Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Substituent influence in phenanthroline-derived ancillary ligands on the excited state nature of novel cationic Ir(III) complexes

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Experimental Section

All reagents and solvents commercially available were used as received, unless otherwise specified. Iridium dimers ($[Ir(ppy)_2(\mu Cl)]_2$ and $[Ir(F_2\text{-}ppy)_2(\mu Cl)]_2$.) were synthesized according to previous literature procedures.[1, 2] NMR spectra were recorded on NMR Bruker AV 400. Chemical shifts are given in parts per million relative to TMS [^{1}H and ^{13}C, $\delta(SiMe_4) = 0$] or an external standard [$\delta(CFCl_3) = 0$ for ^{19}F NMR]. Most NMR assignments were supported by additional 2D experiments. HR-MS(ESI) experiments were carried out using a Thermo Scientific Exactive Plus Orbitrap Spectrometer. FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel. Column chromatography was carried out using Merck silica gel 60 (70–230 mesh).

UV-Vis spectra were registered using a Shimadzu UV-Vis-NIR 3101 PC spectrophotometer. Photoluminescence spectra at 77 K were taken on an *Edinburgh Instrument* spectrofluorimeter equipped with a 900 W Xe arc lamp as excitation source, a photomultiplier tube and an InGaAs detector for the visible and the NIR detection, respectively. Dichloromethane solutions of the complexes were previously degassed with N_2 for approximately 20 min. A cryostat mounted on the spectrofluorimeter was used.

Cyclic voltammograms were obtained using a PalmSens 3 Instruments Potentiostat in a three-electrode cell configuration with a platinum disc working electrode having a geometric area of 0.02 cm^2, a saturated Ag/AgCl reference electrode and a platinum wire counter electrode. All electrochemical measurements were carried out in anhydrous acetonitrile solutions of Ir(III) complexes (1 mM) with 0.1 M of $TBAPF_6$ as supporting electrolyte at a scan rate of 0.1 Vs^{-1}. Nanosecond transient measurements were performed with a custom laser spectrometer comprised of a *Continuum Surelite II* Nd:YAG laser (FWHM = 6-8 ns) with frequency doubled, (532 nm, 330 mJ) or tripled, (355 nm, 160 mJ) option, an *Applied Photophysics* xenon light source including a mod. 720 150 W lamp housing, a mod. 620 power controlled lamp supply and a mod. 03-102 arc

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[1] H. J. Bolink, L. Cappelli, S. Cheylan, E. Coronado, R. D. Costa, N. Lardies, M. K. Nazeeruddin and E. Orti, *Journal of Materials Chemistry*, **2007**, *17*, 5032-5041.

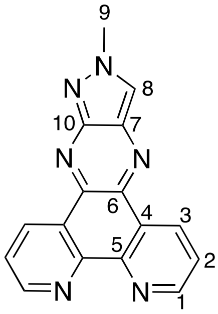
[2] Q. Zhao, T. Cao, F. Li, X. Li, H. Jing, T. Yi and C. Huang, *Organometallics*, **2007**, *26*, 2077-2081.

lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light transmitted or emitted by the sample was focused onto the entrance slit of a 300 mm focal length *Acton SpectraPro 2300i* triple grating, flat field, double exit monochromator equipped with a photomultiplier detector (*Hamamatsu R3896*). Signals from the photomultiplier (kinetic traces) were processed by means of a *LeCroy 9360* (600 MHz, 5 Gs/s) digital oscilloscope.

Synthesis and Characterization of Compounds.

1-methyl-1*H*-pyrazolo[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline **(L1)**

1,10-phenanthroline-5,6-dione (200 mg, 0.95 mmol) was added to a solution of 1-methyl-1*H*-pyrazole-3,4-diamine (2HCl) (176 mg, 0.95 mmol) in absolute ethanol (100 mL). The mixture was refluxed for 1h with vigorous stirring. The resulting solution was cooled to room temperature, filtered and the isolated solid was washed with cold ethanol. The filtrate was then diluted with water and extracted with CH_2Cl_2. The solvent was evaporated under vacuum to dryness. The resulting solid was dissolved in CH_2Cl_2 and precipitated it with dry diethyl ether. **L1** was isolated as an orange solid in 85 % yield (231 mg, 0.81 mmol).



^{1}H NMR (400 MHz, DMSO-d$_6$, 298 K): δ/ppm = 9.53 (d, *J* = 8.1 Hz, 2H, H1), 9.45 (d, *J* = 8.1 Hz, 2H, H3), 8.99 (s, 1H, H8), 7.90 (broad, 2H, H2), 4.47 (s, 3H, H9).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$, 298 K): δ/ppm = 154.8 (C10), 150.8 (C6), 140.8 (C5), 133.0 (C1), 132.4 (C3), 131.5 (C7), 127.35 (C4), 125.2 (C8), 123.8 (C2), 41.4 (C9).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, DMSO-d$_6$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.99 / 131.5 (H8 / C7), 4.47 / 125.2 (H9 / C8).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, DMSO-d$_6$, 298 K): δ (^{1}H) / δ (^{13}C) = 9.53 / 133.0 (H1 / C1), 9.45 / 132.4 (H3 / C3), 8.99 / 125.2 (H8 / C8), 7.90 / 123.8 (H2 / C2), 4.47 / 41.4 (H9 / C9).

COSY (400 MHz / 400 MHz, DMSO-d$_6$, 298 K): δ (^{1}H) / δ (^{1}H) = 9.53 / 7.90 (H1 / H2), 9.45 / 7.90 (H3 / H2).

HR-MS(ESI): ($C_{16}H_{11}N_6$ $[M + H]^+$) Calc: 287.1045 ; Found: 287.1027

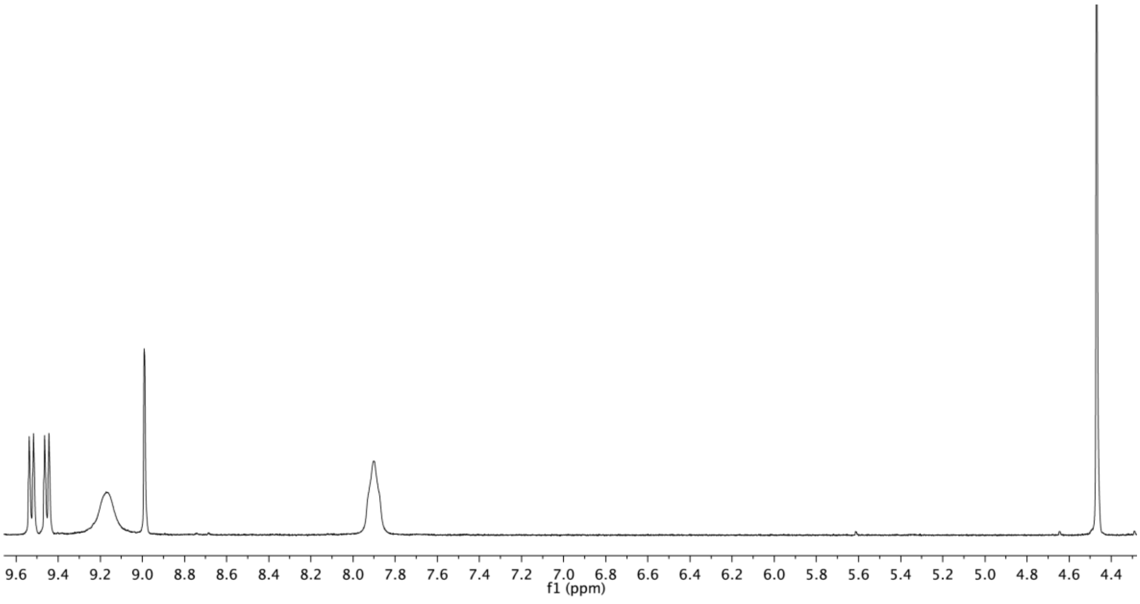


Figure S1: ^1H NMR (400 MHz, DMSO-d_6, 298 K)

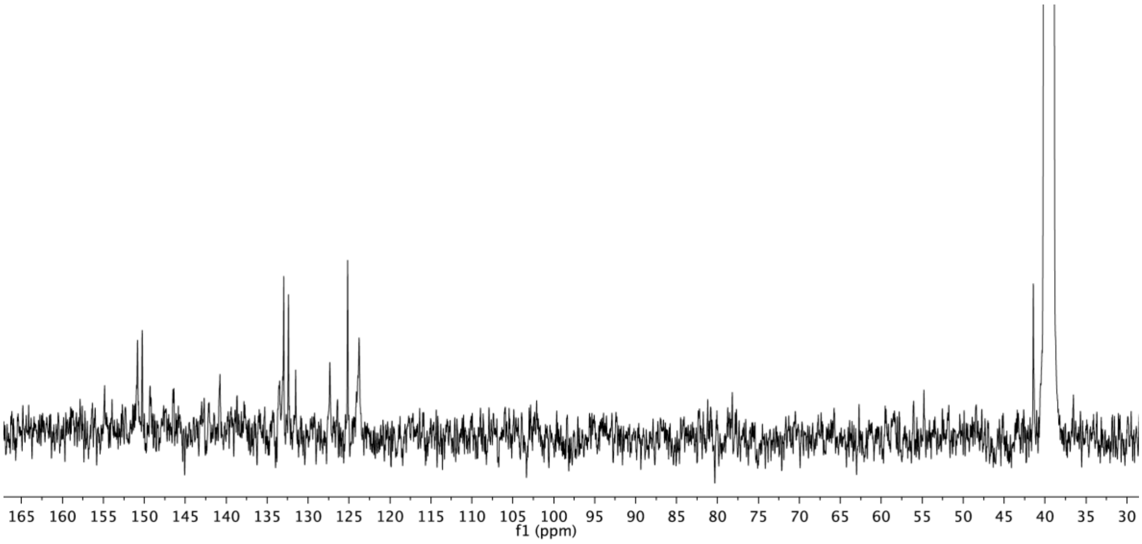
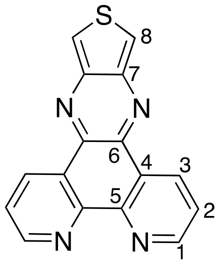


Figure S2: $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 298 K)

Thieno[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline **(L2)**

1,10-phenanthroline-5,6-dione (200 mg, 0.95 mmol) was added to a solution of thiophene-3,4-diamine (2HCl) (178 mg, 0.95 mmol) in absolute ethanol (100 mL). The mixture was refluxed for 1h with vigorous stirring. The resulting solution was cooled to room temperature, filtered and the isolated solid was washed with cold ethanol. The filtrate was then diluted with water and extracted with CH_2Cl_2. The solvent was evaporated under vacuum to dryness. The resulting solid was dissolved in CH_2Cl_2 and precipitated it with dry diethyl ether. **L2** was isolated as an orange solid in 67 % yield (184 mg, 0.63 mmol).



^{1}H NMR (400 MHz, DMSO-d$_6$, 298 K): δ/ppm = 9.44 (d, *J* = 8.1 Hz, 2H, H1), 9.20 (d, *J* = 4.5 Hz, 2H, H3), 8.28 (s, 2H, H8), 7.71 (dd, *J* = 4.5 Hz / 8.1 Hz, 2H, H2).

^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$, 298 K): δ/ppm = 152.8 (C3), 148.9 (C6), 142.6 (C7), 141.6 (C5), 133.9 (C1), 128.2 (C4), 124.4 (C2), 117.4 (C8).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, DMSO-d$_6$, 298 K): δ (^{1}H) / δ (^{13}C) = 9.44 / 152.8 (H1 / C3), 9.20 / 133.9 (H3 / C1), 8.28 / 142.6 (H8 / C7), 7.71 / 128.2 (H2 / C4).

^{1}H, ^{13}C-HMQC (400 MHz / 100 MHz, DMSO-d$_6$, 298 K): δ (^{1}H) / δ (^{13}C) = 9.44 / 133.9 (H1 / C1), 9.20 / 152.8 (H3 / C3), 8.28 / 117.4 (H8 / C8), 7.71 / 124.4 (H2 / C2).

COSY (400 MHz / 400 MHz, DMSO-d$_6$, 298 K): δ (^{1}H) / δ (^{1}H) = 9.44 / 7.71 (H1 / H2), 9.20 / 7.71 (H3 / H2).

HR-MS(ESI): ($C_{16}H_9N_4S$ $[M + H]^+$) Calc: 289.0548; Found: 289.1274.

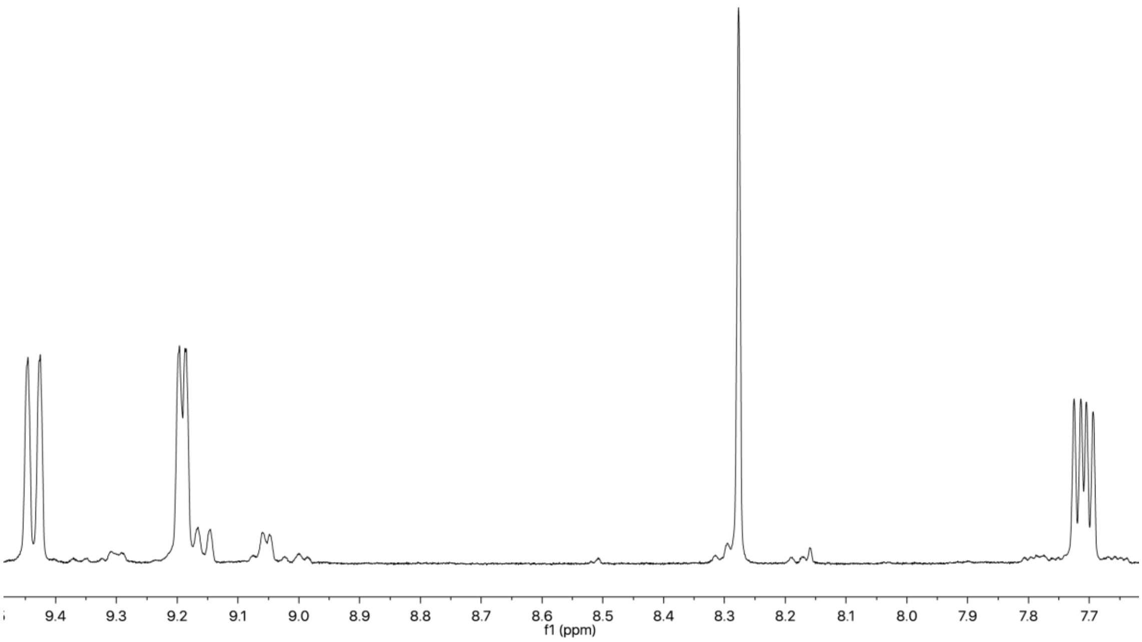


Figure S3: ^{1}H NMR (400 MHz, DMSO-d$_6$, 298 K)

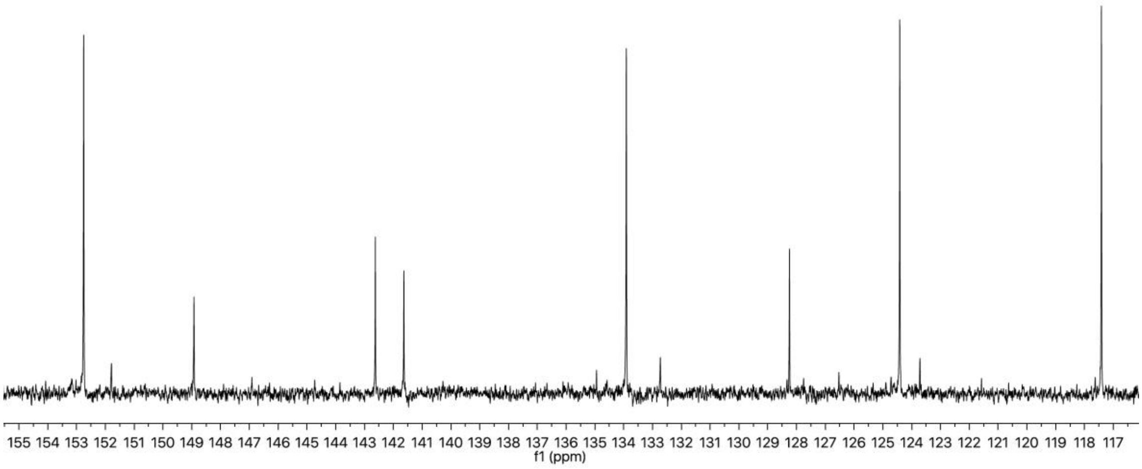
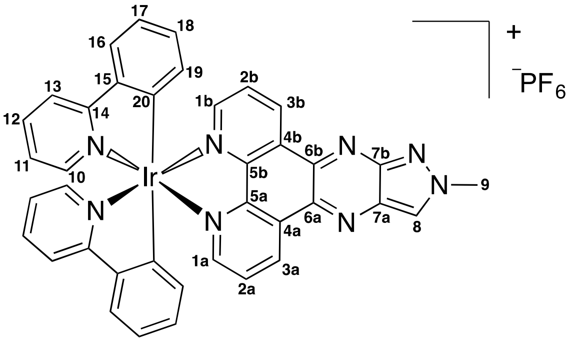


Figure S4: ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$, 298 K)

[(1-methyl-1*H*-pyrazolo[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline**)bis(2-phenyl pyridine)Ir(III)]PF_6. (C1)**

A solution of 1-methyl-1*H*-pyrazolo[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline (**L1**) (100 mg, 0.35 mmol) in acetonitrile was added dropwise to a solution of $[Ir(2\text{-phenylpyridine})_2]_2$-μ-$Cl_2$ (187 mg, 0.17 mmol) in MeOH/CH_2Cl_2 (1:3). The mixture was stirred and refluxed for 12 h under nitrogen atmosphere in darkness. Then, the volatiles were removed under vacuum and 500 mL of water was added to the crude product. The mixture was filtered and 2 equivalents of KPF_6 were added to the obtained solution, obtaining a yellow-orange precipitate. This solid was filtered and washed with water, dried and re-crystallized through CH_2Cl_2/diethyl ether diffusion, obtaining **C1** as yellow crystalline material in 71 % yield (112 mg, 0.17 mmol).



^{1}H NMR (400 MHz, Acetone-d_6, 298 K): δ/ppm = 9.77 (d, *J* = 8.1 Hz, 1H, H3a), 9.71 (d, *J* = 8.1 Hz, 1H, H3b), 9.16 (s, 1H, H8), 8.48 (dd, *J* = 5.1 Hz, 2H, H1a, H1b), 8.26 (d, *J* = 8.1 Hz, 2H, H10), 8.16 (td, *J* = 5.3 Hz / 8.1 Hz, 2H, H2a, H2b), 7.94 (m, 4H, H11, H17), 7.88 (d, *J* = 5.8 Hz, 2H, H16), 7.09 (t, *J* = 7.5 Hz, 2H, H12), 7.00 (m, 4H, H13, H18), 6.46 (d, *J* = 7.5 Hz, 2H, H19), 4.61 (s, 3H, H9).

^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6, 298 K): δ/ppm = 168.4 (C14), 153.1 (C1a), 152.6 (C1b), 151.0 (C16), 150.8 (C20), 150.5 (C5a), 150.3 (C5b), 149.4 (C7b), 145.1 (C15), 140.5 (C6b), 139.6 (C17), 138.3 (C6a), 135.5 (C3a), 134.9 (C3b), 133.6 (C4a, C4b), 132.6 (C19), 131.9 (C7a), 131.2 (C13), 128.8 (C2a, C2b), 127.1 (C8), 125.8 (C11), 124.6 (C18), 123.5 (C12), 120.7 (C10), 43.2 (C9).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.77 / 153.1, 150.5, 138.3 (H3a / C1a, C5a, C6a), 9.71 / 152.6, 150.3, 140.5 (H3b / C1b, C5b, C6b), 9.16 / 149.4, 131.9 (H8 / C7b, C7a), 8.48 / 128.8 (H1a-H1b / C2a-C2b), 8.26 / 168.4 (H10 / C14), 8.16 / 153.1, 152.6, 133.6 (H2a-H2b / C1a, C1b, C4a-C4b), 6.46 / 145.1 (H19 / C15), 4.61 / 127.1 (H9 / C8).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.77 / 135.5 (H3a / C3a), 9.71 / 134.9 (H3b / C3b), 9.16 / 127.1 (H8 / C8), 8.48 / 153.1 (H1a-H1b / C1a), 8.48 / 152.6 (H1a-H1b / C1b), 8.26 / 120.7 (H10 / C10), 8.16 / 128.8 (H2a-H2b / C2a-C2b), 7.94 / 125.8 (H11 / C11), 7.94 / 139.6 (H17 / C17), 7.88 / 150.9 (H16 / C16), 7.09 / 123.5 (H12 / C12), 7.00 / 131.2 (H13 / C13), 7.00 / 124.6 (H18 / C18), 6.46 / 132.6 (H19 / C19), 4.61 / 43.2 (H9 / C9).

COSY (400 MHz / 400 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{1}H) = 9.77 / 8.16 (H3a / H2a-H2b), 9.71 / 8.16 (H3b / H2a-H2b), 8.48 / 8.16 (H1a-H1b / H2a-H2b), 8.26 / 7.94 (H10 / H11), 7.94 / 7.88 (H17 / H16), 7.94 / 7.09 (H11 / H12), 7.94 / 7.00 (H17 / H18), 7.09 / 7.00 (H12 / H13), 7.00 / 6.46 (H18 / H19).

^{19}F NMR (400 MHz, Acetone-d_6, 298 K): δ/ppm = -70.1 (d, J^{F-P} = 712 Hz, PF_6).

^{31}P{^{1}H} NMR (160 MHz, Acetone-d_6, 298 K): δ/ppm = -144.2 (hept, J^{P-F} = 712 Hz, PF_6).

HR-MS(ESI): ($C_{38}H_{26}IrN_8$ $[M]^+$) Calc: 787.1910 ; Found: 787.1864.

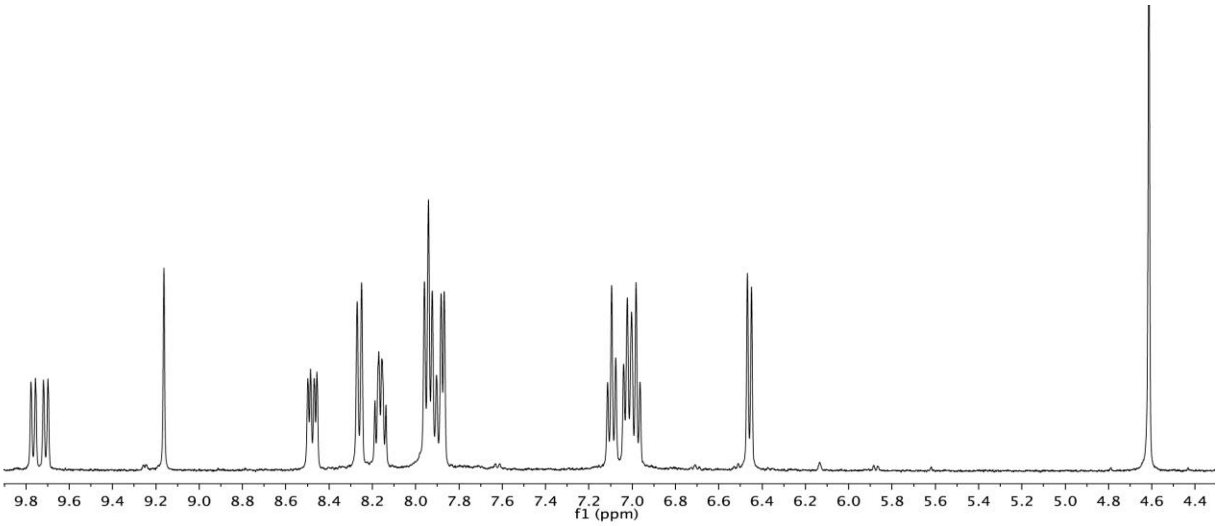


Figure S5: ^{1}H NMR (400 MHz, Acetone-d_6, 298 K)

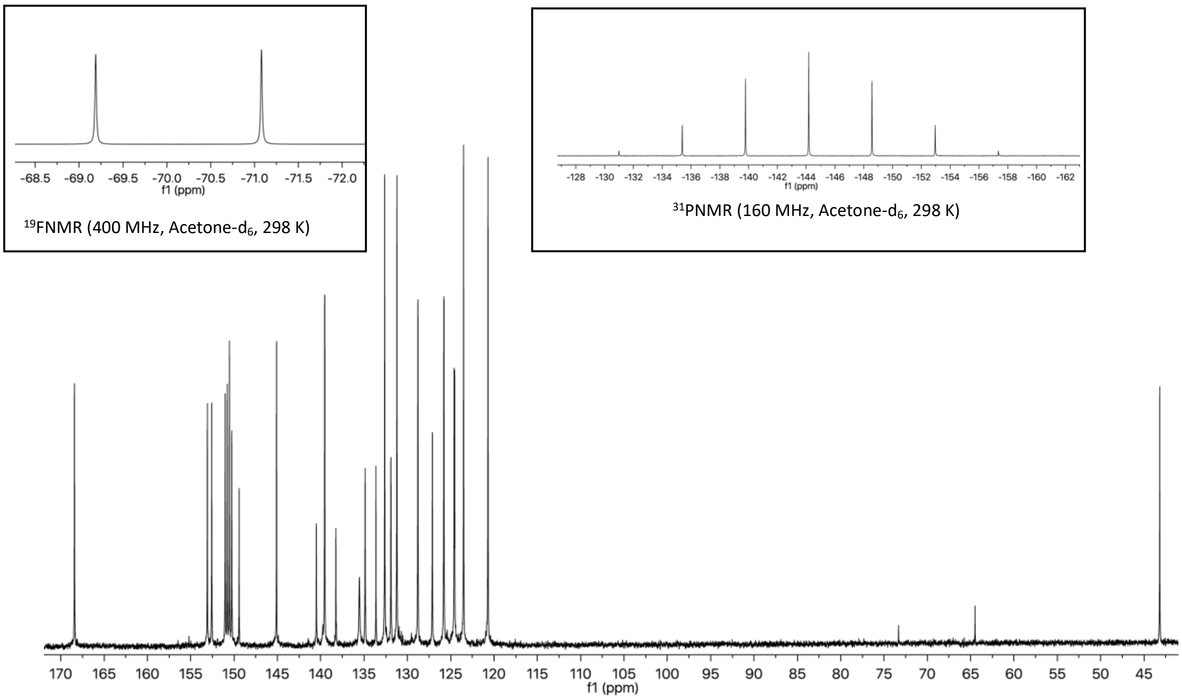
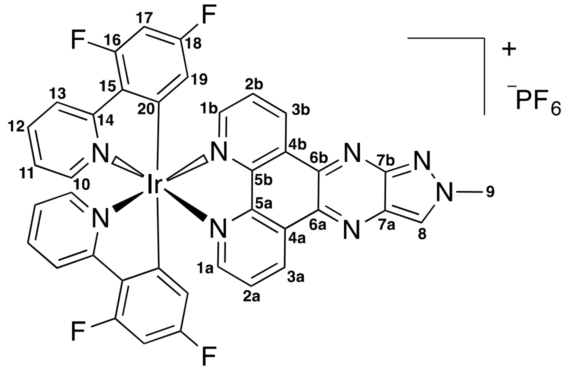


Figure S6: $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d_6, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR

[(1-methyl-1*H*-pyrazolo[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline)bis(2-(2,4-difluorophenyl)pyridine)Ir(III)]PF_6. (C2)

A solution of 11-methyl-11*H*-pyrazolo[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline (**L1**) (94mg, 0.32 mmol) in acetonitrile was added dropwise to a solution of $[Ir(2\text{-}(2,4\text{-difluorophenyl})pyridine)_2]_2$-$\mu$-$Cl_2$ (200mg, 0.16 mmol) in MeOH/CH_2Cl_2 (1:3). The mixture was stirred and refluxed for 12 h under nitrogen atmosphere in darkness. Then, the volatiles were removed under vacuum and 500 mL of water was added to the crude product. The mixture was filtered and 2 equivalents of KPF_6 were added to the obtained solution, obtaining a yellow-orange precipitate. This solid was filtered and washed with water, dried and re-crystallized through CH_2Cl_2/diethyl ether diffusion, obtaining **C2** as yellow crystalline material in 73% yield (117 mg, 0.16 mmol).



^{1}H NMR (400 MHz, Acetone-d_6, 298 K): δ/ppm = 9.74 (d, *J* = 8.2 Hz, 1H, H3a), 9.70 (d, *J* = 8.2 Hz, 1H, H3b), 9.14 (s, 1H, H8), 8.64 (d, *J* = 5.2 Hz, 1H, H1a), 8.61 (d, *J* = 5.2 Hz, 1H, H1b), 8.41 (d, *J* = 8.5 Hz, 2H, H10), 8.18 (m, 2H, H2a, H2b), 8.03 (t, *J* = 8.0 Hz, 2H, H11), 7.98 (broad, 2H, H13), 7.11 (t, *J* = 6.7 Hz, 2H, H12), 6.82 (t, J^{H-F} = 11.1 Hz, 2H, H17), 5.91 (d, J^{H-F} = 8.5 Hz, 2H, H19), 4.60 (s, 3H, H9).

^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6, 298 K): δ/ppm = 163.5 (dd, J^{C-F} = 13.3 Hz / 216.9 Hz, C18), 163.2 (d, J^{C-F} = 4.5 Hz, C14), 160.9 (dd, J^{C-F} = 12.5 Hz / 220.2 Hz, C16), 154.8 (d, J^{C-F} = 5.9 Hz, C20), 153.6 (C1a), 153.0 (C1b), 151.3 (d, J^{C-F} = 11.1 Hz, C13), 150.6 (C5a), 150.3 (C5b), 149.4 (C7b), 140.7 (C11), 139.8 (C6b), 138.7 (C6a), 136.6 (C3b), 135.9 (C3a), 133.9 (C7a), 132.6 (C4a, C4b), 129.3 (C2a, C2b), 129.0 (C15), 127.4 (C8), 125.1 (C12), 124.6 (d, J^{C-F} = 20.1 Hz, C10), 114.8 (d, J^{C-F} = 17.1 Hz, C19), 99.8 (t, J^{C-F} = 26.9 Hz, C17), 43.2 (C9).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.74 / 153.6, 150.6, 138.7 (H3a / C1a, C5a, C6a), 9.70 / 153.0, 150.3, 139.8 (H3b / C1b, C5b, C6b), 9.14 / 149.4, 133.9 (H8 / C7b, C7a), 8.64 / 129.3 (H1a / C2a-C2b), 8.61 / 129.3 (H1b / C2a-C2b), 8.41 / 163.2, 125.1 (H10 / C14, C12), 8.18 / 153.6, 153.0, 132.6 (H2a-H2b / C1a, C1b, C4a-C4b), 8.03 / 151.3 (H11 / C13), 7.89 / 163.2, 140.7, 125.1 (H13 / C14, C11, C12), 7.11 / 151.3, 124.6 (H12 / C13, C10), 6.82 / 163.5, 160.9, 129.0, 114.8 (H17 / C18, C16, C15, C19), 5.91 / 163.5, 129.0, 99.8 (H19 / C18, C15, C17), 4.60 / 127.4 (H9 / C8).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.74 / 135.9 (H3a / C3a), 9.70 / 136.6 (H3b / C3b), 9.14 / 127.4 (H8 / C8), 8.64 / 153.6 (H1a / C1a), 8.61 / 153.0 (H1b / C1b), 8.41 / 124.6 (H10 / C10), 8.18 / 129.3 (H2a, H2b / C2a, C2b), 8.03 / 140.7 (H11 / C11), 7.89 / 151.3 (H13 / C13), 7.11 / 125.1 (H12 / C12), 6.82 / 99.8 (H17 / C17), 5.91 / 114.8 (H19 / C19), 4.60 / 43.2 (H9 / C9).

COSY (400 MHz / 400 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{1}H) = 9.74 / 8.18 (H3a / H2a, H2b), 9.70 / 8.18 (H3b / H2a, H2b), 8.64 / 8.18 (H1a / H2a, H2b), 8.61 / 8.18 (H1b / H2a, H2b), 8.41 / 8.03 (H10 / H11), 8.03 / 7.11 (H11 / H12), 7.89 / 7.11 (H13 / H12).

^{19}F NMR (400 MHz, Acetone-d_6, 298 K): δ/ppm = -70.2 (d, $J^{F\text{-}P}$ = 712 Hz, PF_6), -106.5 (t, $J^{F\text{-}H}$ = 8.0 Hz, F-C18), -108.7 (t, $J^{F\text{-}H}$ = 11.0 Hz, F-C16).

^{31}P{^{1}H} NMR (160 MHz, Acetone-d_6, 298 K): δ/ppm = -144.2 (hept, $J^{P\text{-}F}$ = 712 Hz, PF_6).

HR-MS(ESI): ($C_{38}H_{22}F_4IrN_8$ $[M]^+$) Calc: 859.1533 ; Found: 859.1473.

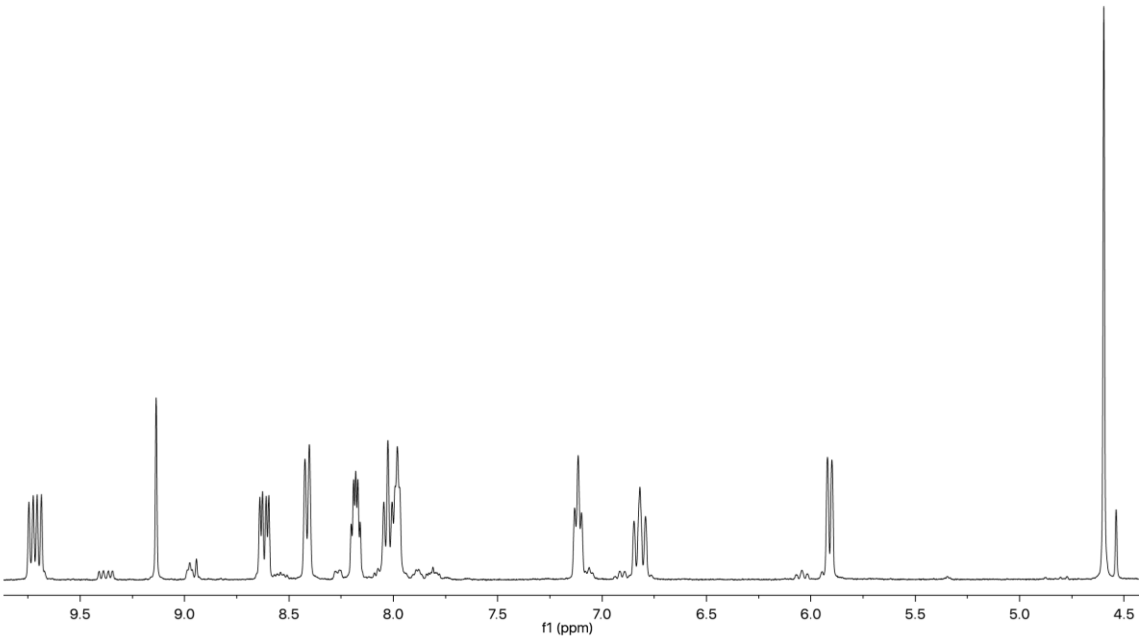


Figure S7: ^{1}H NMR (400 MHz, Acetone-d$_6$, 298 K)

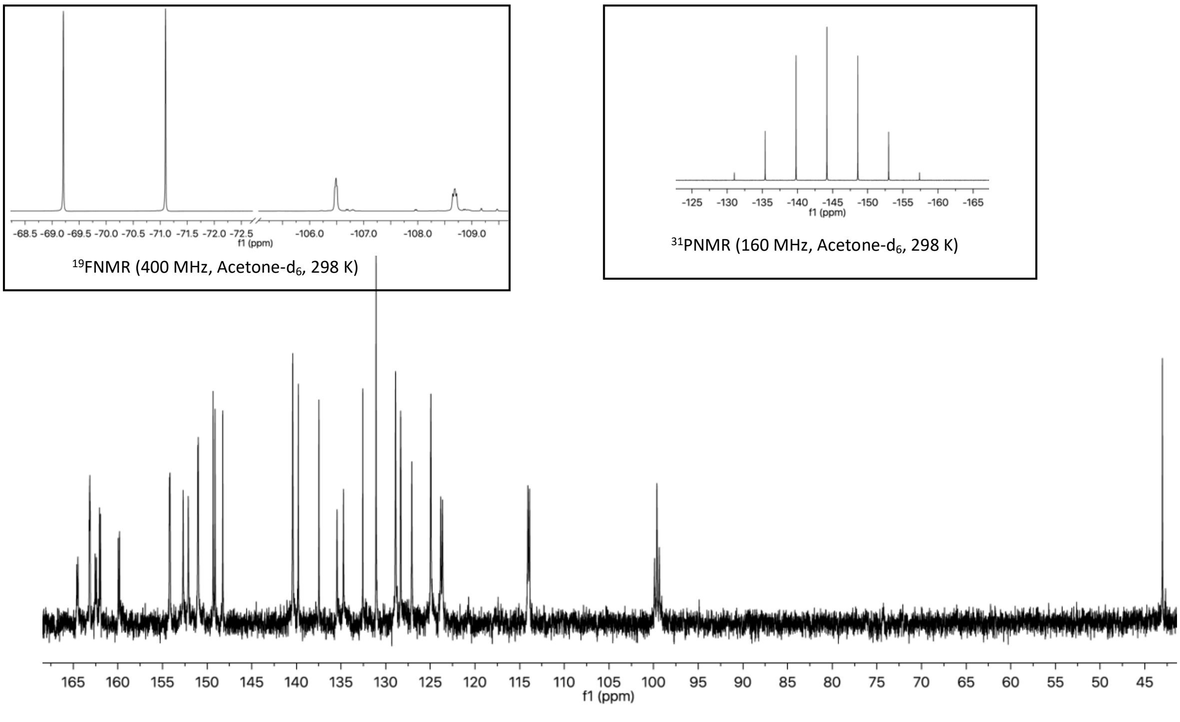
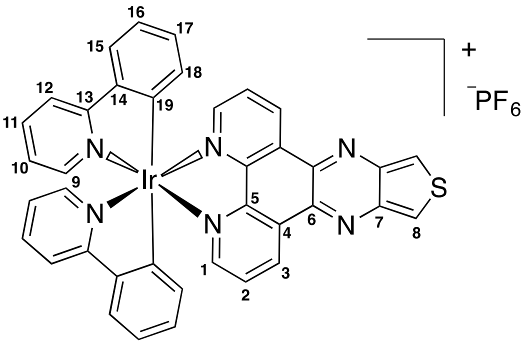


Figure S8: ^{13}C{^{1}H} NMR (100 MHz, Acetone-d$_6$, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR

[(Thieno[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline)bis(2-phenyl pyridine)Ir(III)]PF$_6$. (C3)

A solution of thieno[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline (**L2**) (50 mg, 0.17 mmol) in acetonitrile was added dropwise to a solution of [Ir(2-phenylpyridine)$_2$]$_2$-μ-Cl$_2$ (93 mg, 0.09 mmol) in MeOH/CH$_2$Cl$_2$ (1:3). The mixture was stirred and refluxed for 12 h under nitrogen atmosphere in darkness. Then, the volatiles were removed under vacuum and 500 mL of water was added to the crude product. The mixture was filtered and 2 equivalents of KPF$_6$ were added to the obtained solution, obtaining a yellow-orange precipitate. This solid was filtered and washed with water, dried and re-crystallized through CH$_2$Cl$_2$/diethyl ether diffusion, obtaining **C3** as yellow crystalline material in 65 % yield (52 mg, 0.05 mmol).



^{1}H NMR (400 MHz, Acetone-d$_6$, 298 K): δ/ppm = 9.49 (d, *J* = 8.3 Hz, 2H, H3), 8.58 (s, 2H, H8), 8.26 (d, *J* = 5.3 Hz, 2H, H1), 8.06 (d, *J* = 8.3 Hz, 2H, H9), 7.95 (dd, *J* = 5.3 Hz / 8.3 Hz, 2H, H2), 7.75 (t, *J* = 8.0 Hz, 2H, H10), 7.70 (m, 4H, H16, H15), 6.89 (m, 2H, H11), 6.84 (m, 2H, H12), 6.79 (m, 2H, H17), 6.24 (d, *J* = 7.6 Hz, 2H, H18).

^{13}C{^{1}H} NMR (100 MHz, Acetone-d$_6$, 298 K): δ/ppm = 166.8 (C13), 151.5 (C1), 150.1 (C5), 149.7 (C19), 149.6 (C15), 144.0 (C14), 141.4 (C7), 139.8 (C6), 138.8 (C16), 134.8 (C3), 131.5 (C4), 131.1 (C18), 130.3 (C17), 128.5 (C2), 125.1 (10), 123.8 (C12), 122.5 (C11), 120.1 (C8), 120.0 (C9).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, Acetone-d$_6$, 298 K): δ (^{1}H) / δ (^{13}C) = 9.49 / 151.5, 150.1, 139.8 (H3 / C1, C5, C6), 8.58 / 141.4 (H8 / C7), 8.26 / 150.1, 128.5 (H1 / C5, C2), 8.06 / 166.8, 123.8 (H9 / C13, C11), 7.95 / 131.5 (H2 / C4), 7.70 / 149.6, 131.1 (H16 / C15, C18), 7.70 / 166.8, 138.8, 123.8 (H15 / C13, C16, C12), 6.89 / 120.0 (H11 / C9), 6.84 / 144.0 (H12 / C14), 6.79 / 149.7 (H17 / C19), 6.24 / 144.0 (H18 / C14).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.49 / 134.8 (H3 / C3), 8.58 / 120.1 (H8 / C8), 8.26 / 151.5 (H1 / C1), 8.06 / 120.0 (H9 / C9), 7.95 / 128.5 (H2 / C2), 7.75 / 125.1 (H10 / C10), 7.70 / 149.6 (H15 / C15), 7.70 / 138.8 (H16 / C16), 6.89 / 123.8 (H12 / C12), 6.84 / 122.5 (H11 / C11), 6.79 / 130.3 (H17 / C17), 6.24 / 131.1 (H18 / C18).

COSY (400 MHz / 400 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{1}H) = 9.49 / 7.95 (H3 / H2), 8.26 / 7.95 (H1 / H2), 8.06 / 7.75 (H9 / H10), 7.75 / 6.89 (H10 / H11), 7.70 / 6.79 (H16 / H17), 6.89 / 6.84 (H11 / H12), 6.79 / 6.24 (H17 / H18).

^{19}F NMR (400 MHz, Acetone-d_6, 298 K): δ/ppm = -70.2 (d, $J^{F\text{-}P}$ = 712 Hz, PF_6).

^{31}P{^{1}H} NMR (160 MHz, Acetone-d_6, 298 K): δ/ppm = -144.2 (hept, $J^{P\text{-}F}$ = 712 Hz, PF_6).

HR-MS(ESI): ($C_{38}H_{24}IrN_6S$ $[M]^+$) Calc: 789.1412 ; Found: 789.1371.

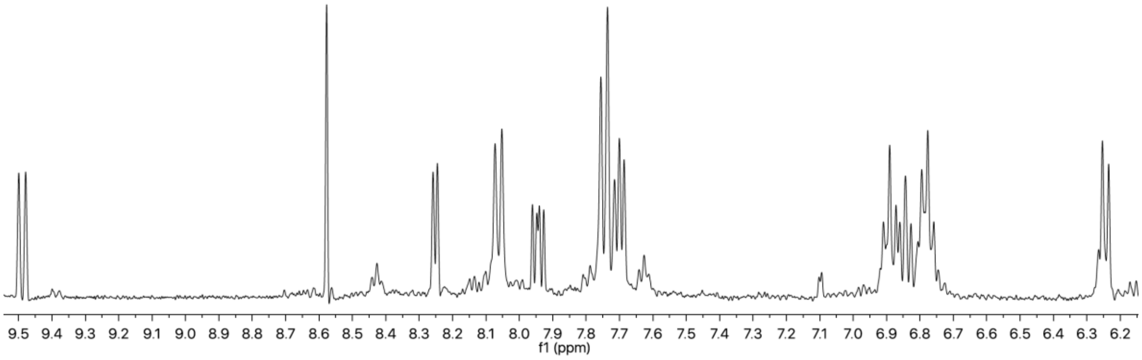


Figure S9: ^{1}H NMR (400 MHz, Acetone-d_6, 298 K)

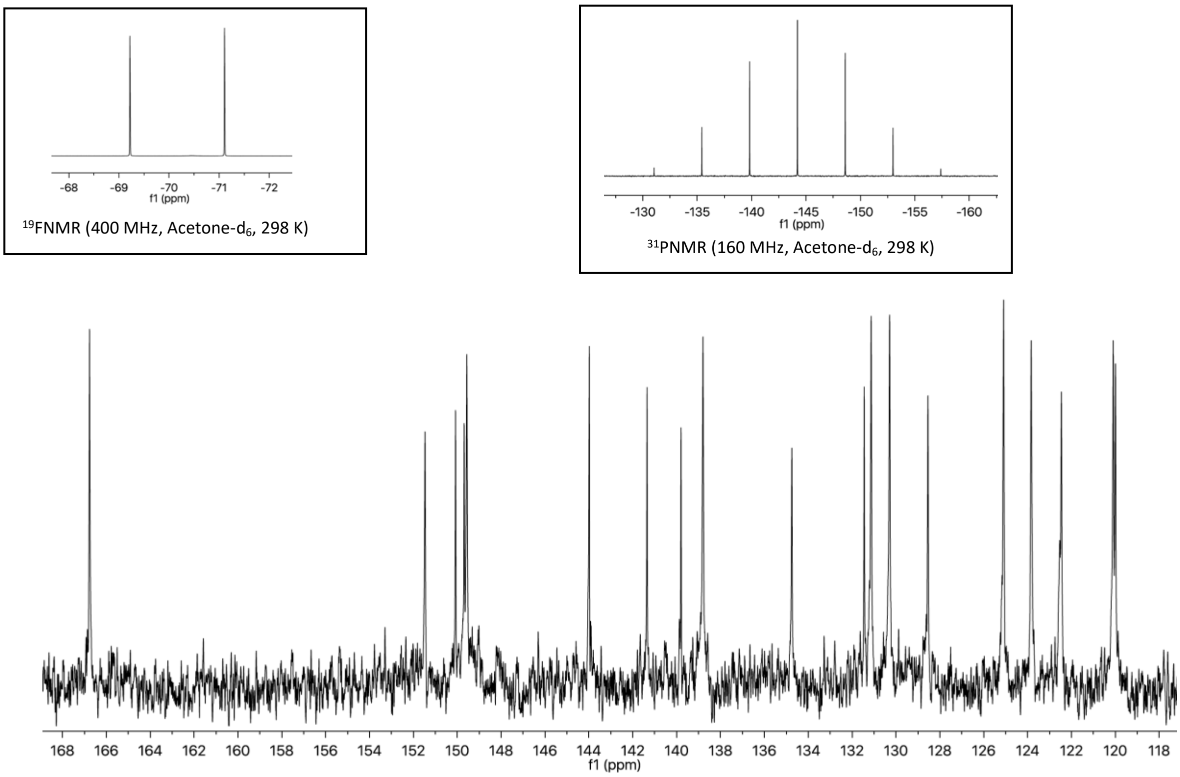
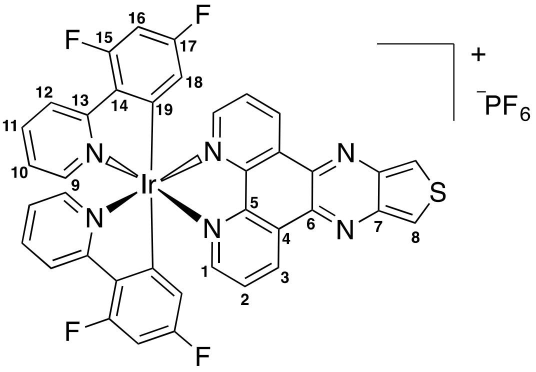


Figure S10: $^{13}C\{^1H\}$ NMR (100 MHz, Acetone-d$_6$, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR

[(Thieno[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline)bis(2-(2,4-difluorophenyl)Ir(III))]PF_6. (C4)

A solution of thieno[3',4':5,6]pyrazino[2,3-*f*][1,10]phenanthroline (**L2**) (50 mg, 0.17 mmol) in acetonitrile was added dropwise to a solution of [Ir(2,4-difluorophenyl)pyridine)$_2$]$_2$-μ-Cl_2 (100 mg, 0.08 mmol) in MeOH/CH_2Cl_2 (1:3). The mixture was stirred and refluxed for 12 h under nitrogen atmosphere in darkness. Then, the volatiles were removed under vacuum and 500 mL of water was added to the crude product. The mixture was filtered and 2 equivalents of KPF_6 were added to the obtained solution, obtaining a yellow-orange precipitate. This solid was filtered and washed with water, dried and re-crystallized through CH_2Cl_2/diethyl ether diffusion, obtaining **C4** as yellow crystalline material in 68 % yield (57 mg, 0.06 mmol).



^{1}H NMR (400 MHz, Acetone-d$_6$, 298 K): δ/ppm = 9.65 (d, *J* = 8.2 Hz, 2H, H3), 8.72 (s, 2H, H8), 8.59 (d, *J* = 5.1 Hz, 2H, H1), 8.41 (d, *J* = 8.3 Hz, 2H, H9), 8.14 (dd, *J* = 5.3 Hz / 7.8 Hz, 2H, H2), 8.03 (t, *J* = 7.8 Hz, 2H, H10), 8.00 (t, *J* = 5.6 Hz, 2H, H12), 7.15 (t, *J* = 6.6 Hz, 2H, H11), 6.81 (dd, $J^{H\text{-}F}$ = 9.7 Hz / 11.4 Hz, 2H, H16), 5.91 (d, $J^{H\text{-}F}$ = 8.6 Hz, 2H, H18).

^{13}C{^{1}H} NMR (100 MHz, Acetone-d$_6$, 298 K): δ/ppm = 164.6 (d, $J^{C\text{-}F}$ = 7.0 Hz, C13), 164.5 (dd, $J^{C\text{-}F}$ = 13.3 Hz / 255.0 Hz, C17), 162.3 (dd, $J^{C\text{-}F}$ = 12.5 Hz / 258.0 Hz, C15), 154.7 (d, $J^{C\text{-}F}$ = 6.6 Hz, C19), 153.6 (C1), 151.1 (C12), 151.1 (C5), 142.9 (C7), 140.7 (C10), 140.6 (C6), 136.6 (C3), 133.1 (C4), 129.6 (C2), 129.0 (d, $J^{C\text{-}F}$ = 4.5 Hz, C14), 125.0 (C11), 124.5 (d, $J^{C\text{-}F}$ = 20.1 Hz, C9), 120.6 (C8), 114.8 (d, $J^{C\text{-}F}$ = 18.0 Hz, C18), 99.8 (t, $J^{C\text{-}F}$ = 27.1 Hz, C16).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.65 / 153.6, 151.1, 140.6 (H3 / C1, C5, C6), 8.72 / 142.9 (H8 / C7), 8.59 / 151.1, 129.6 (H1 / C5, C2), 8.41 / 164.6, 125.0 (H9 / C13, C11), 8.14 / 133.1 (H2 / C4), 8.03 / 151.1 (H10 / C12), 8.00 / 140.7 (H12 / C10), 7.15 / 151.1, 124.5 (H11 / C12, C9), 6.81 / 164.5, 162.3, 129.0 (H16 / C17, C15, C14), 5.91 / 164.5, 129.0 (H18 / C17, C14).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{13}C) = 9.65 / 136.6 (H3 / C3), 8.72 / 120.6 (H8 / C8), 8.59 / 153.6 (H1 / C1), 8.41 / 124.5 (H9 / C9), 8.14 / 129.6 (H2 / C2), 8.03 / 140.7 (H10 / C10), 8.00 / 151.1 (H12 / C12), 7.15 / 125.0 (H11 / C11), 6.81 / 99.8 (H16 / C16), 5.91 / 114.8 (H18 / C18).

COSY (400 MHz / 400 MHz, Acetone-d_6, 298 K): δ (^{1}H) / δ (^{1}H) = 9.65 / 8.14 (H3 / H2), 8.59 / 8.14 (H1 / H2), 8.41 / 8.03 (H9 / H10), 8.03 / 7.15 (H10 / H11), 8.00 / 7.15 (H12 / H11).

^{19}F NMR (400 MHz, Acetone-d_6, 298 K): δ/ppm = -72.6 (d, $J^{F\text{-}P}$ = 708 Hz, PF$_6$), -107.7 (dd, $J^{F\text{-}H}$ = 9.3 Hz / 18.8 Hz, F-C17), -110.0 (t, $J^{F\text{-}H}$ = 11.6 Hz, F-C15).

^{31}P{^{1}H} NMR (160 MHz, Acetone-d_6, 298 K): δ/ppm = -144.4 (hept, $J^{P\text{-}F}$ = 708 Hz, PF$_6$).

HR-MS(ESI): ($C_{38}H_{20}F_4IrN_6S$ [M]$^+$) Calc: 861.1036 ; Found: 861.1036.

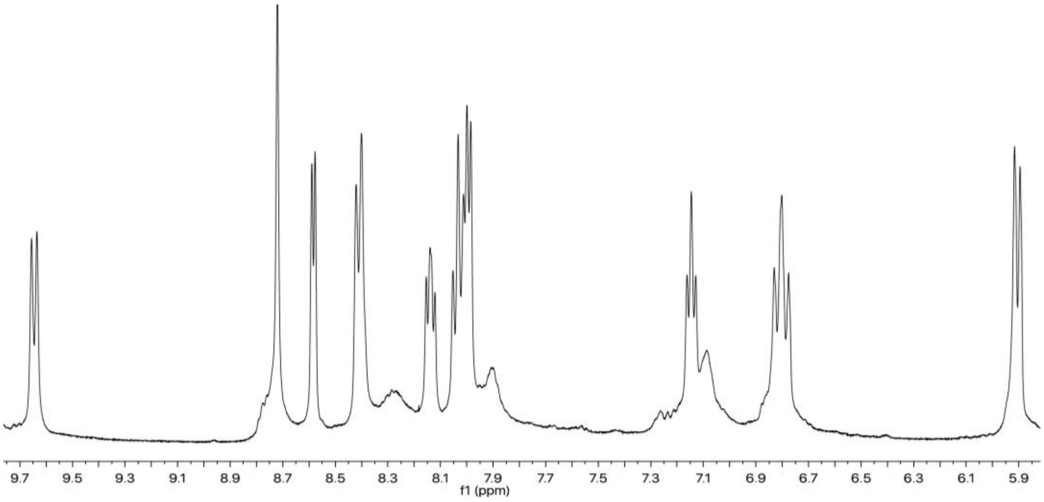
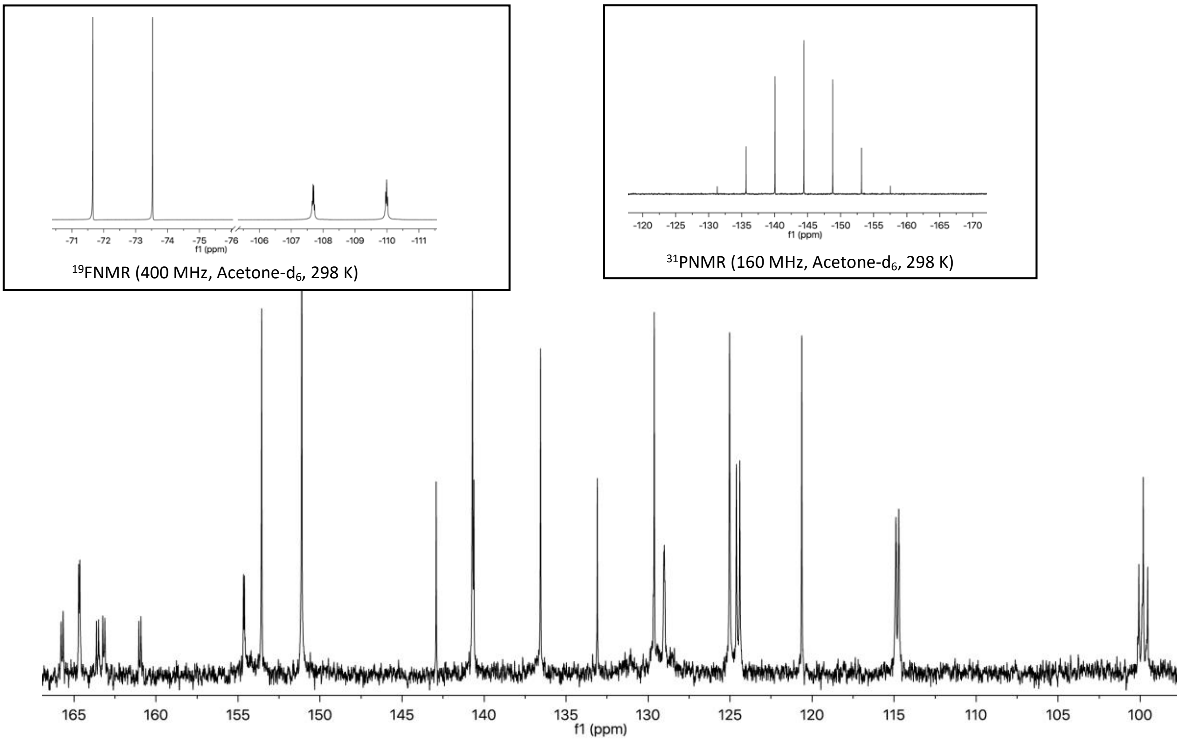


Figure S11: ^{1}HNMR (400 MHz, Acetone-d_6, 298 K)



^{19}FNMR (400 MHz, Acetone-d$_6$, 298 K)

^{31}PNMR (160 MHz, Acetone-d$_6$, 298 K)

Figure S12: $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d$_6$, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR

Absorption and luminescent properties.

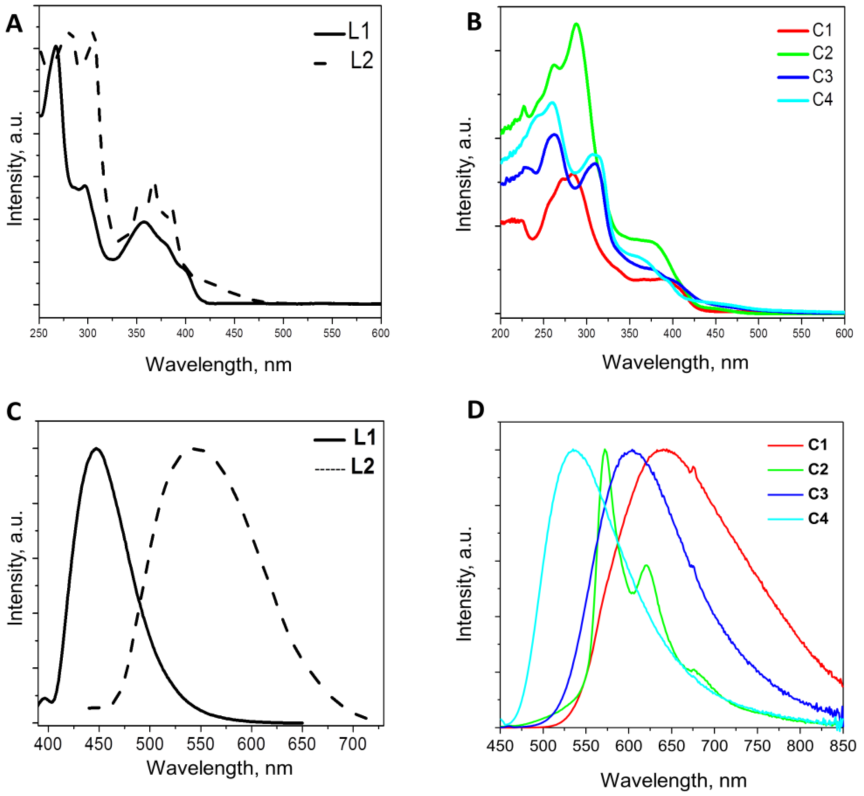


Figure S13. A.) Absorption spectra of L1 and L2. **B.)** Absorption spectra of complexes C1-4. **C.)** Emission spectra of L1 and L2. **B.)** Emission spectra of complexes C1-4. All the absorption and emission spectra registered in dichloromethane solution.

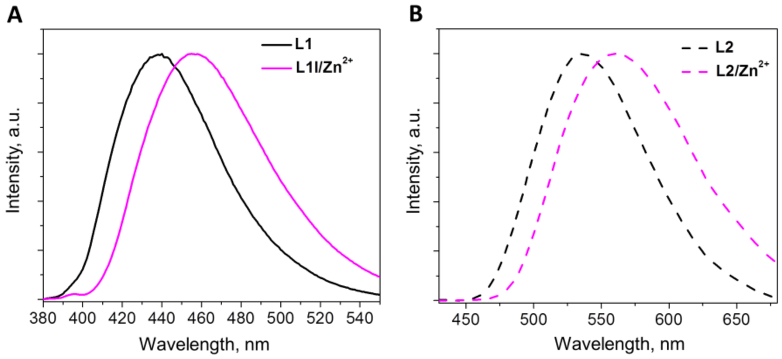


Figure S14. Emission spectra of the free ligands and with addition of Zn^{2+} in acetonitrile solutions for **A.)** L1 and **B.)** L2.

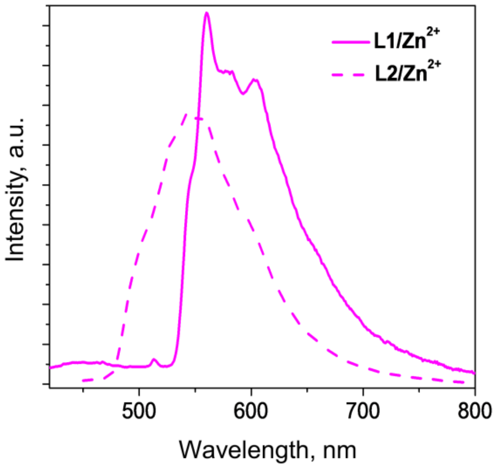


Figure S15. Emission spectra of L1 and L2 with Zn^{2+} in alcoholic glassy matrix at 77 K.

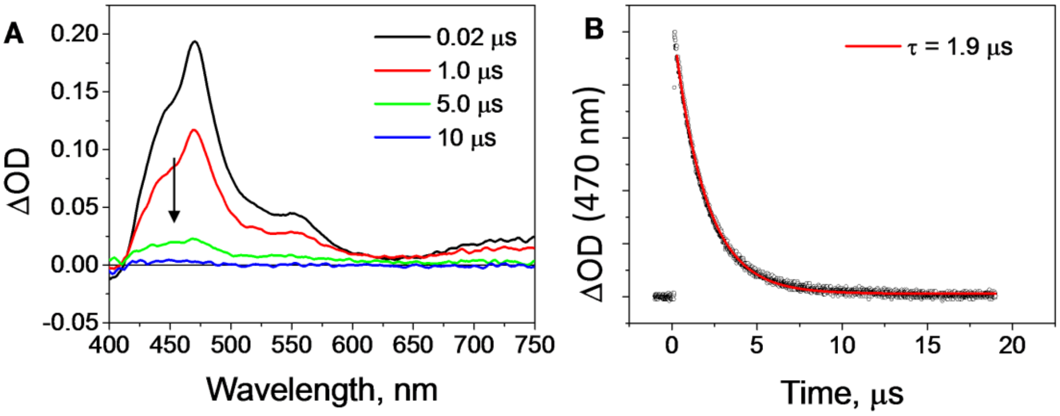


Figure S16. A.) Transient absorption spectra at different time-delays obtained on complex C1 in dichloromethane by laser flash photolysis (excitation at 355 nm) and **B.)** kinetic analysis at 470 nm with related fitting.

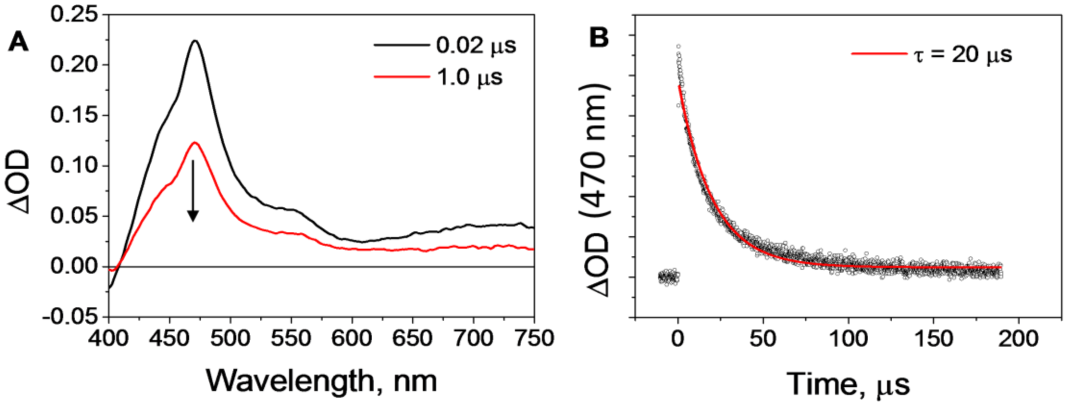


Figure S17. A.) Transient absorption spectra at different time-delays obtained on complex C2 in dichloromethane by laser flash photolysis (excitation at 355 nm) and **B.)** kinetic analysis at 470 nm with related fitting.

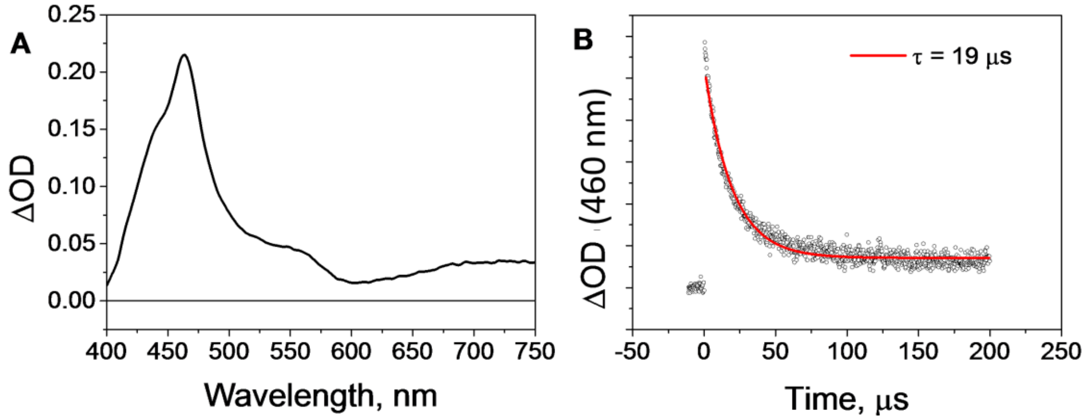


Figure S18. A.) Transient absorption spectrum taken at 1 μs time-delay and **B.)** kinetic trace at 460 nm obtained by flash photolysis (excitation at 355 nm) of ligand L1 in acetonitrile in the presence of $ZnClO_4$.

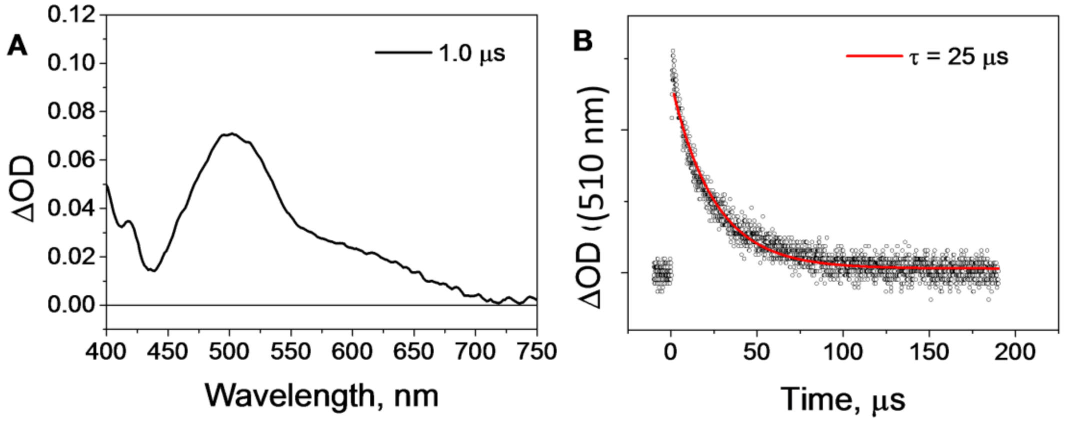


Figure S19. A.) Transient absorption spectrum taken at 1 μs time-delay and **B.)** kinetic trace at 510 nm obtained by flash photolysis (excitation at 355 nm) of ligand L2 in acetonitrile in the presence of $ZnClO_4$.

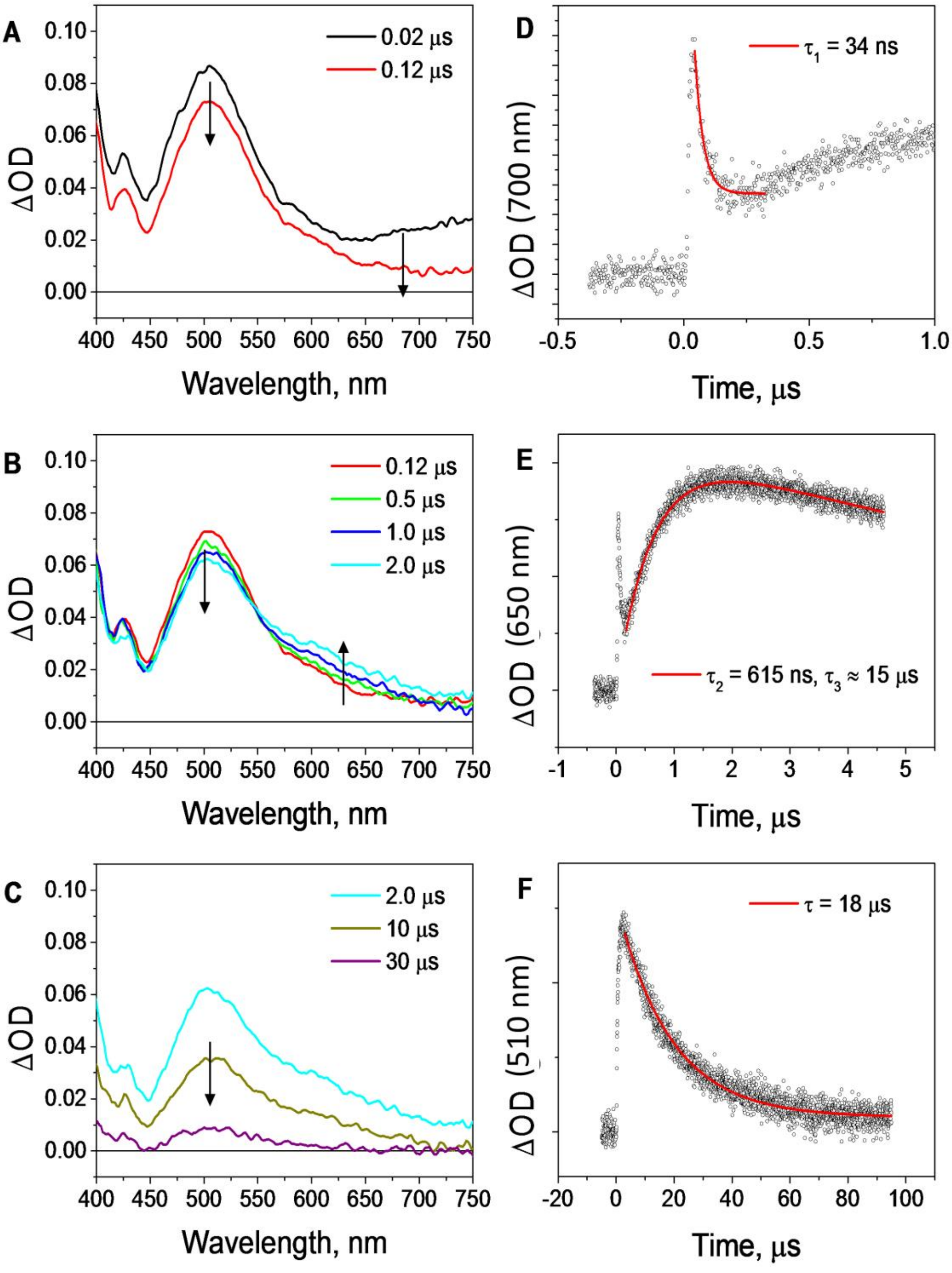


Figure S20. A. B. C.) Transient absorption spectra at different time-delays obtained on complex C3 in dichloromethane by laser flash photolysis (excitation at 355 nm) and kinetic analysis at **D.)** 700 nm, **E.)** 650 nm and **F.)** 510 nm with related fitting.

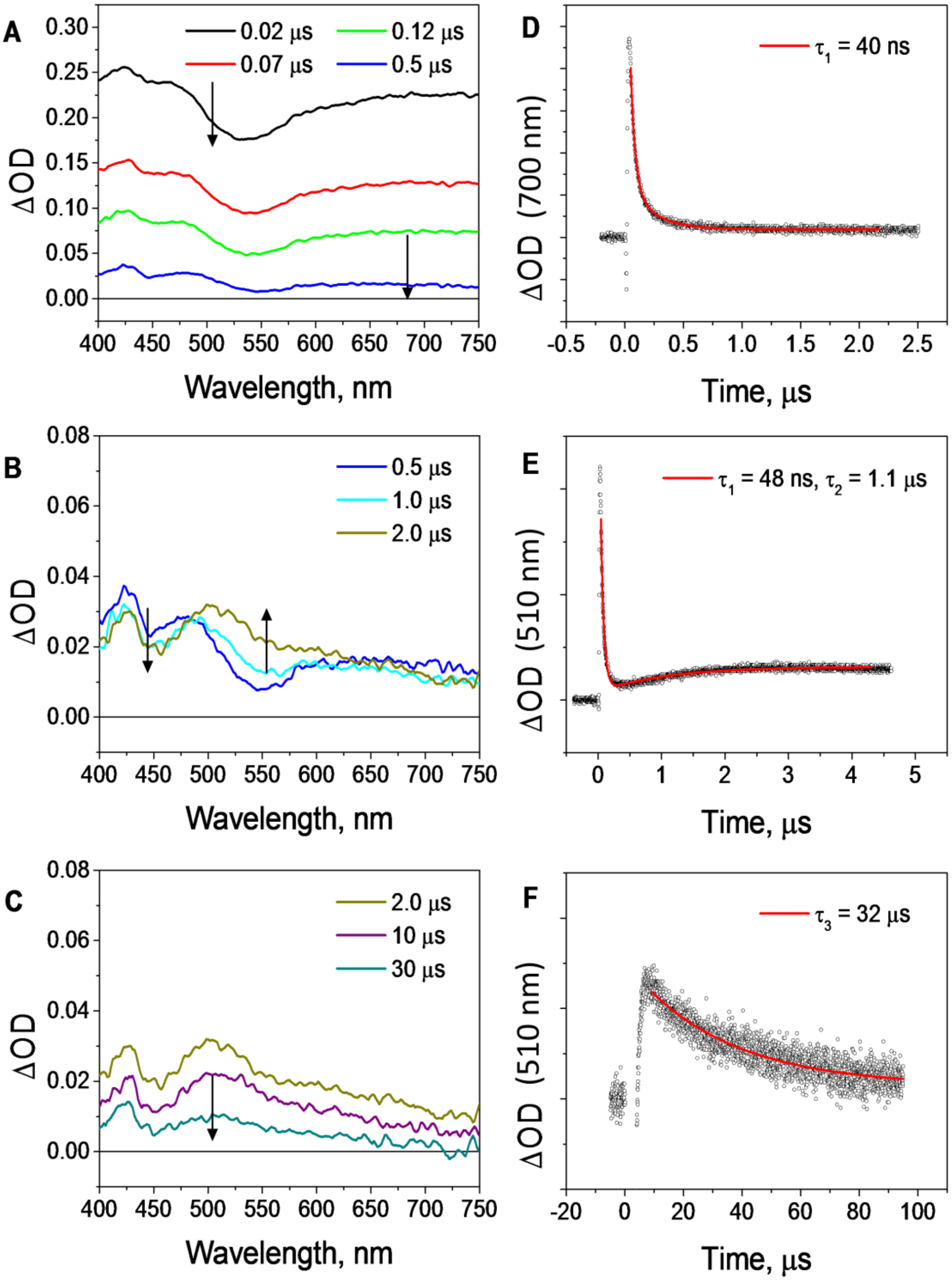


Figure S21. A. B. C.) Transient absorption spectra at different time-delays obtained on complex C4 in dichloromethane by laser flash photolysis (excitation at 355 nm) and kinetic analysis at **D.)** 700 nm, and **E. F.)** 510 nm with related fitting.