, H_8) **δ_C/ppm ($CDCl_3$, 125 MHz)** 154.6 (C_5), 152.3 (C_6), 140.1 (C_3), 120.6 (C_4), 119.5 (C_2), 81.7 ($C_{7/8}$), 80.6 ($C_{7/8}$). **IR** ν_{max}/cm^{-1} 3263, 1585, 1531, 1464, 1365, 1234, 1025, 838, 737, 706, 679, 631, 514. **Elem. Anal.** Calcd for $C_{14}H_8N_2 \cdot 0.1H_2O$: C, 81.61; H, 4.01; N, 13.60. Found**:** C, 81.45; H, 3.94; N 13.75.



To a solution of 5,5'-diethynyl-2,2'-bipyridine (0.09 g, 0.44 mmol) in anhydrous toluene, 5-iodopyridine (0.19 g, 0.88 mmol) and $Pd(PPh_3)_4$ (0.04 g, 0.03 mmol) were added. After degassing the yellow solution several times, diisopropylamine (6 mL) was added. The mixture was heated at 60 °C for two days. The dark red mixture was filtrated through celite and the filtrate was evaporated. The crude product was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 0% to 1%). A powder was obtained and dissolved in a 1M aqueous HCl solution (5 mL) and H_2O (20 mL). The aqueous layer was washed with CH_2Cl_2 (2x30 mL). A 1M aqueous NaOH solution (10 mL) was then added that resulted in precipitation of a white powder. The resulting suspension was extracted with CH_2Cl_2 (2x30 mL) and the organic layers were collected and evaporated to dryness to afford the product as a beige solid (0.087 g, 72%).

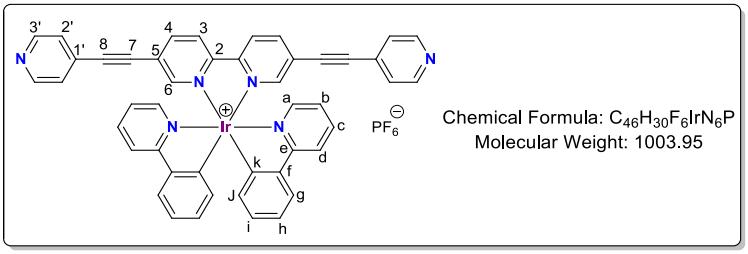
δ_H/ppm ($CDCl_3$, 500 MHz) 8.84 (2H, d, ^4J = 1.7, H_6), 8.65 (4H, dd, ^3J = 4.4, ^5J = 1.5, $H_{3'}$), 8.48 (2H, d, ^3J = 8.3, H_3), 7.98 (2H, dd, ^3J = 8.2, ^4J = 2.1, H_4), 7.43 (4H, dd, ^3J = 4.5, ^5J = 1.5, $H_{2'}$). **δ_C/ppm ($CDCl_3$, 125 MHz)** 154.6 ($C_{5/2}$), 151.9 (C_6), 149.8 ($C_{3'}$), 139.7 (C_4), 130.7 ($C_{1'}$), 125.5 ($C_{2'}$), 120.8 (C_3), 119.5 ($C_{2/5}$),

90.9 ($C_{7/8}$), 90.7 ($C_{7/8}$). NMR assignments according to HSQC and HMBC 2D ^{1}H-^{13}C NMR experiments. **IR** ν_{max}/cm^{-1} 1584, 1529, 1492, 1411, 1364, 1219, 1022, 839, 819, 735, 718, 649, 549, 520, 466. **Elem. Anal.** Calcd for $C_{24}H_{14}N_4 \cdot 0.25H_2O$: C, 79.43; H, 4.03; N, 15.44. Found: C, 79.35; H, 4.02; N, 15.39. **UV-Visible** λ_{max} (CH_2Cl_2)/nm ($\varepsilon/x10^3$ $L.mol^{-1}.cm^{-1}$) 279 (15.6), 340 (64.6).



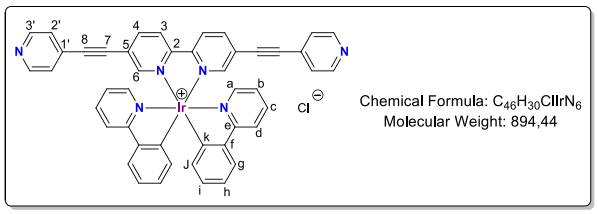
rac-$[Ir(ppy)_2(\mu\text{-}Cl)]_2$ was synthesised in 86 % yield following the reported procedure.[2]

δ_H/ppm ($CDCl_3$, 300 MHz) 9.24 (4H, dd, ^{3}J = 5.7, ^{4}J = 1.0, H_a), 7.86 (4H, d, ^{3}J = 7.8, H_d), 7.73 (4H, td, ^{3}J = 7.5, ^{4}J = 1.5, H_c), 7.48 (4H, dd, ^{3}J = 7.8, ^{4}J = 1.2, H_g), 6.73-6.78 (8H, m, H_b, H_i), 6.56 (4H, ddd, ^{3}J = 8.0, ^{3}J = 8.0, ^{4}J = 1.4, H_h), 5.93 (4H, dd, ^{3}J = 7.7, ^{4}J = 1.0, H_J). **δ_C/ppm ($CDCl_3$, 75 MHz)** 168.6 (C_e), 151.7 (C_a), 145.4 (C_f), 143.7 (C_k), 136.1 (C_J), 130.6 (C_c), 124.1 (C_b), 123.7 (C_d), 122.1 (C_i), 121.3 (C_g) 118.3 (C_h). ^{1}H and ^{13}C NMR assignments according to R. J. Watts *et al.* [3] **IR** ν_{max}/cm^{-1} 1605, 1582, 1477 (C=N), 1416, 1268, 1225, 1160, 1062, 1030, 793, 753, 735, 727



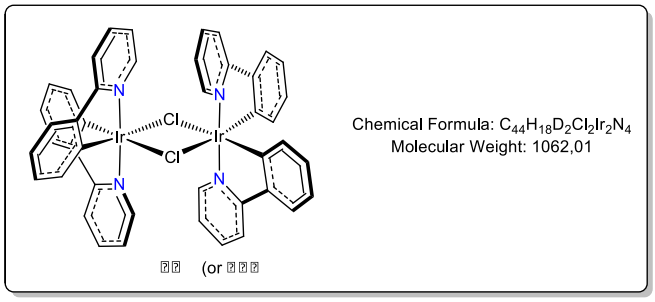
To a solution of *rac*-$[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (0.05 g, 0.046 mmol) in a mixture of MeOH/CH_2Cl_2/CH_3CN (6 mL/6 mL/2 mL) was added 5,5'-diethynylpyridine-2,2'-bipyridine (0.035 g, 0.097 mmol). The yellow solution was heated at 60 °C overnight. After cooling, water (30 mL) was added and the aqueous layer was washed with Et_2O (3x30 mL). The aqueous layer was heated at 70 °C and an aqueous KPF_6 solution (100 mg in 5 mL H_2O) was added. An orange precipitate formed immediately and the suspension was placed in an ice bath for 2 hours. The suspension was filtered, washed with H_2O (5 mL) and Et_2O (5 mL). The product was obtained as a red powder (0.078 g, 85 %) by recrystallization from acetonitrile (1.5 mL) and diethylether (30 mL). Single crystals suitable for X-ray diffraction were obtained by vapour diffusion of Et_2O (15 mL) into an acetonitrile solution containing the Ir complex (5 mg in 1 mL).

δ_H/ppm (CD_3CN, 400 MHz) 8.62 (4H, br s, $H_{3'}$), 8.56 (2H, d, ^3J = 8.6, H_3), 8.27 (2H, dd, ^3J = 8.6, ^4J = 2.0, H_4), 8.06-8.09 (4H, m, H_d, H_6), 7.87 (2H, ddd, ^3J = 7.8, ^3J = 7.8, ^4J = 1.4, H_c), 7.81 (2H, d, ^3J = 7.7, H_g), 7.70 (2H, d, ^3J = 5.8, H_a), 7.36 (4H, d, ^3J = 5.7, $H_{2'}$), 7.04-7.09 (4H, m, H_b, H_h), 6.94 (2H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.0, H_i), 6.27 (2H, d, ^4J = 7.6, H_J). **δ_C/ppm (CD_3CN, 100 MHz)** 168.1 (C_e), 155.6 (C_2),153.5 (C_6), 151.1 ($C_{3'}$), 150.6 (C_a), 150.0 (C_f), 145.0 (C_k), 142.7 (C_4), 139.7 (C_c), 132.4 (C_J), 131.5 (C_i), 129.9 (C_5), 126.3 ($C_{2'}$), 126.0 ($C_{3/g}$), 125.9 ($C_{3/g}$), 124.8 ($C_{1'}$), 124.6 ($C_{b/h}$), 123.9 ($C_{b/h}$), 121.0 (C_d), 94.3 (C_8), 88.4 (C_7). ^{1}H and ^{13}C NMR assignments according to COSY 2D ^{1}H-^{1}H NMR experiments and HSQC and HMBC 2D ^{1}H-^{13}C NMR experiments and in agreement with the assignments reported for $[Ir(ppy)_2(bpy)]^+$.[3] **MS (ESI$^+$)**: calcd for $[M\text{-}PF_6]^+$ $C_{46}H_{30}Ir_1N_6$ 859.22, found 859.22. **UV-Visible** λ_{max} (CH_3CN)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 256 (43.8), 303 (37.4), 359 (45.9). **UV-Visible** λ_{max} (THF)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 302 (40.6), 362 (48.9). **Elem. Anal.** Calcd for $C_{46}H_{30}F_6IrN_6P$: C, 55.03; H, 3.01; N, 8.37. Found**:** C, 54.71; H, 3.27; N 8.71.



To a solution of *rac*-$[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (0.05 g, 0.047 mmol) in a mixture of MeOH/CH_2Cl_2/CH_3CN (5 mL/5 mL/1.5 mL) was added 5,5'-diethynylpyridine-2,2'-bipyridine (0.036 g, 0.100 mmol). The yellow solution was heated at 60 °C overnight. The solvent was evaporated to dryness. Then the mixture was dissolved into 3 mL acetonitrile, filtered and concentrated. *rac*-$[Ir(ppy)_2$(**1**)$][Cl]$ (0.065 g, 78 %) was obtained by recrystallization from acetonitrile (2 mL) and Et_2O (20 mL).

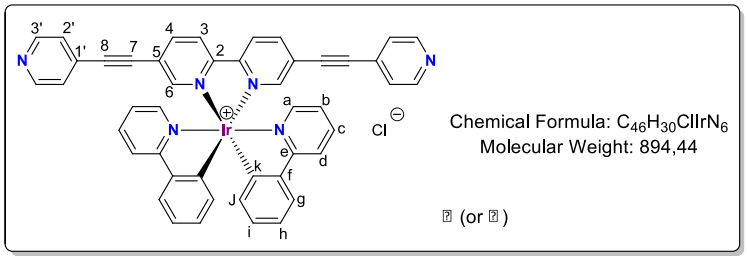
δ_H/ppm (CD_3CN, 400 MHz) 8.64 (2H, d, ^3J = 8.6, H_3), 8.56 (4H, d, ^3J = 5.7, $H_{3'}$), 8.28 (2H, dd, ^3J = 8.6, ^4J = 1.9, H_4), 8.09 (2H, d, ^3J = 8.6, H_d), 8.05 (2H, d, ^3J = 1.9, H_6), 7.88 (2H, ddd, ^3J = 7.8, ^3J = 7.8, ^4J = 1.4, H_c), 7.83 (2H, d, ^3J = 7.7, H_g), 7.70 (2H, d, ^3J = 5.8, H_a), 7.37 (4H, d, ^3J = 5.7, $H_{2'}$), 7.04-7.09 (4H, m, H_b, H_h), 6.95 (2H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.0, H_i), 6.27 (2H, d, ^4J = 7.6, H_J). **δ_C/ppm (CD_3CN, 100 MHz)** 168.1 (C_e), 155.6 (C_2), 153.5 (C_6), 151.1 ($C_{3'}$), 150.6 (C_a), 150.0 (C_f), 145.0 (C_k), 142.7 (C_4), 139.7 (C_c), 132.4 (C_J), 131.5 (C_i), 129.9 (C_5), 126.2 ($C_{2'}$), 126.1 ($C_{3/g}$), 125.9 ($C_{3/g}$), 124.8 ($C_{1'}$), 124.6 ($C_{b/h}$), 123.9 ($C_{b/h}$), 121.0 (C_d), 94.3 (C_8), 88.4 (C_7). **UV-Visible** λ_{max} (CH_3CN)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 256 (43.3), 301 (37.9), 359 (45.4)



The enantiopure iridium dimers ΔΔ-[Ir(ppy)$_2$(μ-Cl)]$_2$ and ΛΛ-[Ir(ppy)$_2$(μ-Cl)]$_2$ were obtained according to the procedure described by Lusby *et al.* [4] with slight modifications. The crude products obtained after reaction of the racemic dimer with L- or D-serine respectively were purified by column chromatography (SiO_2) using a mixture of CH_2Cl_2/CH_3OH/NEt_3 as eluent with a gradient elution of 99:0:1 to 97:3:1 (instead of CH_2Cl_2/CH_3OH/NEt_3 96:3:1 only). ΔΔ-[Ir(ppy)$_2$(μ-Cl)]$_2$ and ΛΛ-[Ir(ppy)$_2$(μ-Cl)]$_2$ were obtained as yellow solids (32 mg and 36 mg respectively) in 43 % and 48 % yields respectively (starting from 150 mg of *rac*-[Ir(ppy)$_2$(μ-Cl)]$_2$).

ΔΔ-[Ir(ppy)$_2$(μ-Cl)]$_2$: **^{1}H** and **^{13}C NMR** spectra were identical to *rac*-[Ir(ppy)$_2$(μ-Cl)]$_2$. **$[\alpha]_D^{20}$** (*c* 0.052 g/100 mL in CH_2Cl_2): +433°.

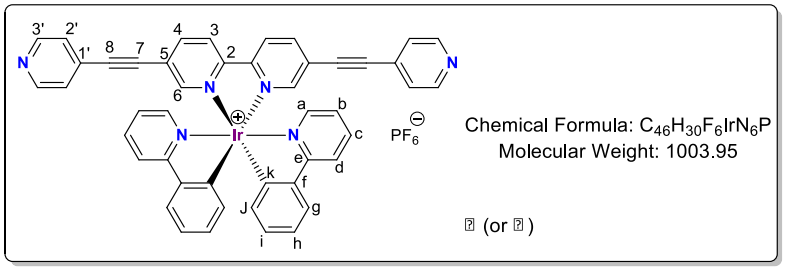
ΛΛ-[Ir(ppy)$_2$(μ-Cl)]$_2$: **^{1}H** and **^{13}C NMR** spectra were identical to *rac*-[Ir(ppy)$_2$(μ-Cl)]$_2$. **$[\alpha]_D^{20}$** (*c* 0.054 g/100 mL in CH_2Cl_2): -468°



The same procedure as the one followed for the racemic compound *rac*-[Ir(ppy)$_2$(**1**)][Cl] was used for the synthesis of Δ- and Λ-[Ir(ppy)$_2$(**1**)][Cl] complexes starting from the enantiopure Iridium dimers (ΔΔ and ΛΛ-[Ir(ppy)$_2$(μ-Cl)]$_2$ respectively; 0.02g, 0.018 mmol). The enantiopure products Δ-[Ir(ppy)$_2$(**1**)][Cl] (0.024 g, 74 %) and Λ-[Ir(ppy)$_2$(**1**)][Cl] (0.025 g, 76 %) were obtained by recrystallization from acetonitrile (2 mL) and Et_2O (20 mL). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of toluene into a toluene/CH_3CN 1/1 solution of the desired complex.

Δ-[Ir(ppy)$_2$(**1**)][Cl]: **^{1}H NMR** and **^{13}C NMR** were identical to *rac*-[Ir(ppy)$_2$(**1**)][Cl]. **$[\alpha]_D^{20}$** (*c* 0.047 g/100 mL in CH_3CN): -317° **UV-Visible** λ_{max} (CH_3CN)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 256 (42.8), 301 (39.6), 359 (47.8).

Λ-[Ir(ppy)$_2$(**1**)][Cl]: **^{1}H NMR** and **^{13}C NMR** were identical to *rac*-[Ir(ppy)$_2$(**1**)][Cl]. **$[\alpha]_D^{20}$** (*c* 0.048 g/100 mL in CH_3CN): +323°. **UV-Visible** λ_{max} (CH_3CN)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 256 (42.2), 301 (39.4), 359 (48.6).



Synthesis of Δ- and Λ-[Ir(ppy)$_2$(**1**)][PF_6] complexes follow the same procedure as for the parent racemic complex starting from the enantiopure Iridium dimers (ΔΔ and ΛΛ-[Ir(ppy)$_2$(μ-Cl)]$_2$ respectively). Red solids (60 mg for Δ-[Ir(ppy)$_2$(**1**)][PF_6] and 62 mg for Λ-[Ir(ppy)$_2$(**4**)][PF_6]) were obtained by recrystallization from acetonitrile (3 mL) and Et_2O (20 mL) in 80 % and 83 % yield respectively.

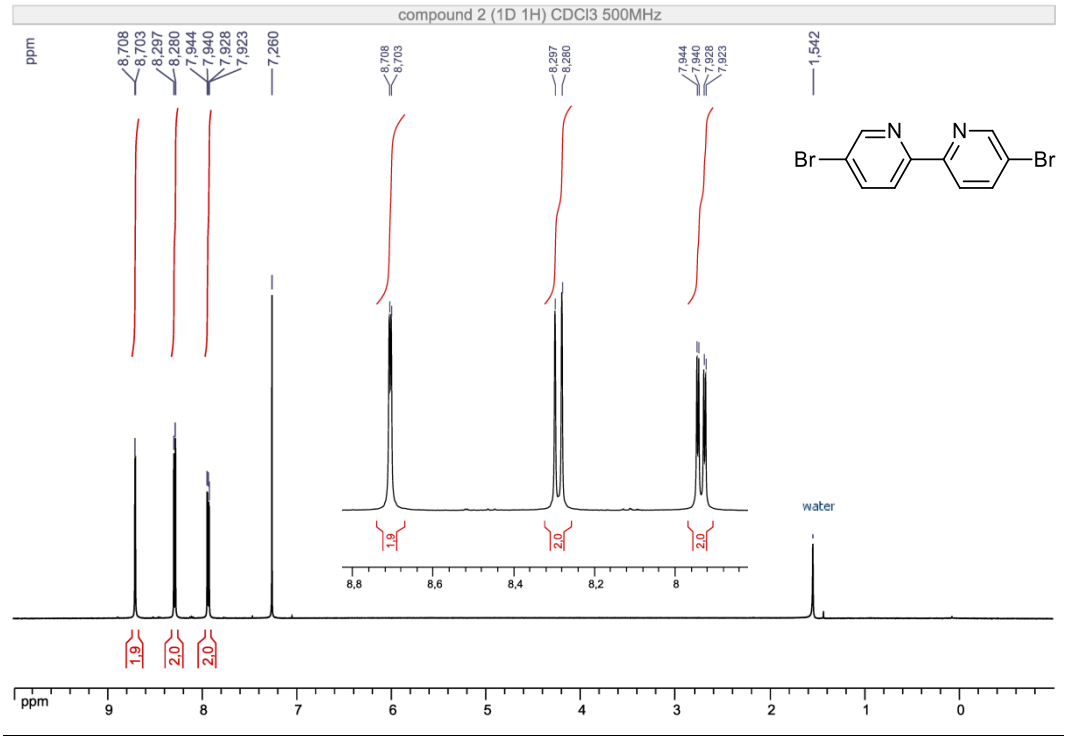
Δ-[Ir(ppy)$_2$(**1**)][PF_6]: **^{1}H NMR** and **^{13}C NMR** were identical to *rac*-[Ir(ppy)$_2$(**1**)][PF_6]. **$[\alpha]_D^{20}$** (*c* 0.068 g/100 mL in CH_3CN): -299°. **UV-Visible** λ_{max} (CH_3CN)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 256 (45.4), 301 (40.3), 359 (47.7).

Λ-[Ir(ppy)$_2$(**1**)][PF_6]: **^{1}H NMR** and **^{13}C NMR** were identical to *rac*-[Ir(ppy)$_2$(**1**)][PF_6]. **$[\alpha]_D^{20}$** (*c* 0.064 g/100 mL in CH_3CN): +238°. **UV-Visible** λ_{max} (CH_3CN)/nm (ε/x10^3 L.mol^{-1}.cm^{-1}) 256 (44.5), 301 (40.5), 359 (47.1).

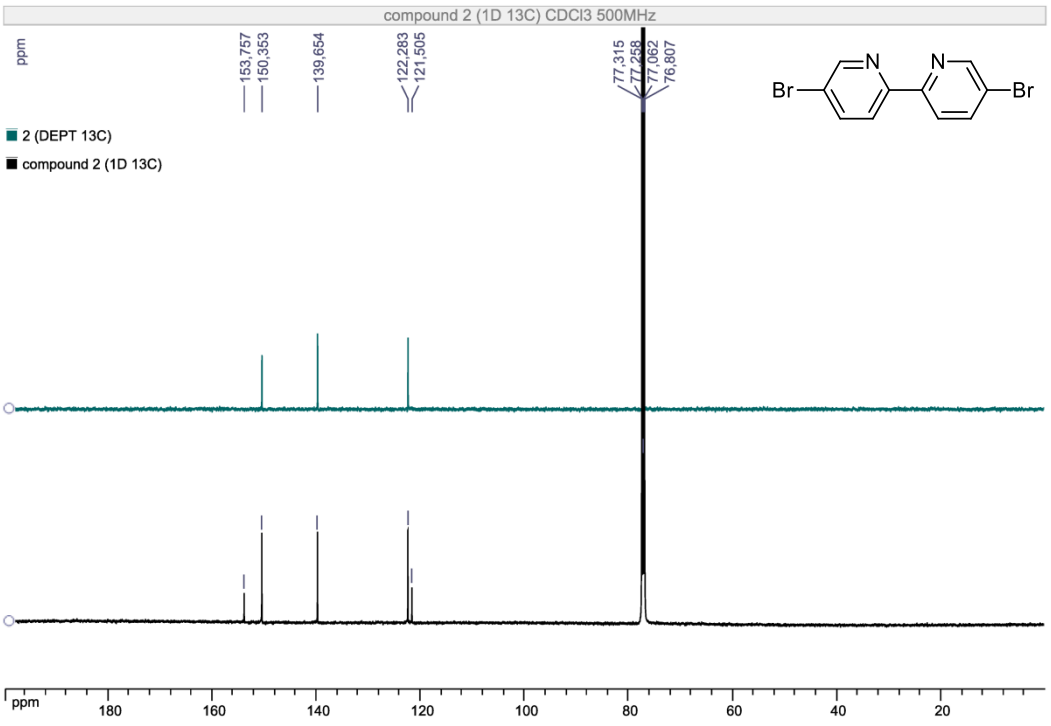
NMR spectra

Compound **2**

^{1}H NMR ($CDCl_3$, 500MHz)

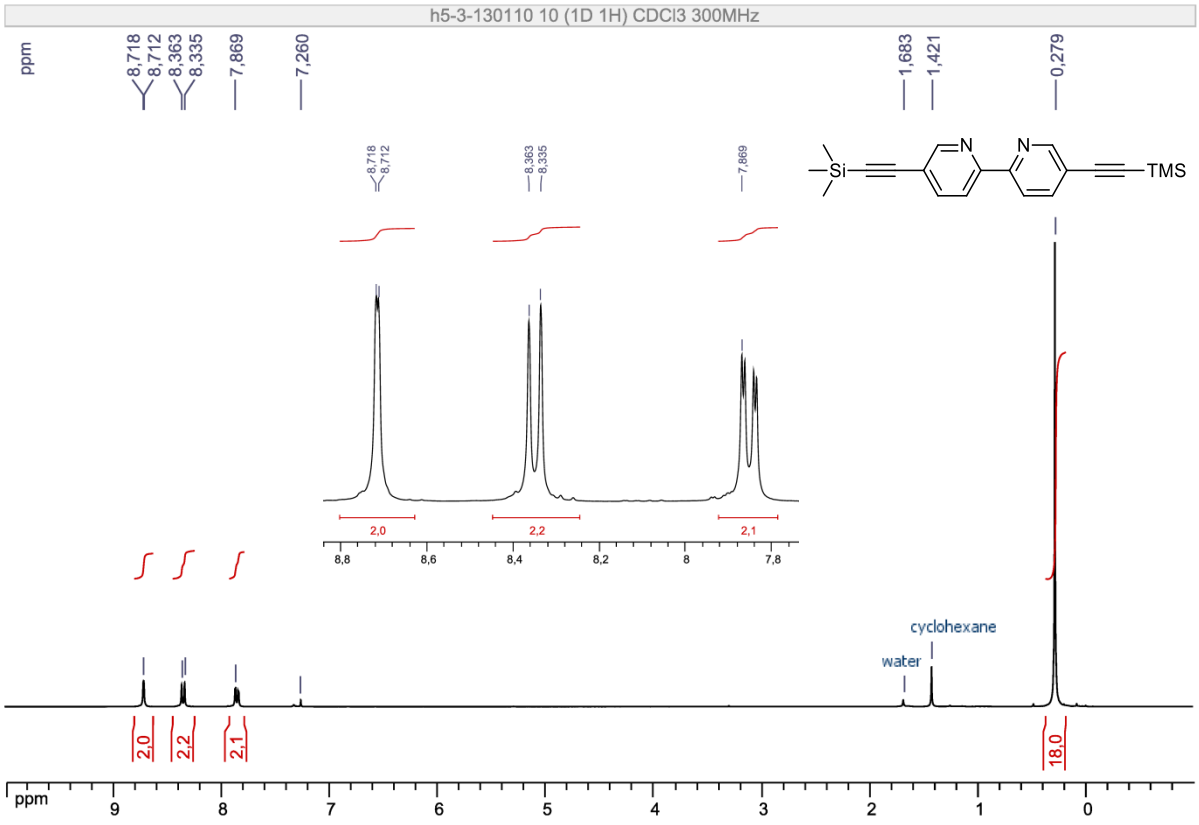


^{13}C NMR ($CDCl_3$, 125MHz)

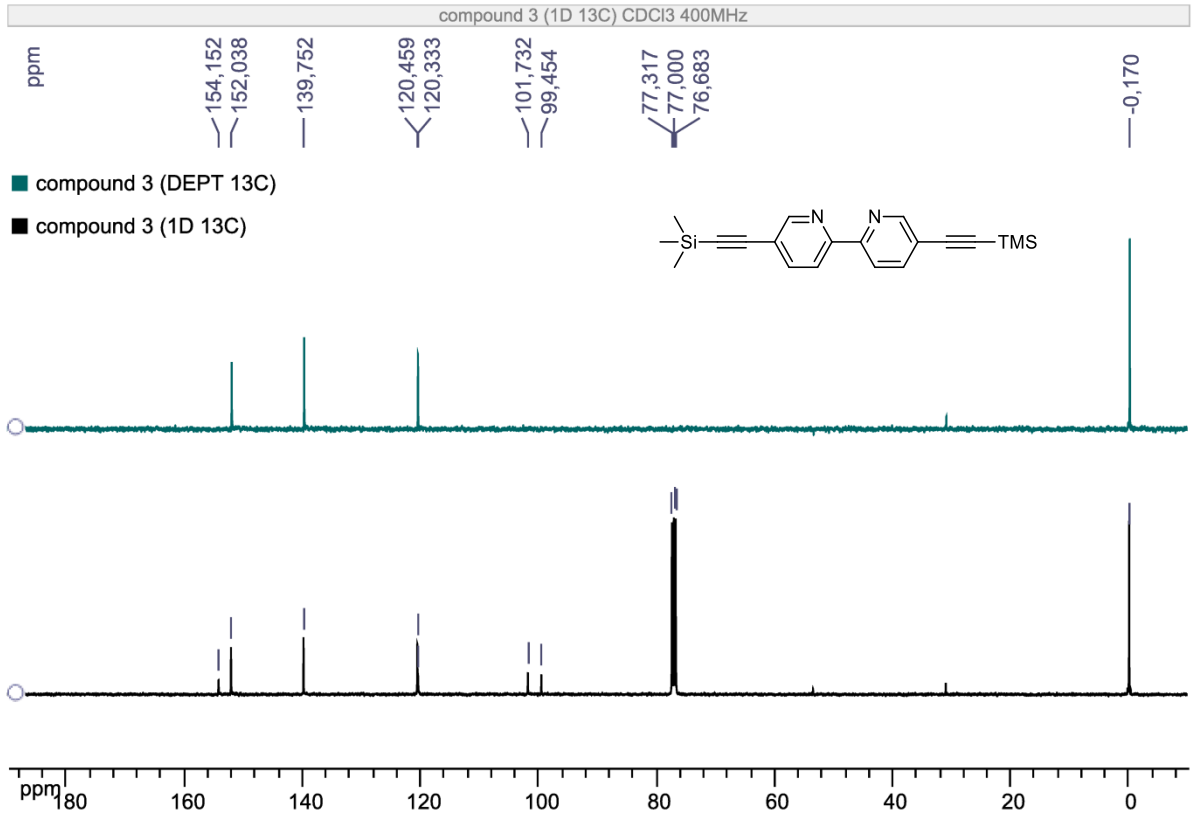


Compound **3**

^{1}H NMR ($CDCl_3$, 300MHz)

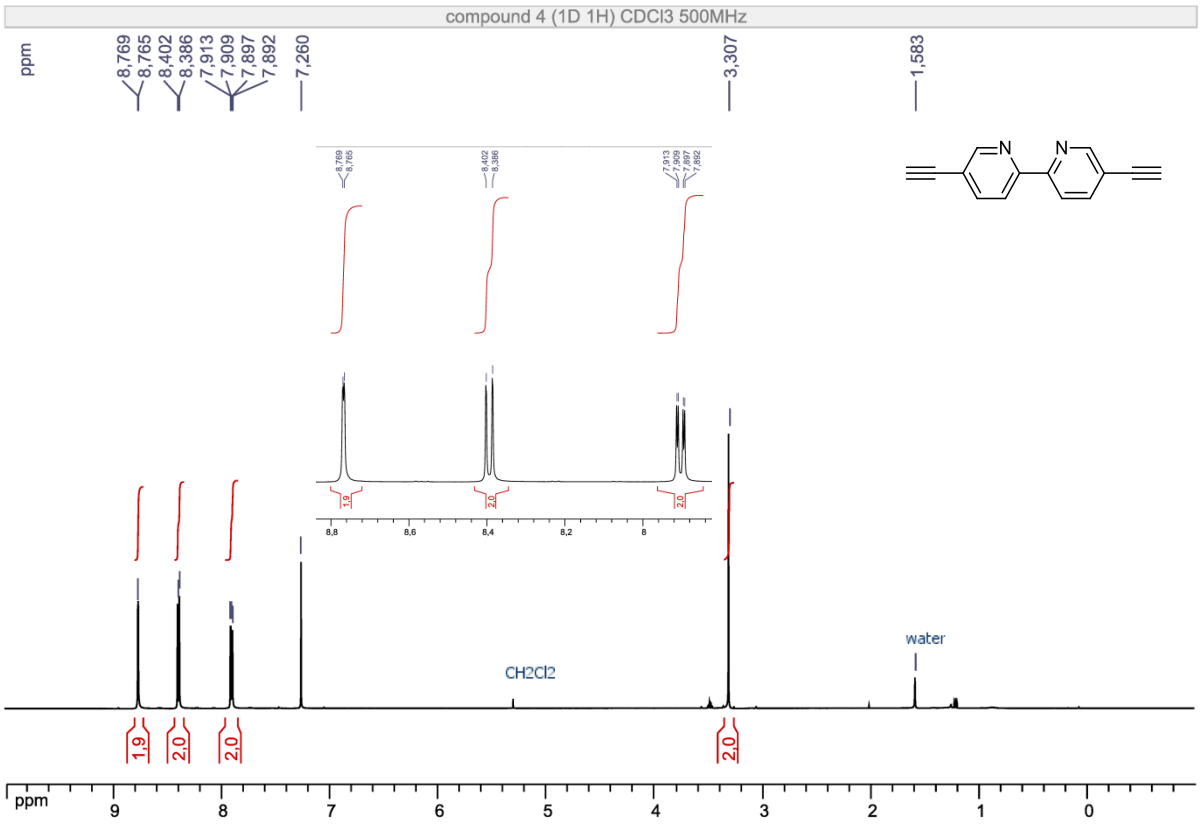


^{13}C NMR ($CDCl_3$, 100MHz)

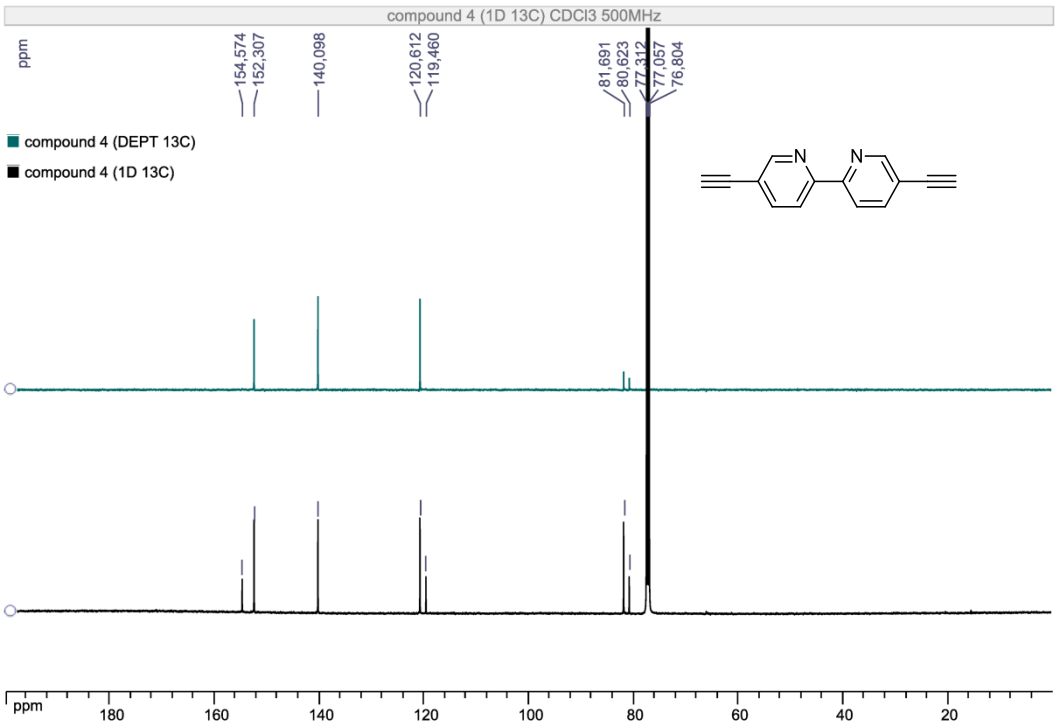


Compound **4**

^{1}H NMR ($CDCl_3$, 500MHz)

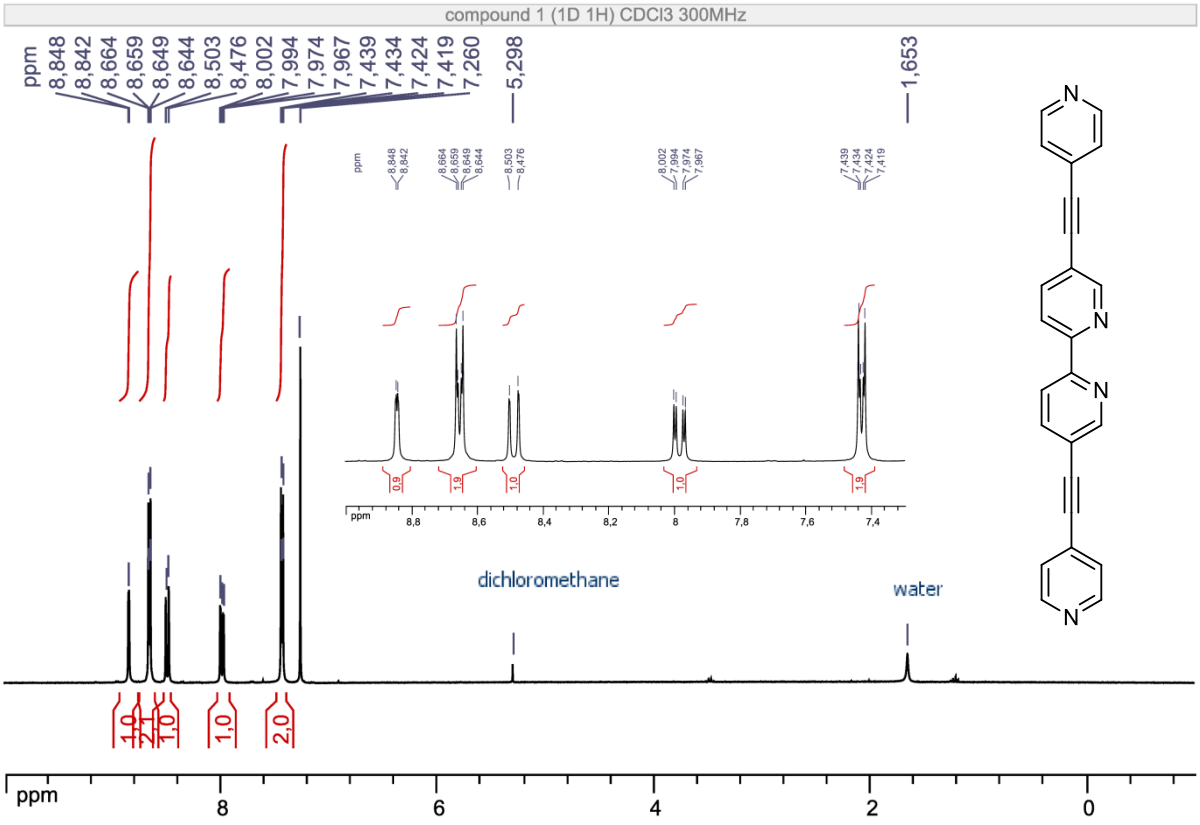


^{13}C NMR ($CDCl_3$, 125MHz)

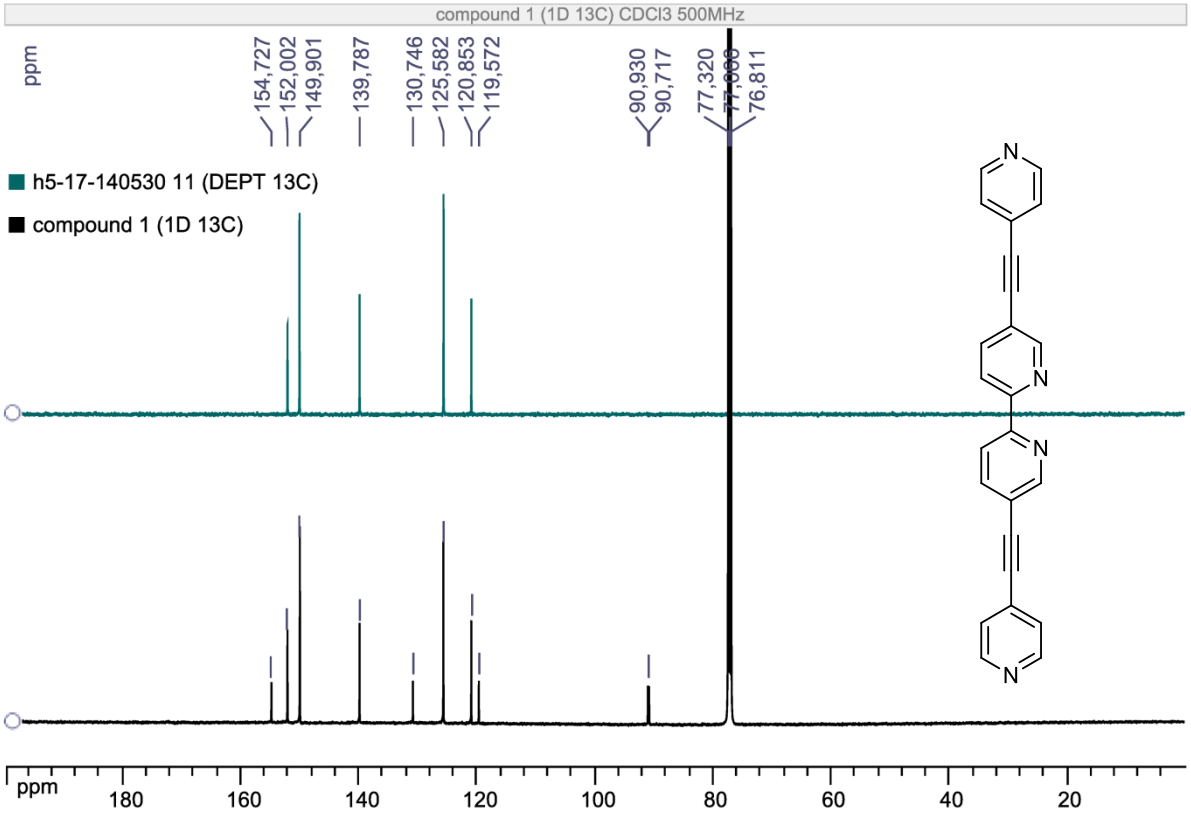


Compound **1**

^{1}H NMR ($CDCl_3$, 500MHz)

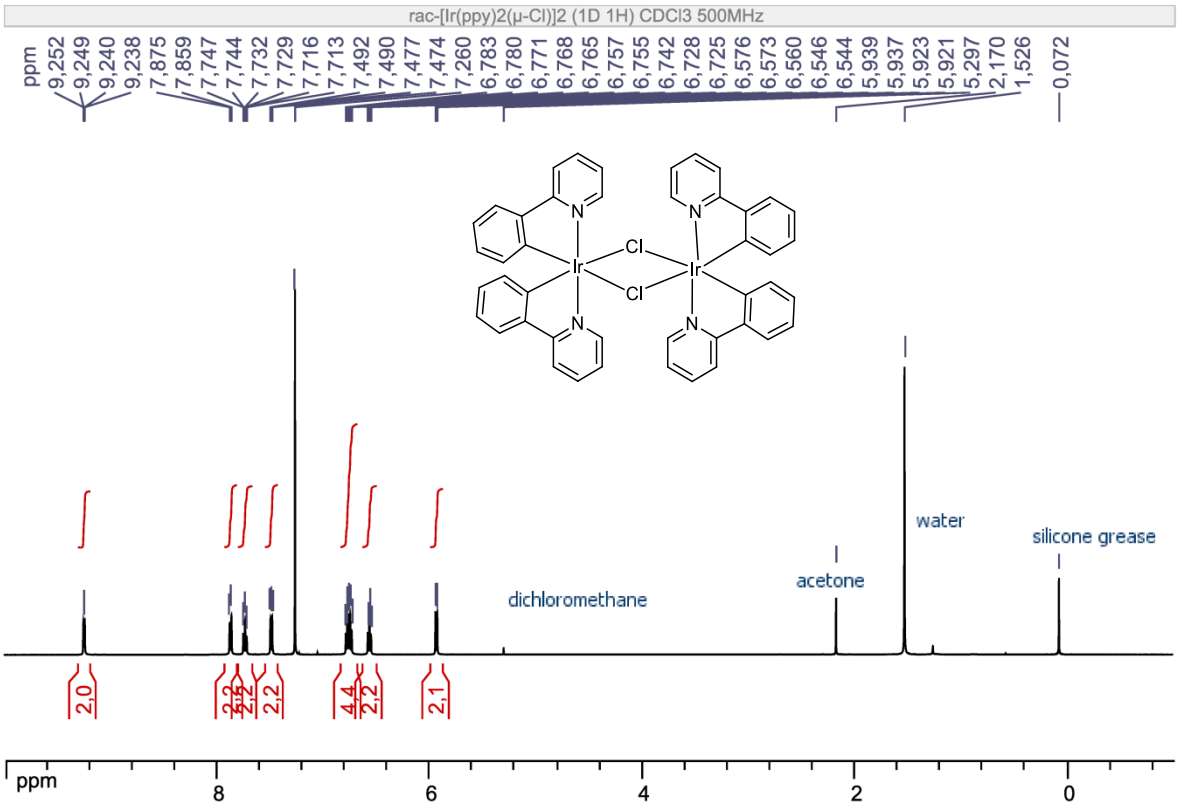


^{13}C NMR ($CDCl_3$, 125MHz)

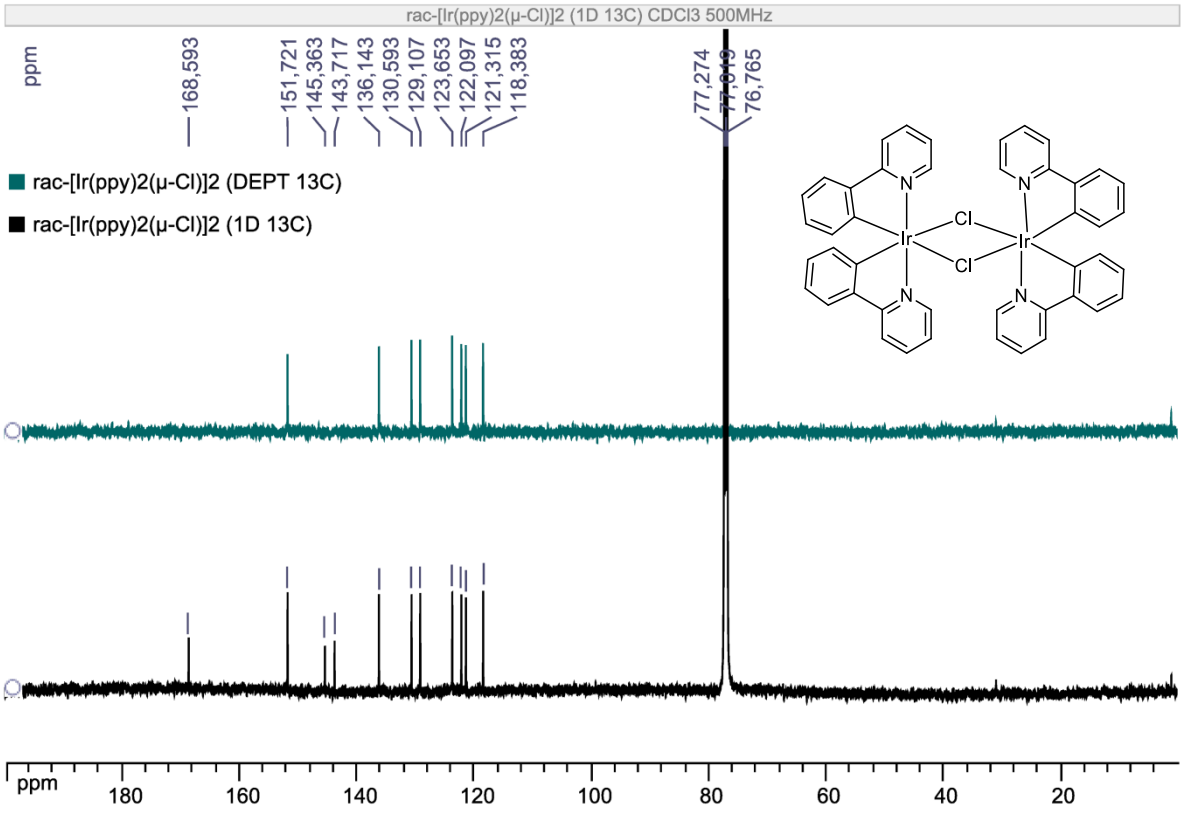


rac-$[Ir(ppy)_2(\mu\text{-}Cl)]_2$

^{1}H NMR ($CDCl_3$, 500MHz)

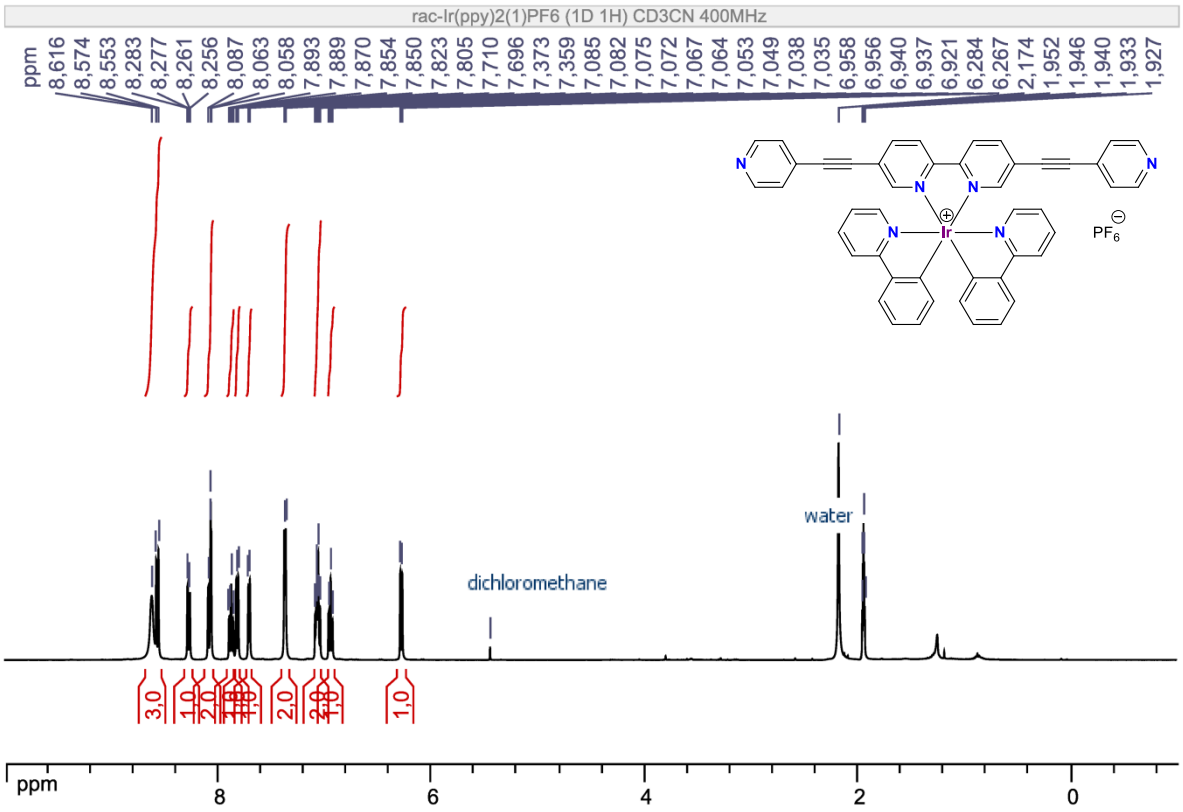


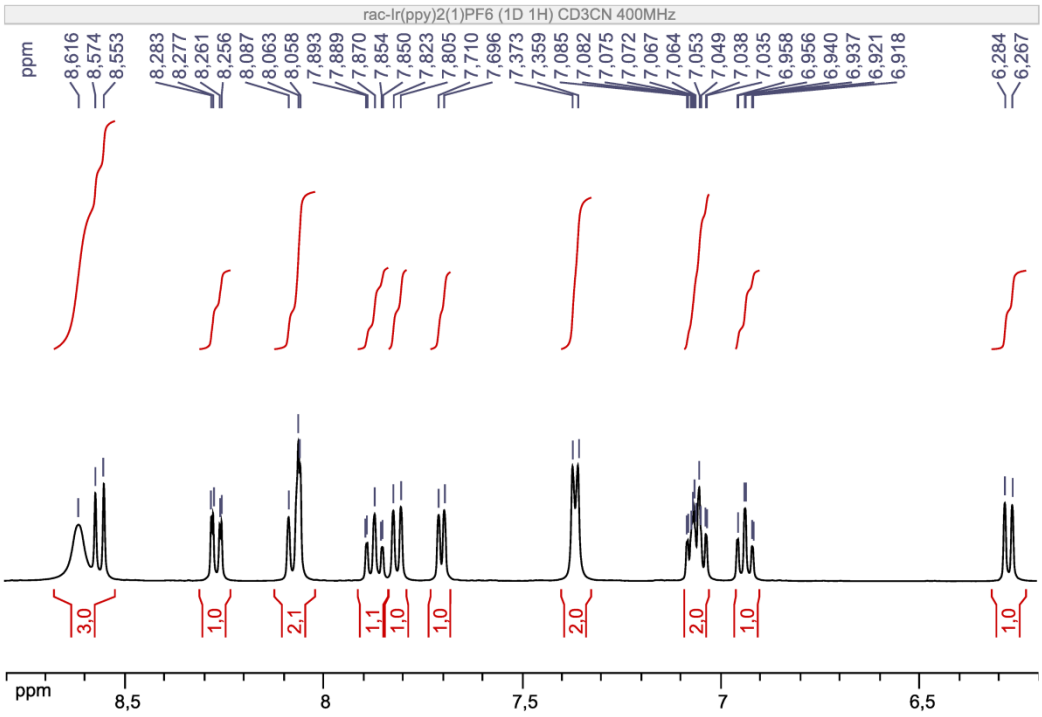
^{13}C NMR ($CDCl_3$, 500MHz)



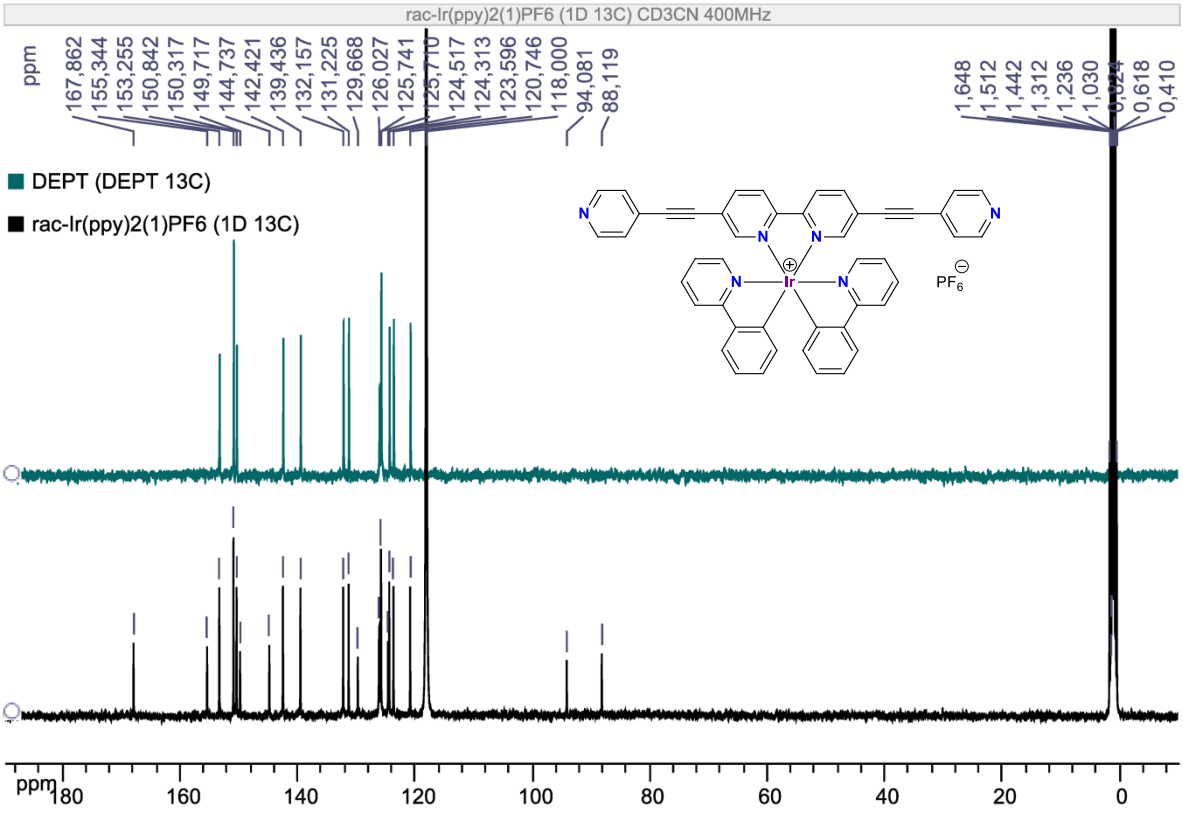
rac-[Ir(ppy)$_2$(**1**)][PF$_6$]

^{1}H NMR (CD$_3$CN, 400MHz)



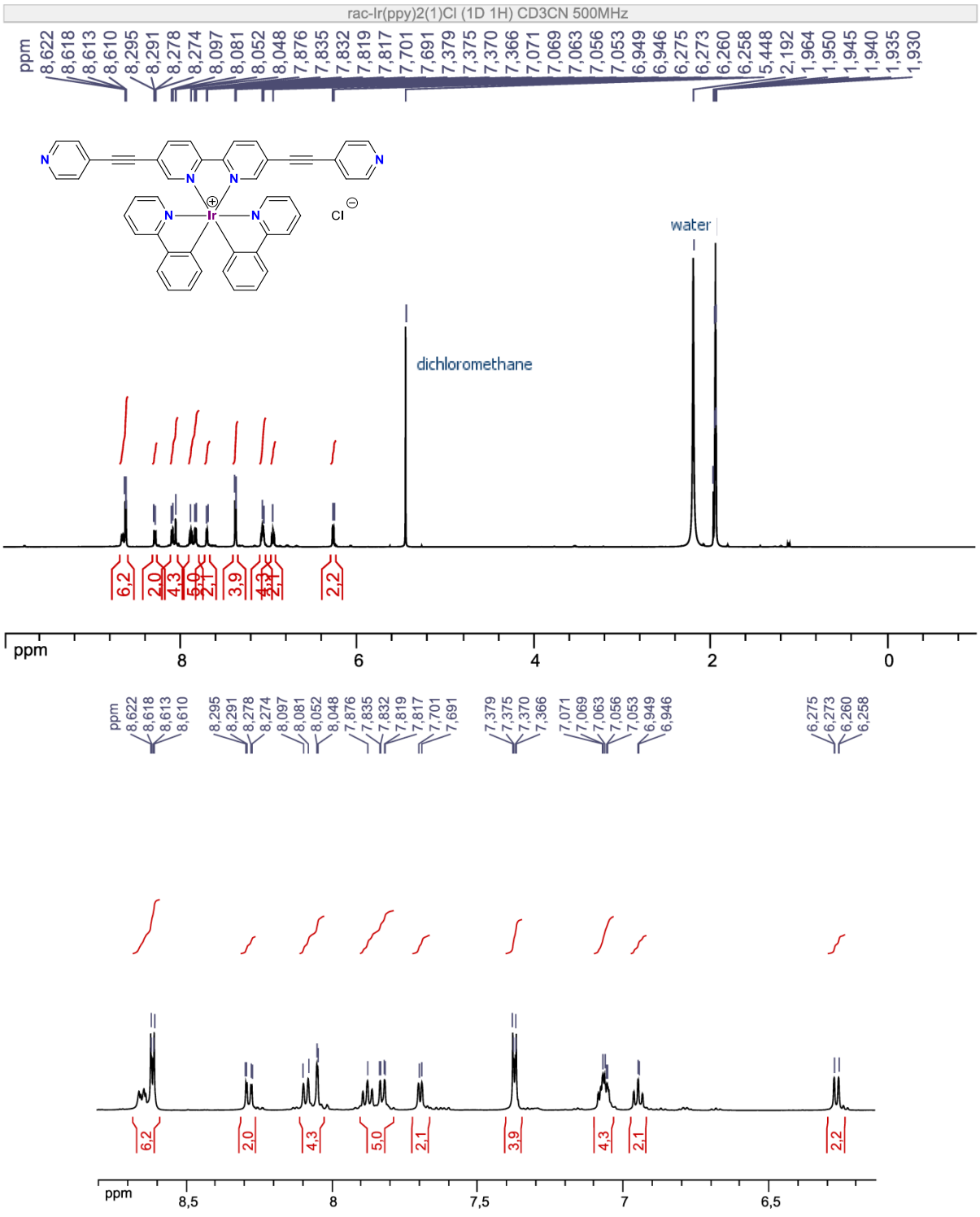


^{13}C NMR (CD_3CN, 100MHz)

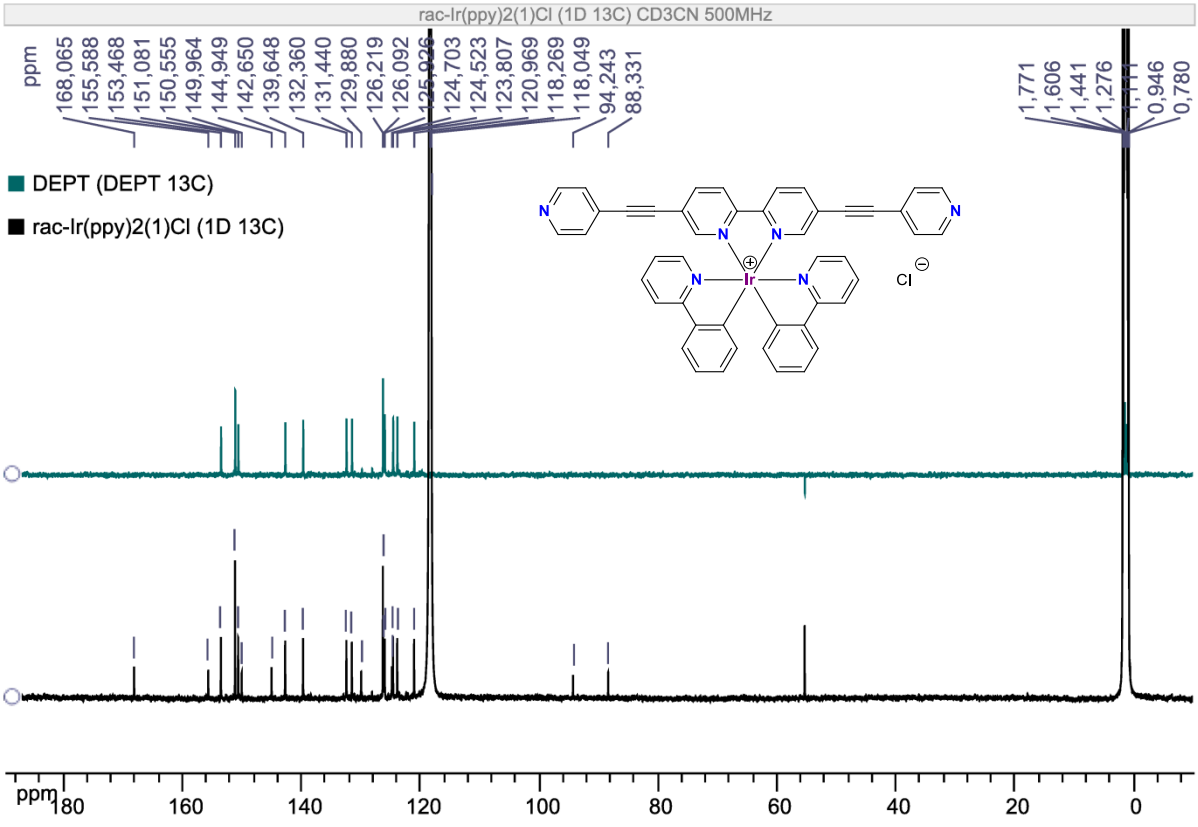


rac-[Ir(ppy)$_2$(**1**)][Cl]

^{1}H NMR (CD$_3$CN, 400MHz)



^{13}C NMR (CD_3CN, 100MHz)



Crystallographic data

Name	*rac*-[Ir(ppy)$_2$(**1**)][PF$_6$]	Δ-[Ir(ppy)$_2$(**1**)][Cl]	Λ-[Ir(ppy)$_2$(**1**)][Cl]	*rac*-[Ir(ppy)$_2$(**1**)]·[Cu(BF$_4$)$_2$]
Formula	$C_{46}H_{32}F_6IrN_6OP$	$C_{60}H_{48}ClIrN_6O$	$C_{60}H_{48}ClIrN_6O$	$C_{97}H_{68}B_2Cl_{12}CuF_{20}Ir_2N_{12}OP_2$
FW	1021.95	1096.69	1096.69	2754.53
Crystal system	Triclinic	Orthorhombic	orthorhombic	Monoclinic
Space group	P-1	P2(1)2(1)2	P 21 21 2	C2/c
a, Å	13.9900(3)	32.5454(6)	32.7712(7)	33.6718(17)
b, Å	15.4250(3)	12.2814(2)	12.3271(4)	33.6481(16)
c, Å	23.9686(7)	13.9420(2)	13.9638(4)	13.8979(6)
α, °	104.5710(10)	90	90	90
ß, °	106.4530(10)	90	90	110.2790(10)
γ, °	93.4910(10)	90	90	90
V, Å^3	4752.1(2)	5572.66(16)	5641.0(3)	14770.2(12)
Z	4	4	4	4
T, K	173(2)	173(2)	173(2)	173(2)
μ, mm^{-1}	2.906 mm^{-1}	2.487 mm^{-1}	2.457 mm^{-1}	2.242
Refls. coll.	24960	15818	15562	20368
Ind. Refls. (R_{int})	24960 (0.0210)	15815 (0.0345)	15257 (0.032)	20368 (0.0456)
R_1 (I>2σ(I))[a]	0.0421	0.0322	0.0337	0.0737
wR_2 (I>2σ(I))[a]	0.0964	0.0566	0.0659	0.1925
R_1 (all data)[a]	0.0722	0.0383	0.0427	0.1251
wR_2 (all data)[a]	0.1038	0.0569	0.0685	0.2082
GOF	1.004	1.098	0.923	1.043
Absolute structure parameter		0.008(4)	0.008(4)	

[a] $R_1 = \sum\big||F_0| - |F_c|\big|/\sum|F_0|$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum wF_0^4]^{1/2}$

Selected average bond lengths and angles for rac-[Ir(ppy)$_2$(1)][PF$_6$]:

Ir-C_{ppy} 2.007 Å, Ir-N_{ppy} 2.043 Å, Ir-N_{bpy} 2.143 Å, N_{ppy}-Ir-N_{ppy} 172.31°, N_{ppy}-Ir-C_{ppy} 80.25°, N_{bpy}-Ir-N_{bpy} 76.50°;

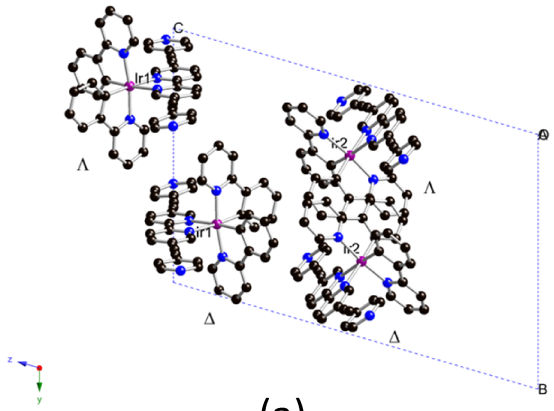
Selected average bond lengths and angles for Δ-[Ir(ppy)$_2$(1)][Cl] :

Ir-C_{ppy} 2.017 Å, Ir-N_{ppy} 2.053 Å, Ir-N_{bpy} 2.146 Å, N_{ppy}-Ir-N_{ppy} 172.11°, N_{ppy}-Ir-C_{ppy} 80.39°, N_{bpy}-Ir-N_{bpy} 76.53°;

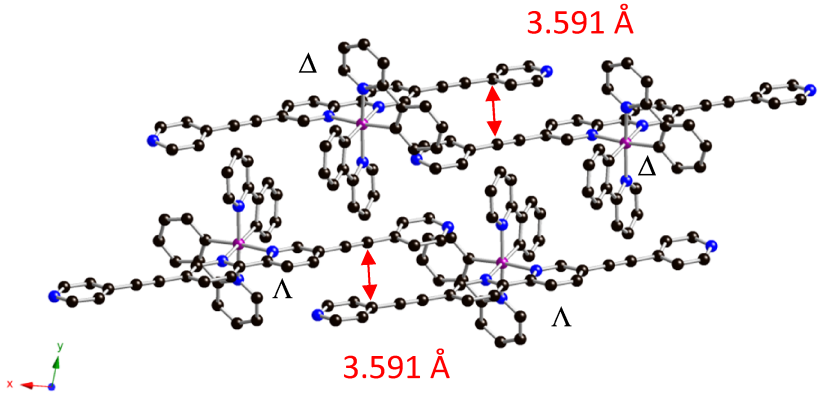
Selected average bond lengths and angles for Λ-[Ir(ppy)$_2$(1)][Cl] :

Ir-C_{ppy} 2.016 Å, Ir-N_{ppy} 2.053 Å, Ir-N_{bpy} 2.140 Å, N_{ppy}-Ir-N_{ppy} 171.98°, N_{ppy}-Ir-C_{ppy} 80.31°, N_{bpy}-Ir-N_{bpy} 76.57°.

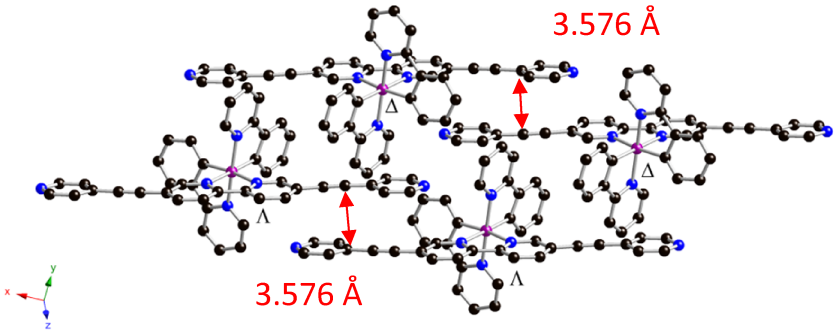
Crystal packing for rac-[Ir(ppy)$_2$(1)][PF$_6$] (solvent molecules, H atoms and PF_6 anions have been omitted for clarity) highlighting the π-π interactions within the lattice.



(a)



(b)

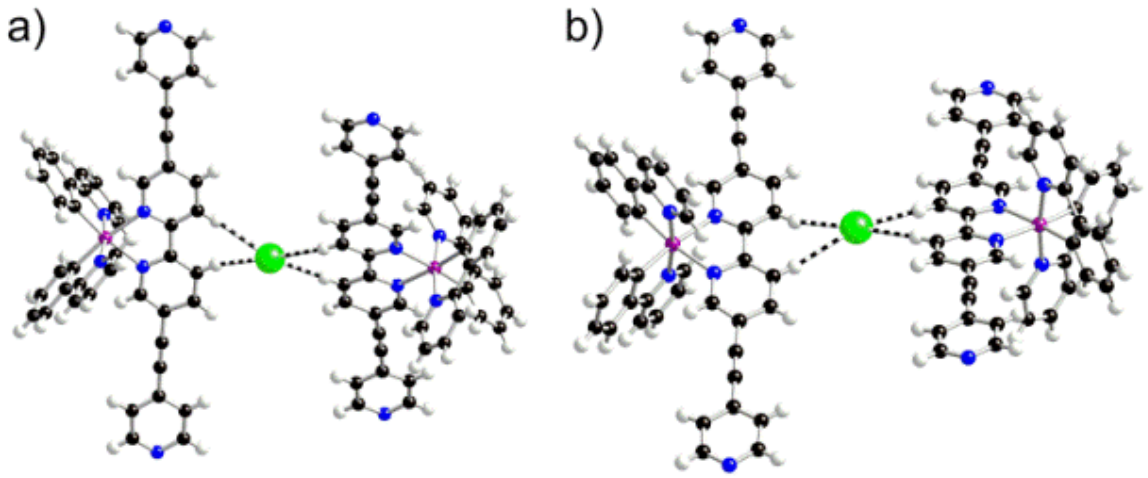


(c)

Within the crystal, two cristallographically non-equivalent Ir complexes are present labelled Ir1 and Ir2 respectively (a). The chirality of each center is indicated on the figure. π-π interactions between two substituted bpy ligand belonging either to two neighbouring Δ (or Λ) enantiomers with a shortest C-C distance of 3.591 Å and 3.576 Å for Ir 1 and Ir2 centers respectively (Figures b and c respectively) are observed.

Crystal structures of Δ-[Ir(ppy)$_2$(1)][Cl] (a) and Λ-[Ir(ppy)$_2$(1)][Cl] (b) highlighting the Hydrogen bonds between the chloride anion and the bipyridine units of the metallatecton.

Solvent molecules have been omitted for clarity. Only the H-bonds between the bipyridine ligand and one chloride ion Cl_1 are represented. The other chloride ion Cl_2 is not shown for clarity.

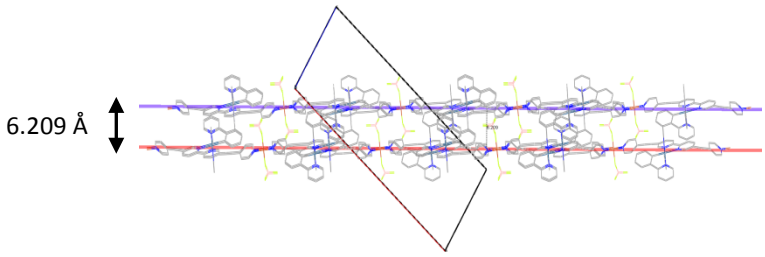


It should be noted that no suitable single crystals for X-Ray diffraction could be obtained for the PF_6 salt. This may be related to the non-innocent role played by the chloride ion in the crystal phase, in particular through hydrogen bonds with the bipyridine ligand bridging thus two Iridium complexes. Such observation has already been reported by E. Constable *et al.*[5] for similar Ir(III) complexes in the solid state and in solution.

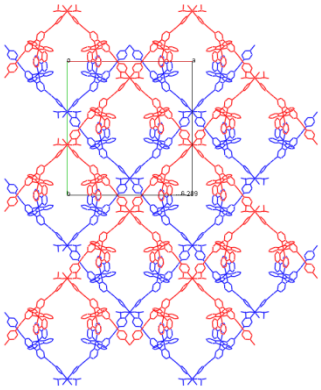
One of the two anions present in the lattice is chelated by the bipyridine ligand through hydrogen bonds bridging thus two Iridium complexes. The other chloride ion is disordered over two positions and is also hydrogen-bonded to H atoms of one ppy ligand, one toluene molecule and one terminal pyridine unit of the bpy ligand.[‡] Such observation has already been reported by E. Constable *et al.*[5] for similar Ir(III) complexes in the solid state and in solution. As a matter of fact, the ^{1}H NMR spectra of [Ir(ppy)$_2$(**1**)][PF_6] and [Ir(ppy)$_2$(**1**)][Cl] in CD_3CN are almost similar except for the signal of proton H_3 which exhibits a downfield shift of *ca.* 0.08 ppm when going from the PF_6 salt to the Cl salt (see NMR above in the synthesis part).

Crystal packing for the coordination network rac-Ir(ppy)$_2$(1)·Cu(BF$_4$)$_2$ (solvent molecules, H atoms and PF_6 anions have been omitted for clarity; the Λ enantiomer is depicted in red while the Δ enantiomer is coloured in blue)

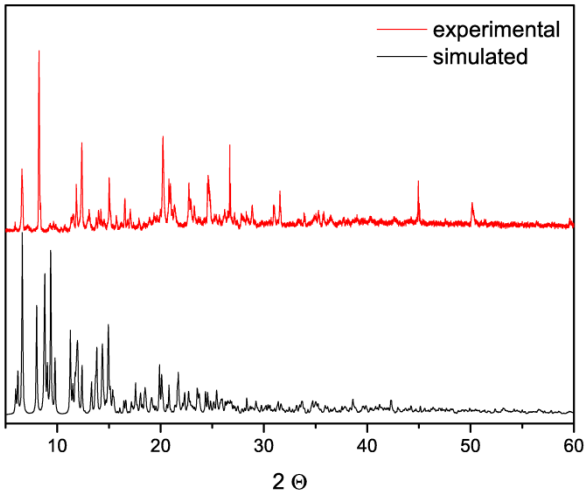
View along the b axis



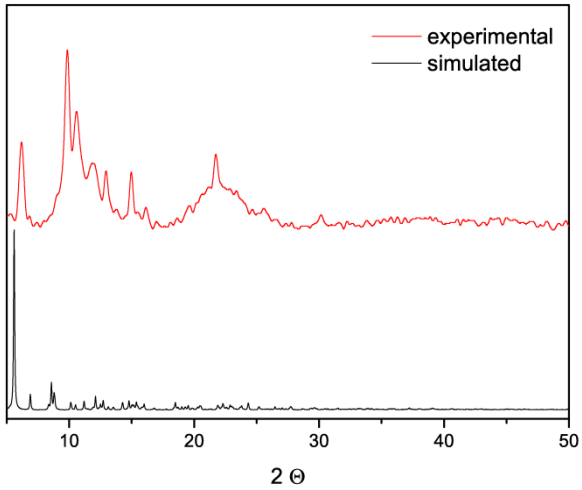
View along the c axis



PXRD patterns



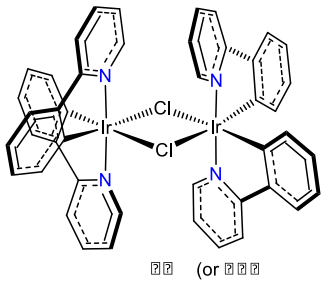
PXRD patterns simulated from single-crystal data (black) and experimentally obtained on crystalline material (red) for *rac*-[Ir(ppy)$_2$(**1**)][PF$_6$].

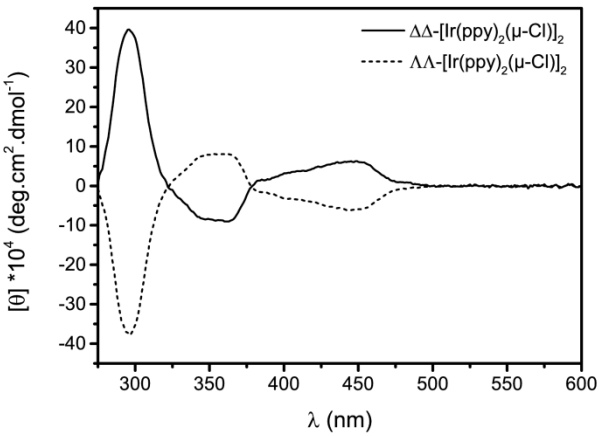


PXRD patterns simulated from single-crystal data (black) and experimentally obtained on crystalline material after 30 minutes in air (red) for the coordination network *rac*-Ir(ppy)$_2$(**1**)·Cu(BF$_4$)$_2$.

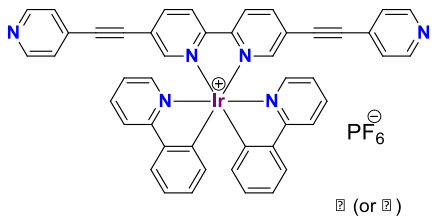
CD spectra

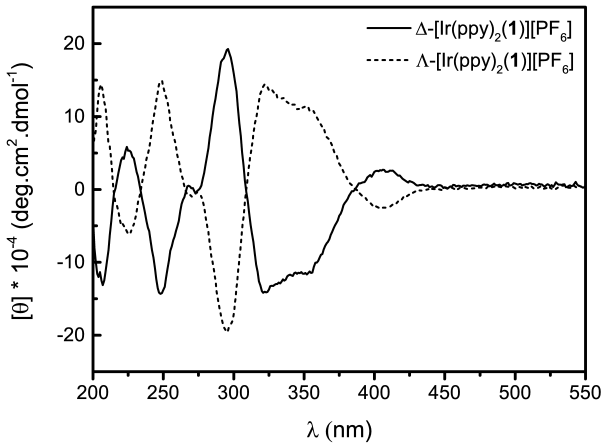
CD spectra of ΔΔ- and ΛΛ-[Ir(ppy)$_2$(μ-Cl)]$_2$ (293K, 20μM) in CH_2Cl_2



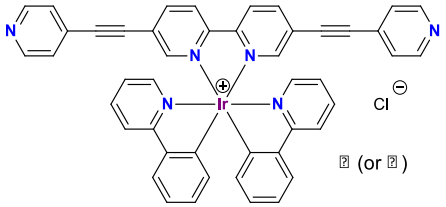


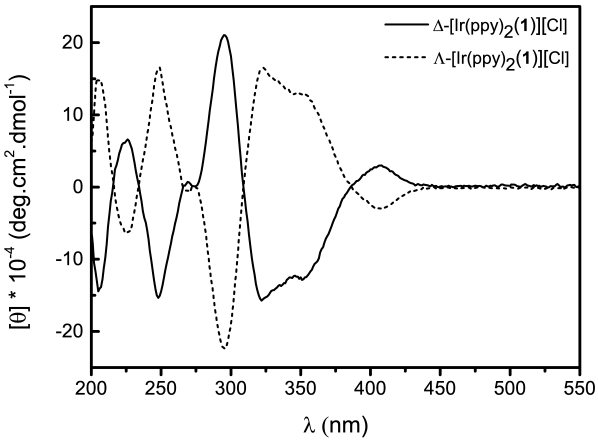
CD spectra of Δ- and Λ-[Ir(ppy)$_2$(**1**)][PF_6] (293K, 10μM) in CH_3CN





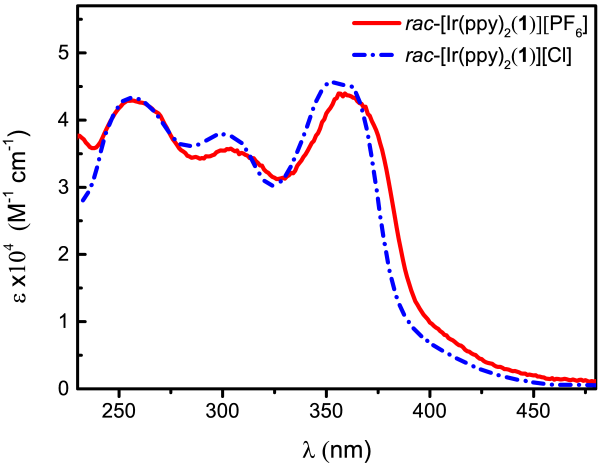
CD spectra of Δ- and Λ-[Ir(ppy)$_2$(**1**)][Cl] (293K, 10μM) in CH_3CN



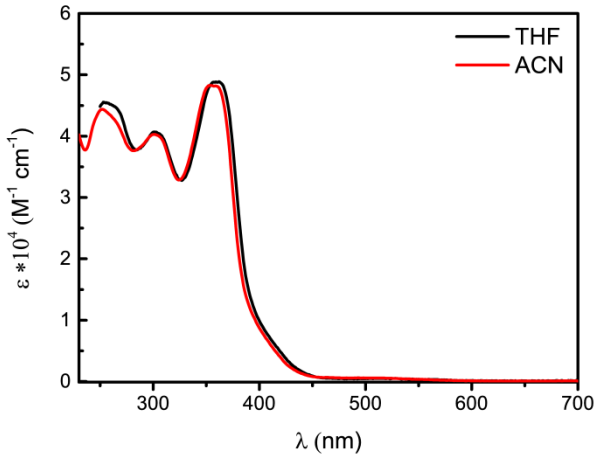


Absorption and Emission spectra in solution

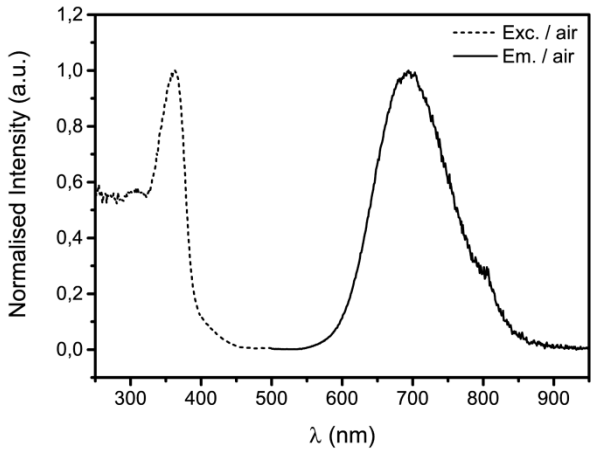
Absorption spectra of *rac*-[Ir(ppy)$_2$(**1**)][PF$_6$] and *rac*-[Ir(ppy)$_2$(**1**)][Cl] in CH_3CN.



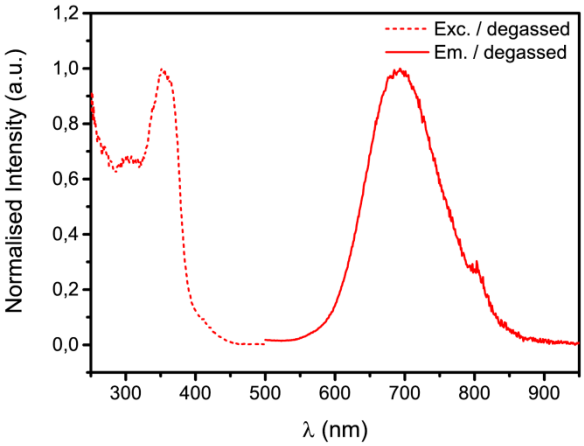
Absorption spectra of *rac*-[Ir(ppy)$_2$(**1**)][PF$_6$] in CH_3CN (red) and in THF (black).



Excitation (dashed, λ_{em} = 694 nm) and emission (solid, λ_{exc} = 360 nm) spectra of *rac*-[Ir(ppy)$_2$(**1**)][PF$_6$] in aerated THF.



Excitation (dashed, λ_{em} = 694 nm) and emission (solid, λ_{exc} = 360 nm) spectra of *rac*-[Ir(ppy)$_2$(**1**)][PF$_6$] in degassed THF.



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