Essential Role of The Ancillary Ligand in the Color Tuning of Iridium Tetrazolate Complexes

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SUPPORTING INFORMATION

I. ^{1}H and ^{13}C NMR spectra

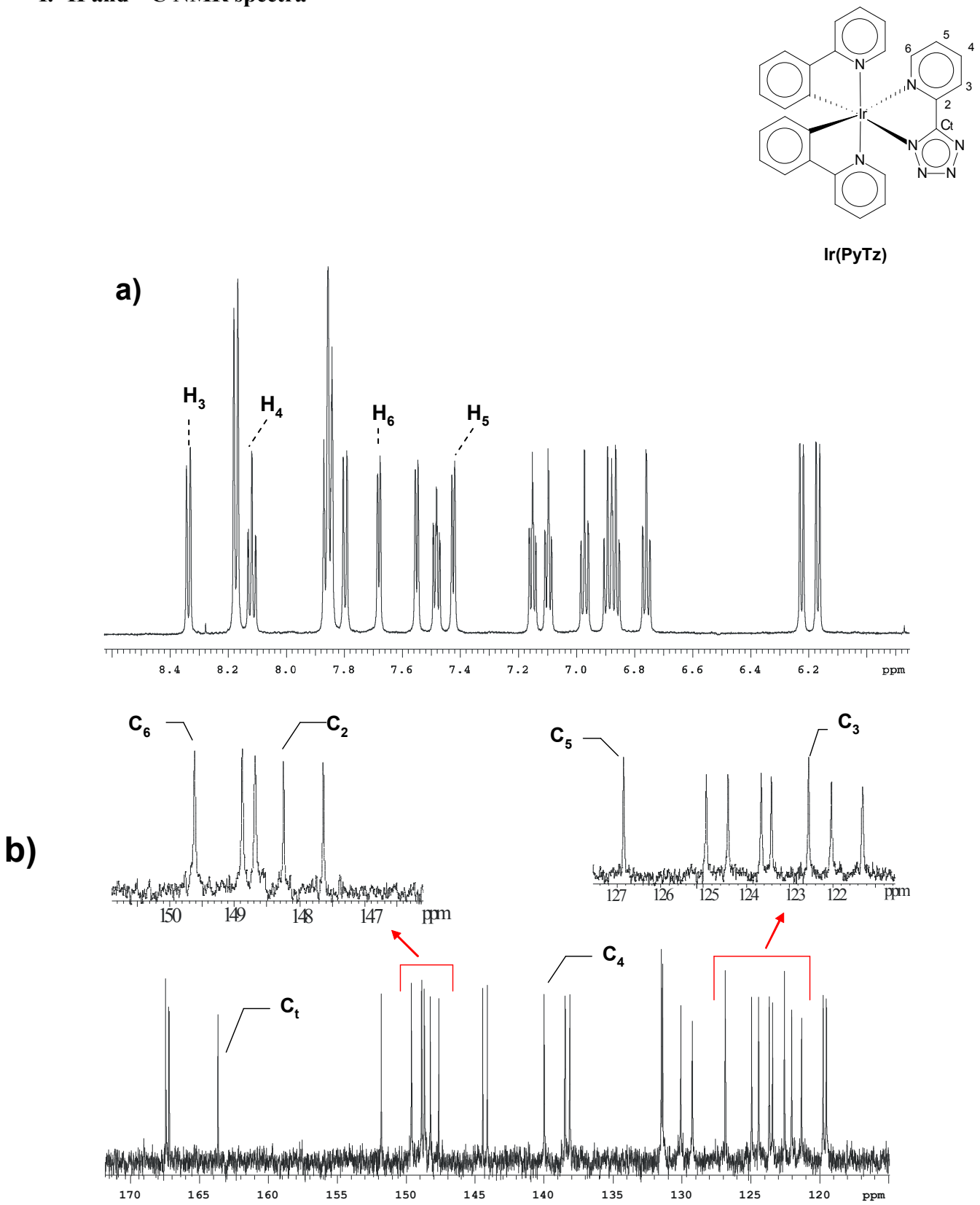


Figure S1. **Ir(PyTz)**: (a) ^{1}H NMR spectrum (600 MHz, DMSO-d6); (b) ^{13}C NMR spectrum (100 MHz, DMSO-d6, r.t.).

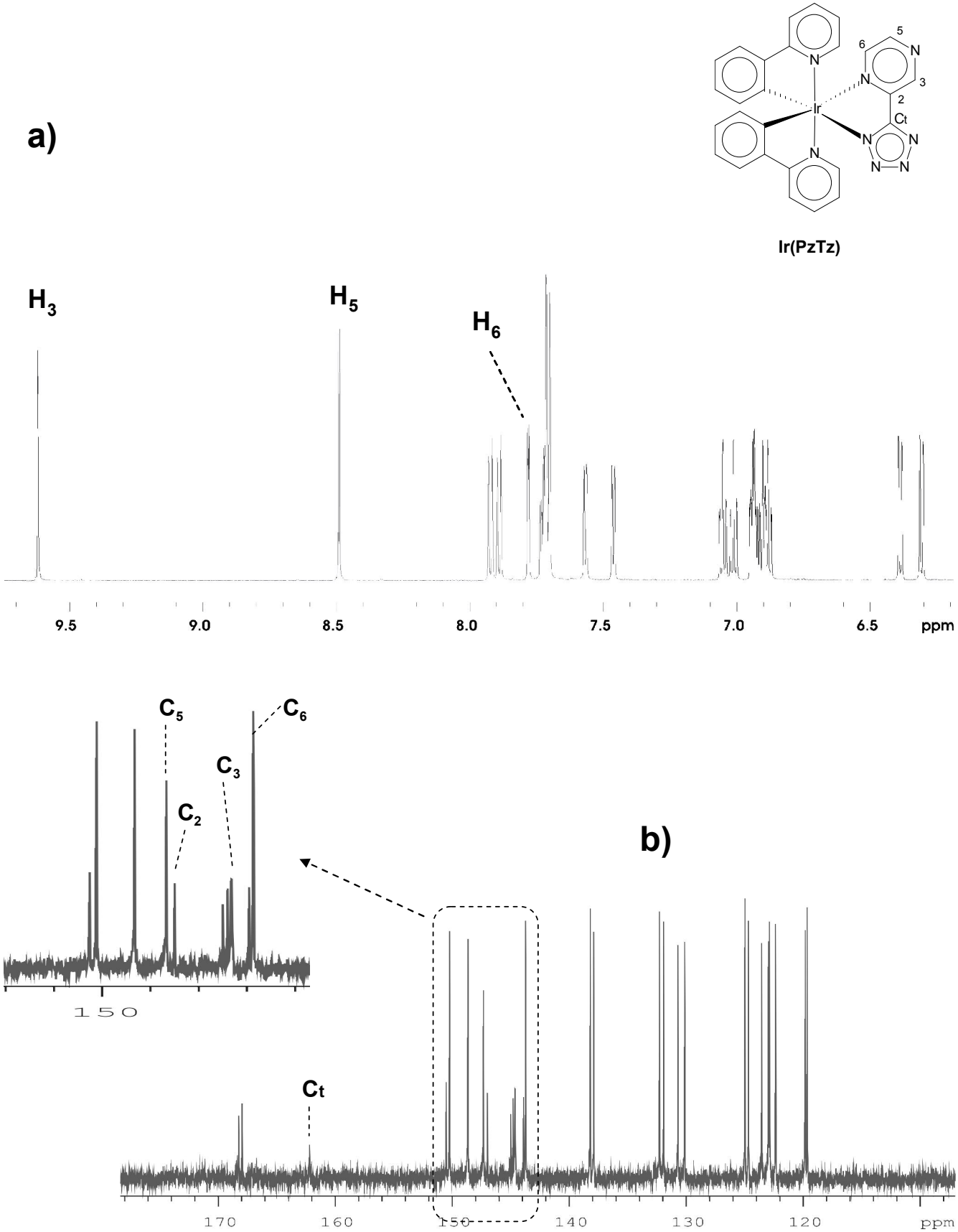


Figure S2. **Ir(PzTz)** (a) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2); (b) ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, r.t.).

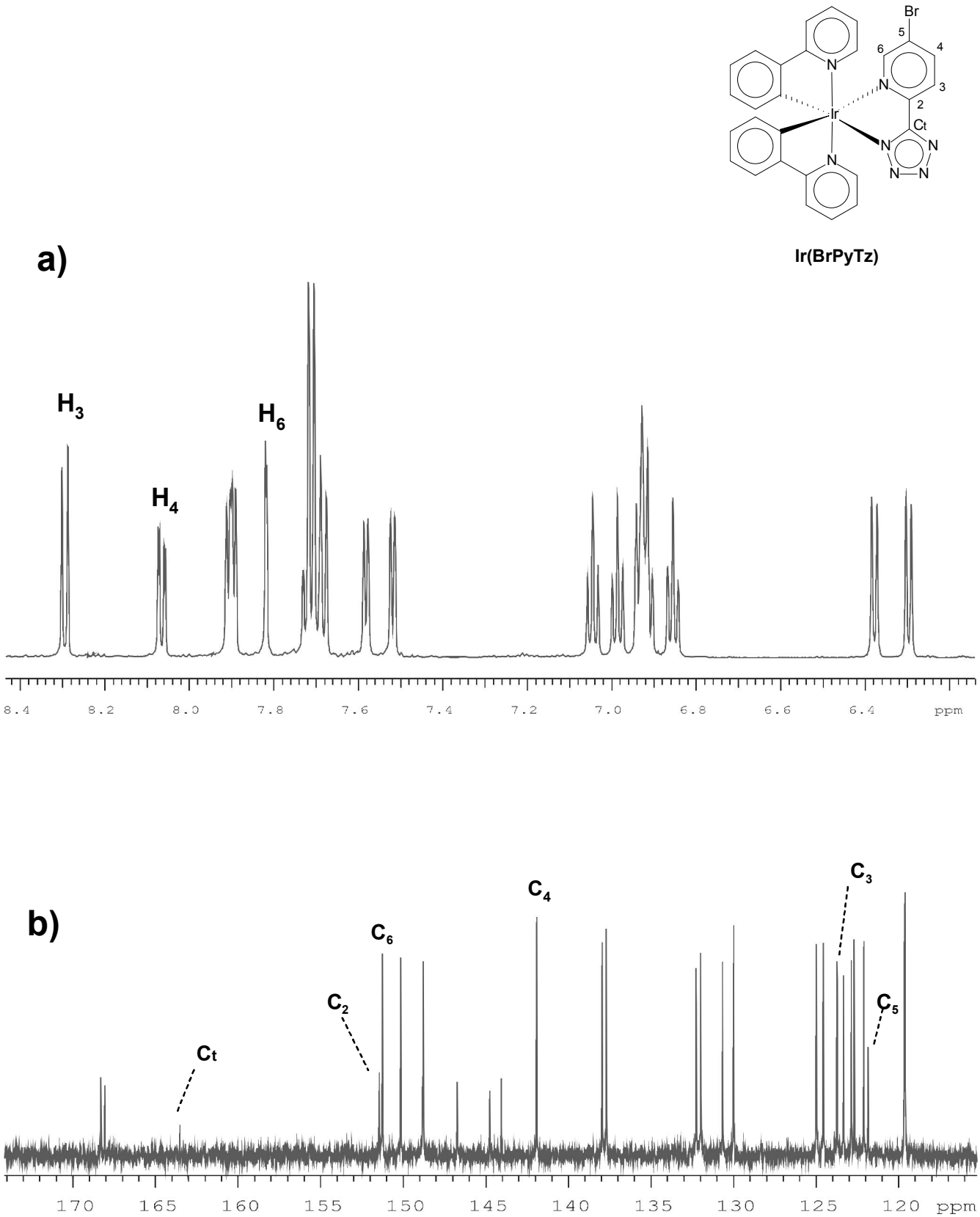


Figure S3. **Ir(BrPyTz)** (a) ^{1}H NMR spectrum (600 MHz, CD_2Cl_2); (b) ^{13}C NMR spectrum (150.8 MHz, CD_2Cl_2, r.t.).

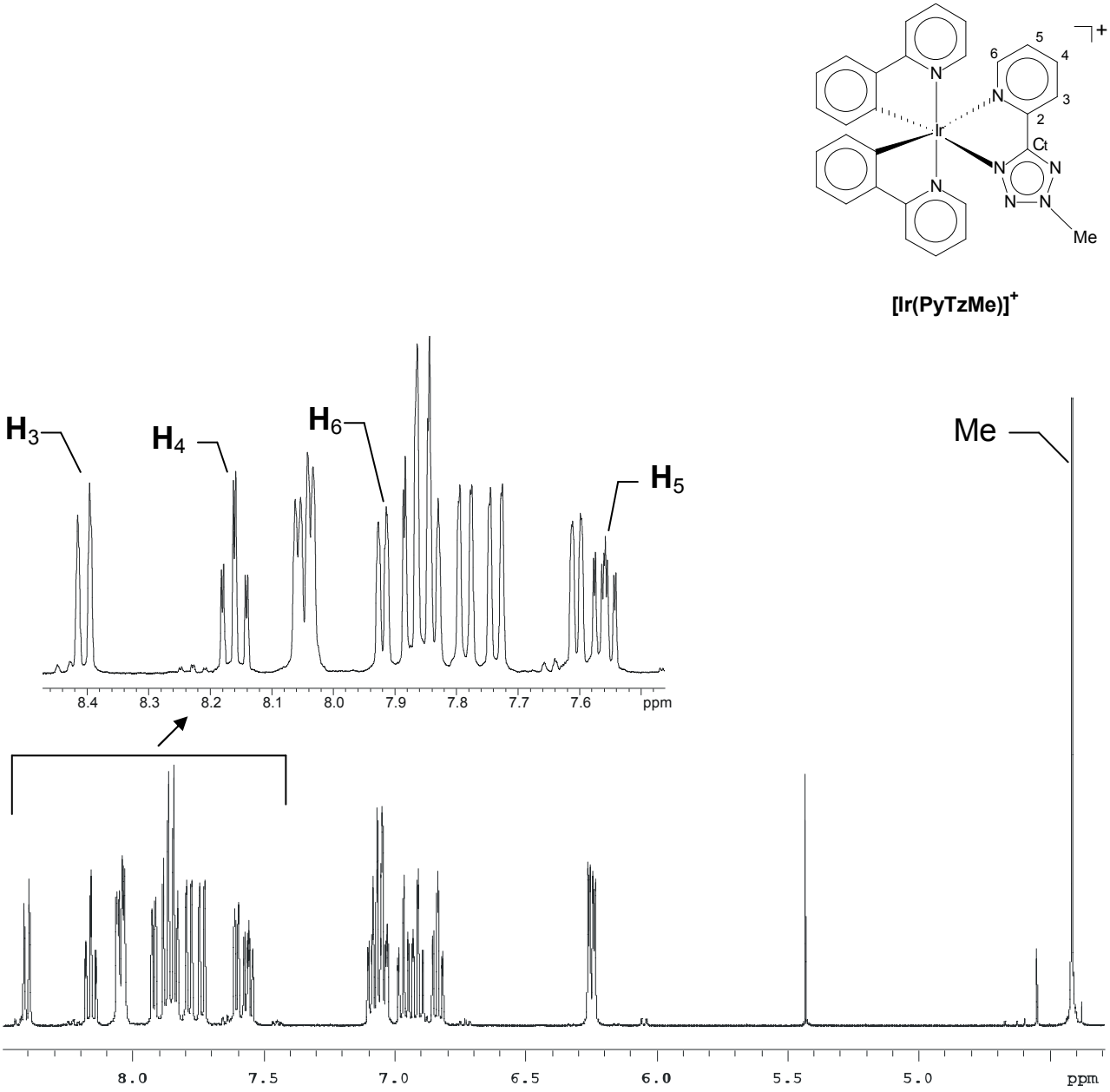
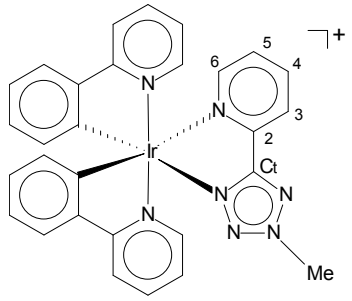
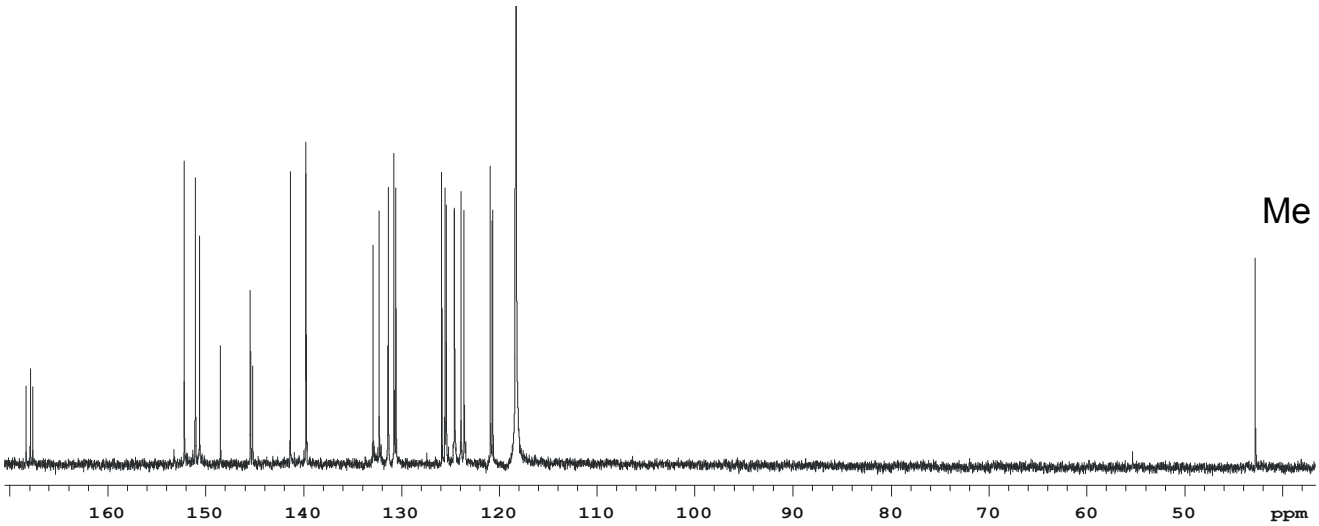


Figure S4. **[Ir(PyTzMe)]$^+$** ^{1}H NMR spectrum (400 MHz, CD_3CN, r.t.).



[Ir(PyTzMe)]$^+$



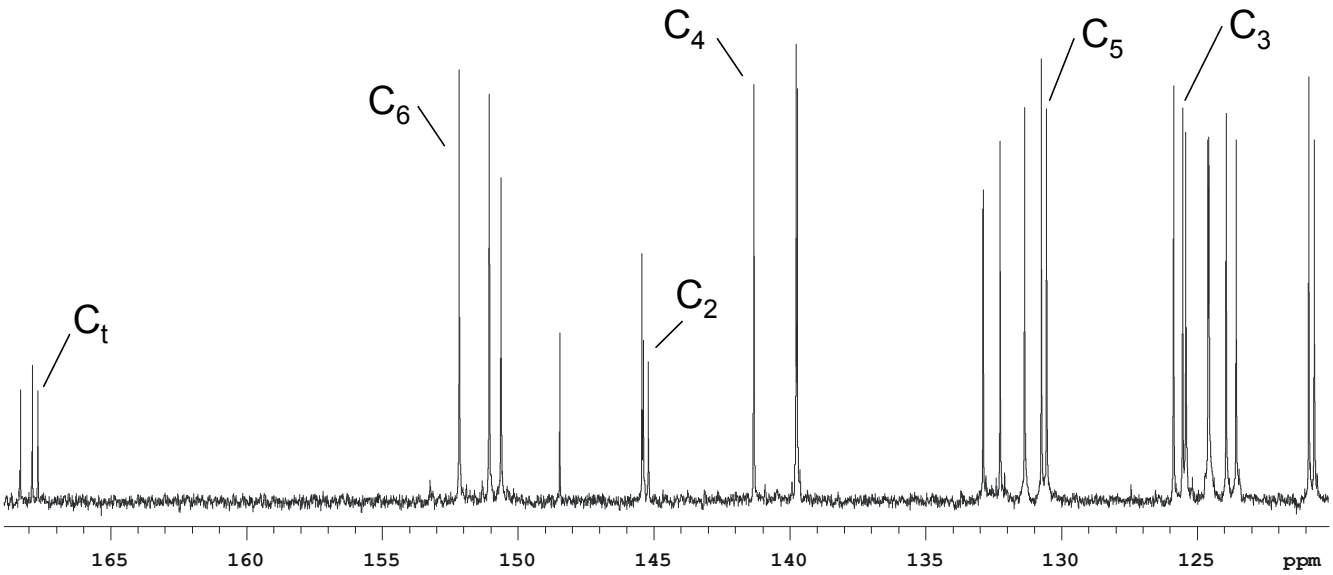
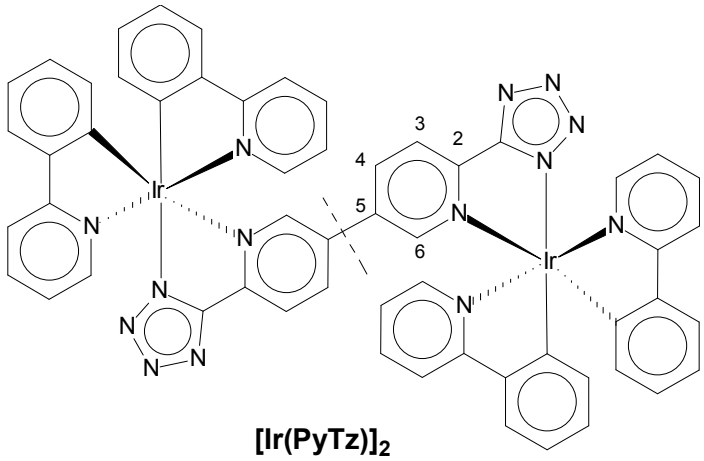


Figure S5. **[Ir(PyTzMe)]$^+$** ^{13}C NMR spectrum (100 MHz, CD_3CN, r.t.).



[Ir(PyTz)]$_2$

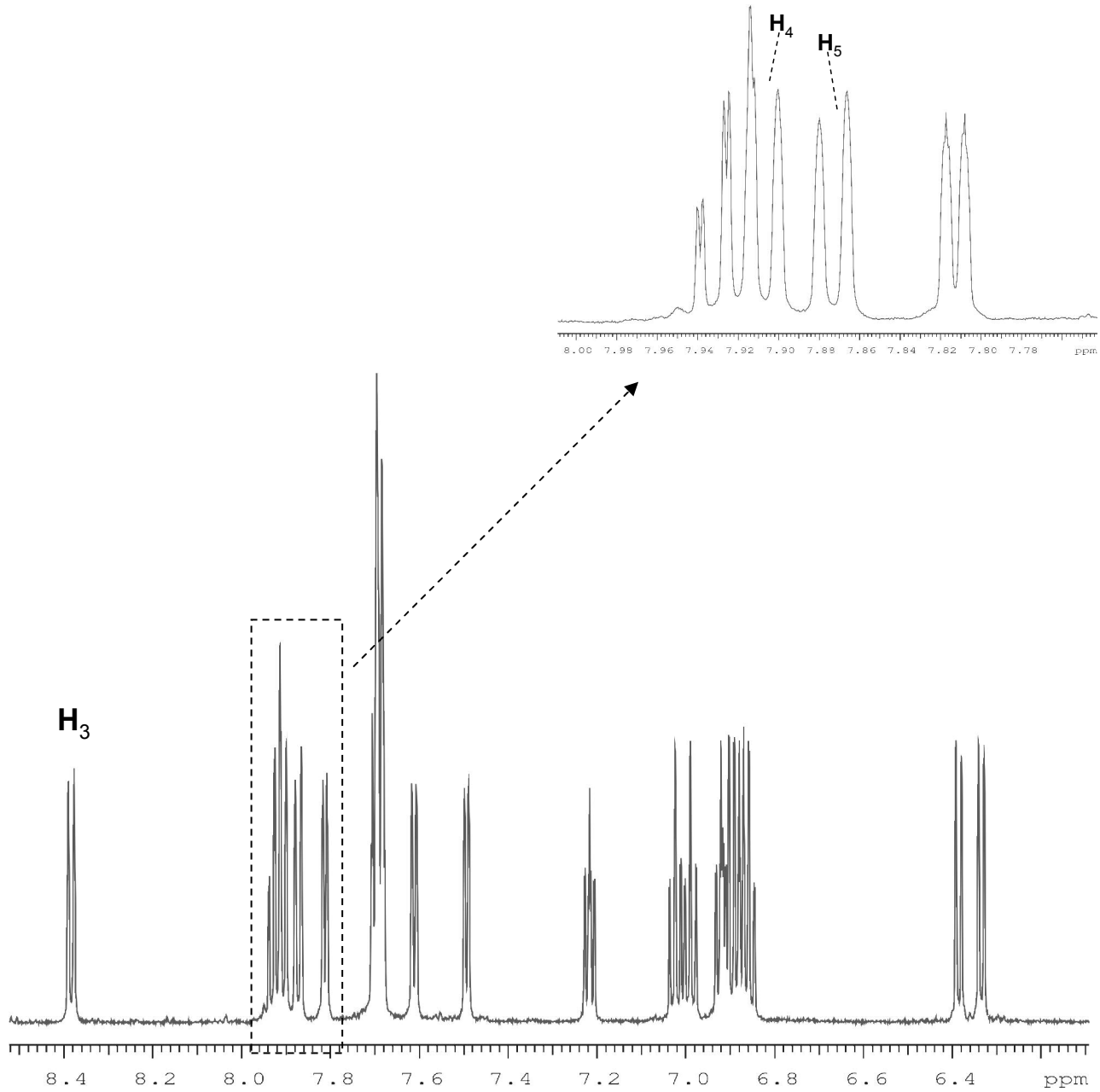
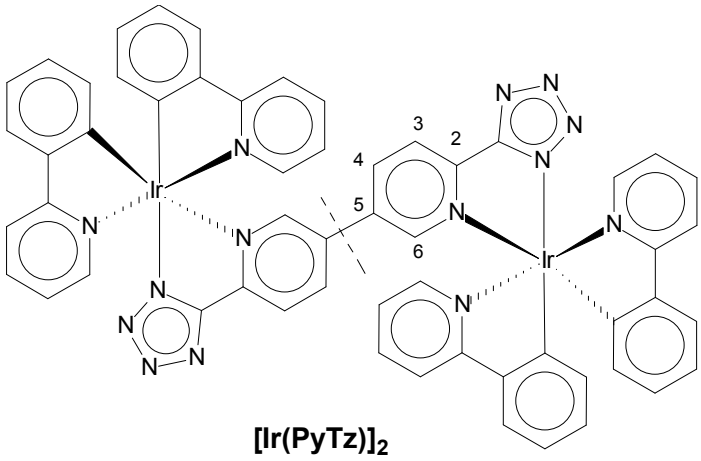


Figure S6. **[Ir(PyTz)]$_2$** ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, r.t.).



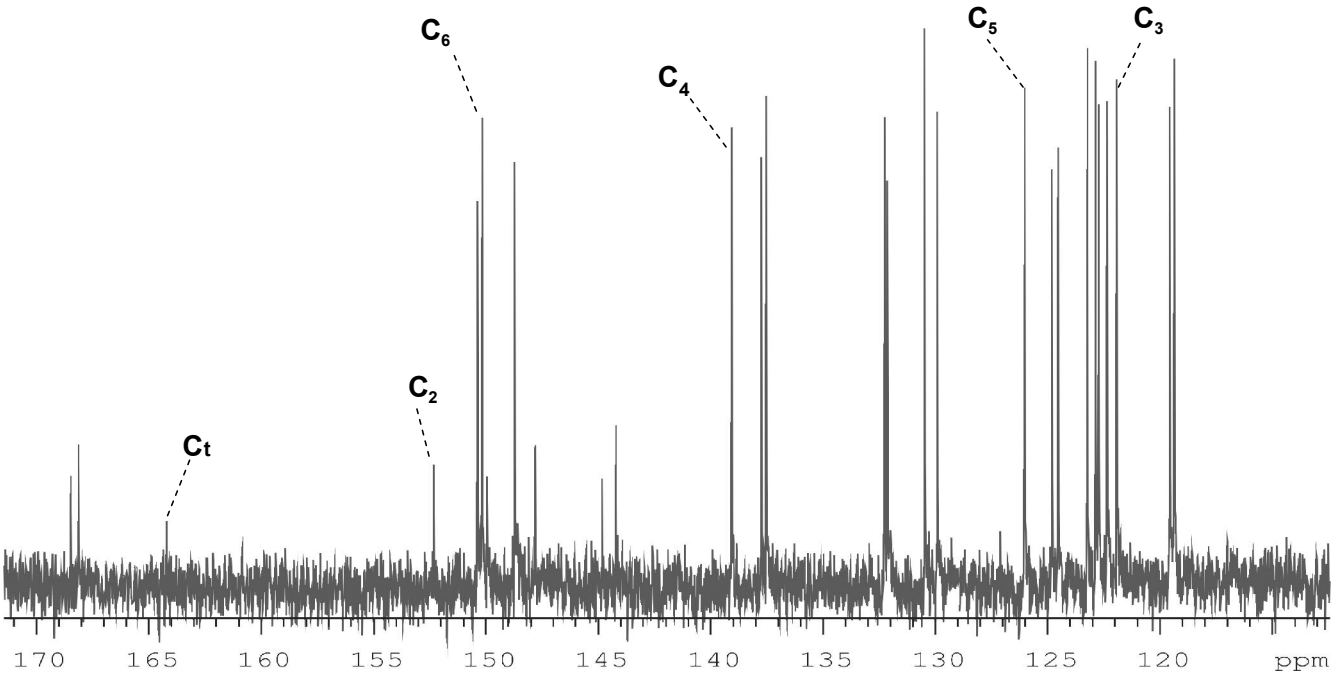
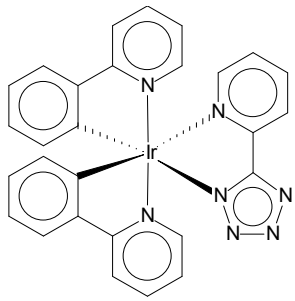


Figure S7. **[Ir(PyTz)]$_2$** ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, r.t.).

II. Absorption and emission spectra



Ir(PyTz)

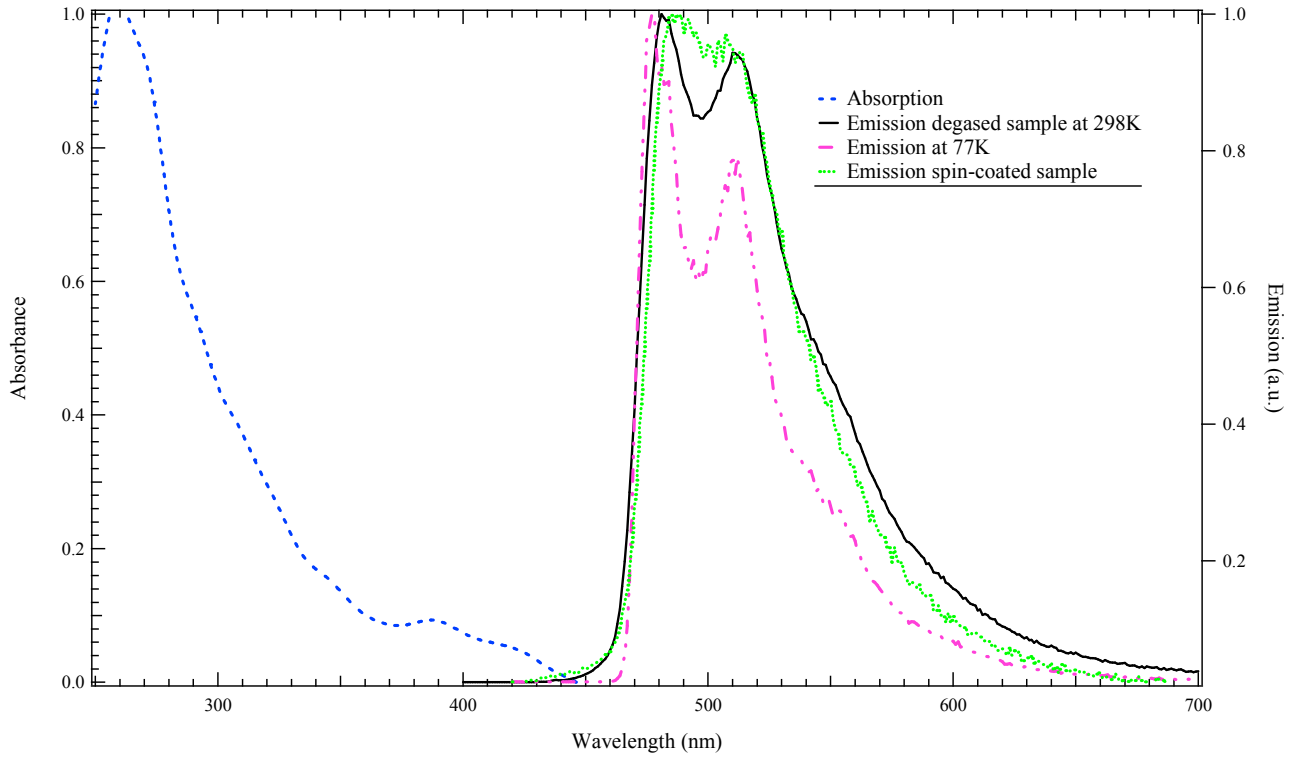
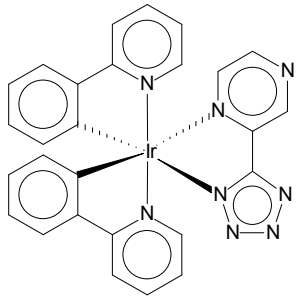


Figure S8. **Ir(PyTz)**: Absorption (2.5 10^{-5} M in CH_2Cl_2) and solution (degassed CH_2Cl_2) and solid state (77 K in butyronitrile glass; spin coated with PMMA, polymethyl-metacrylate).



Ir(PzTz)

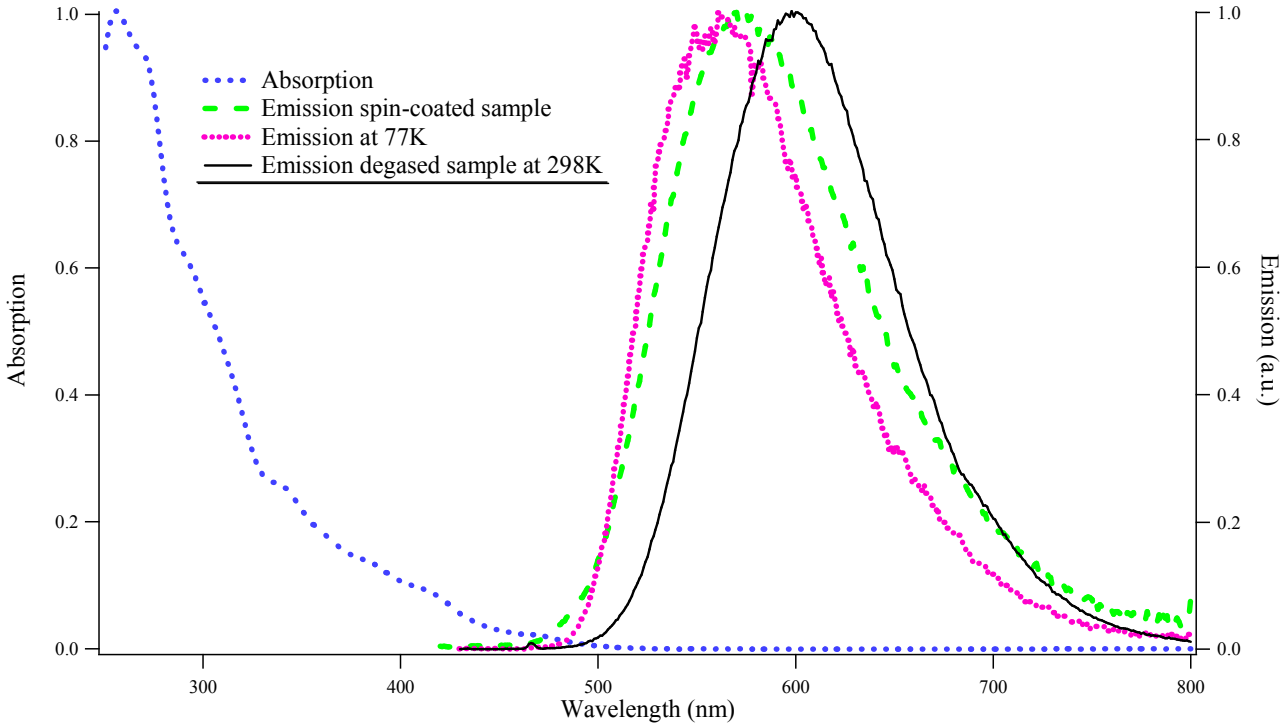
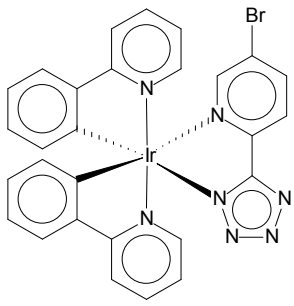


Figure S9. **Ir(PzTz)**: Absorption (2.5 10^{-5} M in CH_2Cl_2) and solution (degassed CH_2Cl_2) and solid state (77 K in butyronitrile glass; spin coated with PMMA, polymethyl-metacrylate).



Ir(BrPyTz)

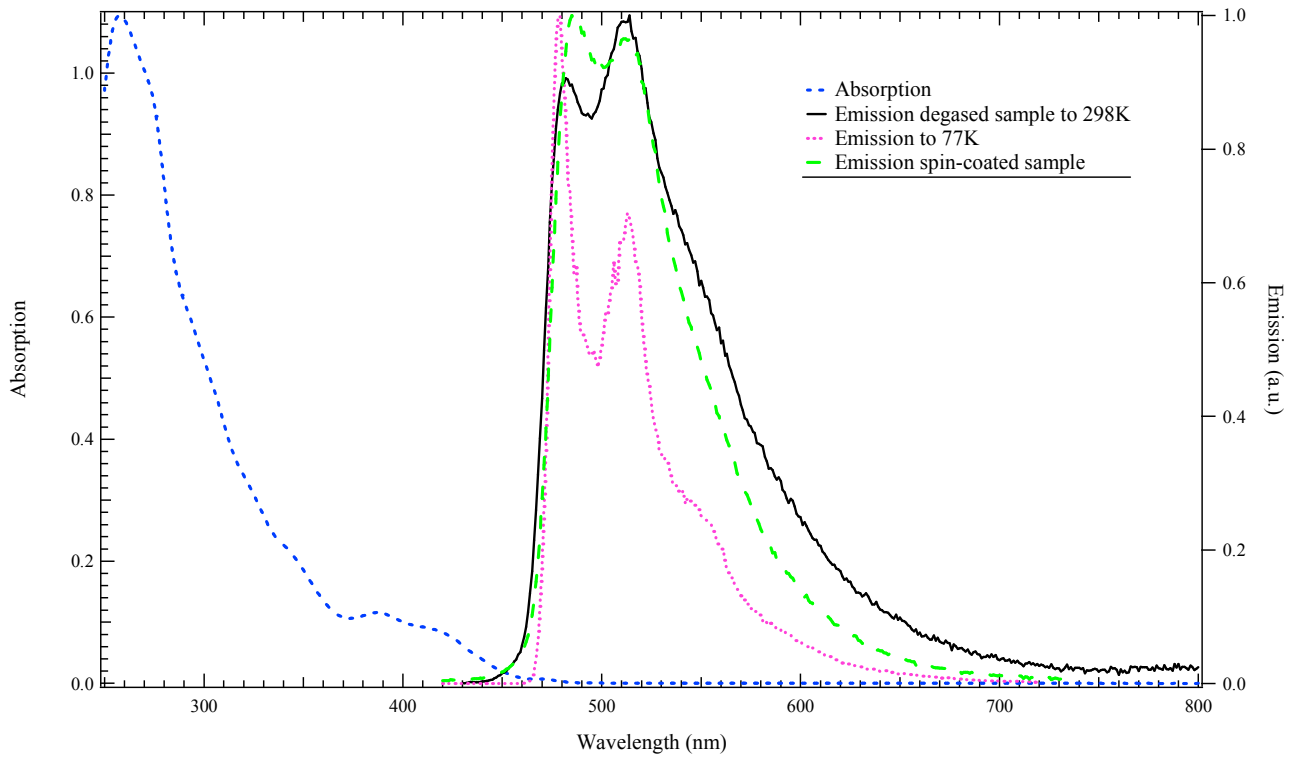
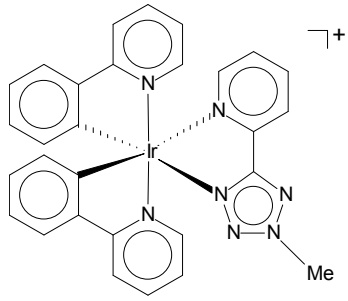


Figure S10. **Ir(BrPyTz)**: Absorption (2.5 10^{-5} M in CH_2Cl_2) and solution (degassed CH_2Cl_2) and solid state (77 K in butyronitrile glass; spin coated with PMMA, polymethyl-metacrylate).



[Ir(PyTzMe)]$^+$

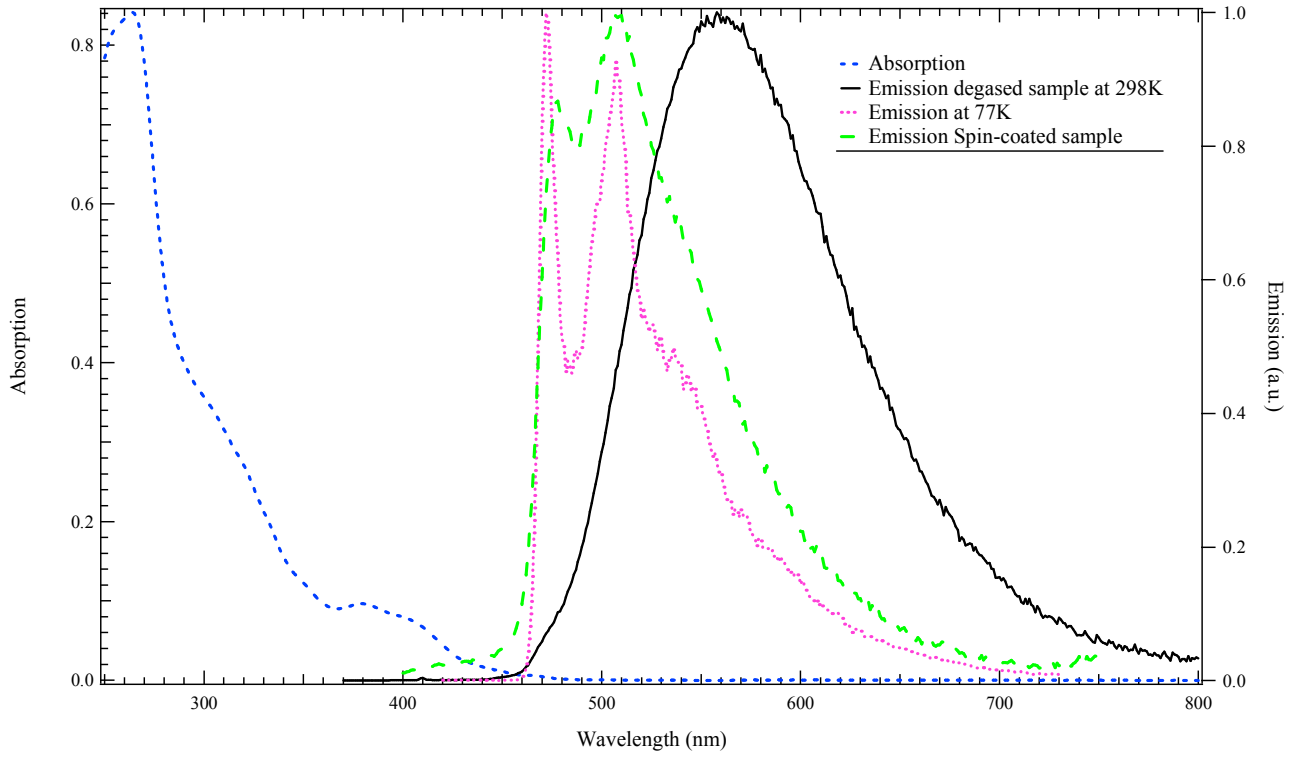
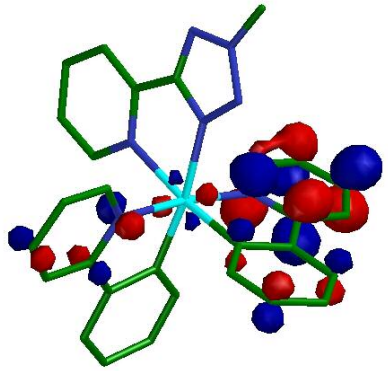


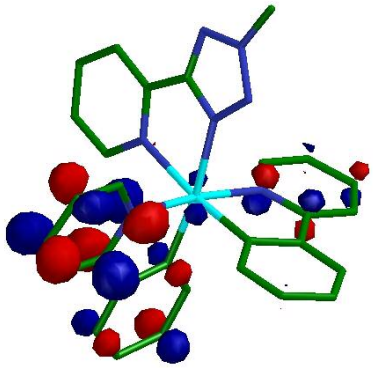
Figure S11. **[Ir(BrPyTz)]$^+$**: Absorption (2.8 10^{-5} M in CH_2Cl_2) and solution (degassed CH_2Cl_2) and solid state (77 K in butyronitrile glass; spin coated with PMMA, polymethyl-metacrylate).

Table S1. Selection of calculated bond lengths (Å) and angles (deg) for **Ir(PyTz)**, **Ir(PzTz)**, **Ir(BrPyTz)** and **[Ir(PyTzMe)]$^+$**.

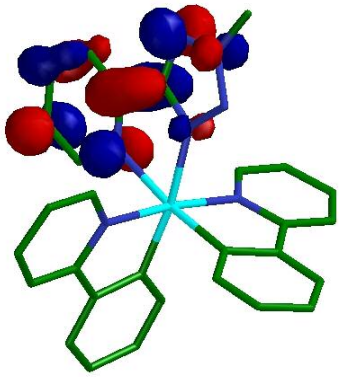
	Ir(PyTz) calc (exp)	**Ir(PzTz) calc (exp)**	**Ir(BrPyTz) calc (exp)**	**[Ir(PyTzMe)]$^+$ calc (exp)**
Ir(1)–N(1)	2.148 (2.140)	2.152 (2.147)	2.150 (2.137)	2.175 (2.143)
Ir(1)–N(5)	2.241 (2.161)	2.228 (2.156)	2.246 (2.196)	2.251 (2.182)
Ir(1)–N(6)	2.068 (2.049)	2.072 (2.041)	2.069 (2.033)	2.080 (2.042)
Ir(1)–N(7)	2.069 (2.047)	2.069 (2.046)	2.072 (2.048)	2.079 (2.048)
Ir(1)–C(17)	2.032 (2.016)	2.032 (2.007)	2.032 (1.987)	2.026 (1.999)
Ir(1)–C(28)	2.025 (2.008)	2.026 (2.002)	2.024 (1.991)	2.029 (2.008)



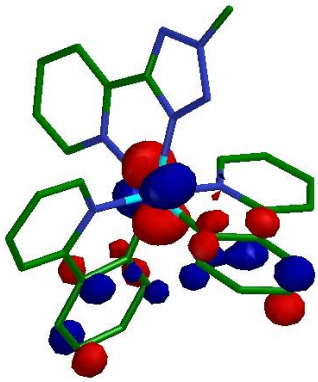
LUMO+1



LUMO



SOMO



HOMO

Figure S12. Plots of the HOMO, the singularly occupied molecular orbital (SOMO) and the two LUMO's of the fully optimized **[Ir(PyTzMe)]** (i.e., the one-electron reduced species) calculated at the UB3LYP/6-31G* (except for Ir, for which the LANL2DZ was used) level of theory. As expected, the SOMO resides on the tetrazolate ligand, while the LUMO and LUMO+1 are both localized on the two phenylpyridines.