A small cationic donor–acceptor iridium complex with a long-lived charge-separated state

Cyclic Voltammetry. Cyclic voltammogramms were measured with a computer controlled BAS CV50W potentiostat under an argon atmosphere in dry and oxygen-free solvents with 0.2 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. The concentration of the solute was about 0.5 mM. A conventional three electrode set-up consisting of a platinum disc working electrode, a Ag/AgCl pseudoreference electrode and a platinum wire counter electrode was used. The redox potentials were referenced against the ferrocene/ferrocenium redox couple as an internal standard.

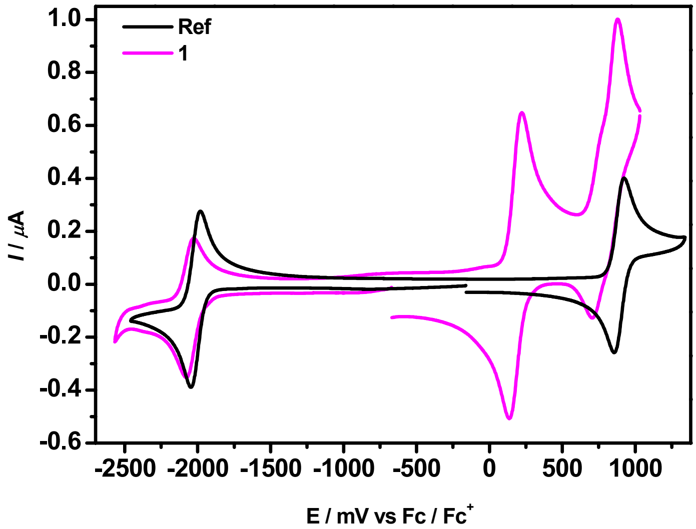


Fig. 1 Cyclic voltammetry of **1** and **Ref** in MeCN. The oxidation wave of 1 at 800 mV is overlaid by another oxidation process, presumably that of the second oxidation of a triarylamine moiety.

Spectroelectrochemistry. The spectroelectrochemical measurements were carried out in a thin-layer cell with a gold minigrid working electrode.[1] The potential (EG & G potentiostat/galvanostat model 363) applied to the electrode was varied in steps of 50 – 100 mV and an UV/vis/NIR spectrum was recorded with a JASCO V-570 UV/vis/NIR spectrometer ca. 1 min after each potential change.

UV/vis Spectoscopy. All solvents were of spectroscopic grade and were used without further purification. Absorption spectra were recorded with a JASCO V-570 UV/vis/NIR spectrometer in 1 cm quartz cuvettes.

Transient Absorption Measurements. Nanosecond transient absorption spectra were acquired on an Edinburgh LP 920 Laser Flash spectrometer. All solvents were of spectroscopic grade and used without purification. Measurements were carried out in a 1 cm quartz cell. The samples were degassed by bubbling through inert gas for 5 min. The samples were excited with 5 ns laser pulses at 24000 cm^{-1} (416 nm) or 28200 cm^{-1} (355 nm). The excitation pulse was produced by a Continuum Minilite II Nd:YAG laser operating at 10 Hz and the probe pulse was provided by a pulsed Xe flash lamp. For experiments at 24000 cm^{-1} the THG of the fundamental of 9400 cm^{-1} (1064 nm) was shifted to lower energy by means of a 50 cm Raman shifter which was charged with hydrogen (50 bar). The corresponding energy was selected by a Pellin-Broca prism. The 24000 cm^{-1} pump energy was used in order to avoid ionization of the triarylamine moieties.[2] The instrument response (ca. 8 ns) of the setup was determined by measuring the scattered light using an empty quartz cell. The decay curves were deconvoluted with the IRF using the corresponding spectrometer software. Residuals and autocorrelation function (without any significant structure) served as the main criteria in the evaluation of the fit.[2]

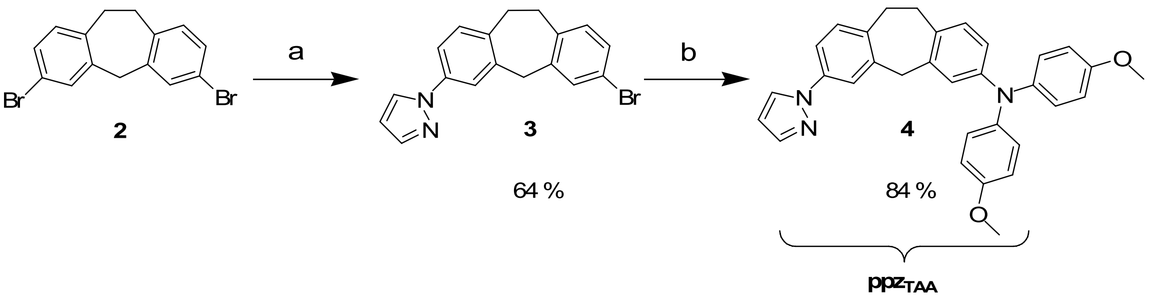
The quantum yield of CS state formation was estimated by $\Phi_{CS} = 1-(\Phi_1 / \Phi_{Ref})$. With Φ_1 >0.005 and $\Phi_1 = 0.31$ a quantum yield $\Phi_{CS} > 0.98$ results.

Measurements were performed at different concentrations (1.1-1.8 x 10^{-4} mol l^{-1}) and laser power (1.8 mJ – 3.2 mJ). Within these ranges there is no significant variation of lifetimes or amplitudes which excludes the presence of bimolecular deactivation processes. However, we found a noticeable temperature dependence primarily on the amplitudes which indicates an equilibrium in the excited state. Qualitatively, the amplitude of the longer lifetime decreases with increasing temperature. Further work to elucidate this phenomenon is currently in progress.

Fluorescence Spectroscopy. Steady state fluorescence spectra at RT were recorded on a PTI (Photon Technology International) fluorescence spectrometer QM-2000-4 with a cooled photomultiplier (R928 P) and a 75 W xenon short arc lamp in 1 cm quartz cells. All solvents were of spectroscopic grade and were used without further purification. The concentration was ca. 10^{-5} – 10^{-6} M and oxygen was removed by bubbling inert gas through the solutions for about 5 minutes before each measurement. The fluorescence quantum yields were determined relative to Rhodamine 101.[3]

Steady state emission experiments at 77 K were performed with an Edinburgh LP 920 Laser Flash spectrometer. The samples were dissolved in 2-MeTHF, filtered, filled in an EPR quartz tube and cooled down with liquid N_2 in an EPR dewar vessel. The wavelength dependence of the detector was corrected with the known spectrum of *N,N'*-Dimethylamino-*m*-nitrobenzene (*N,N'*- DMANB).[4]

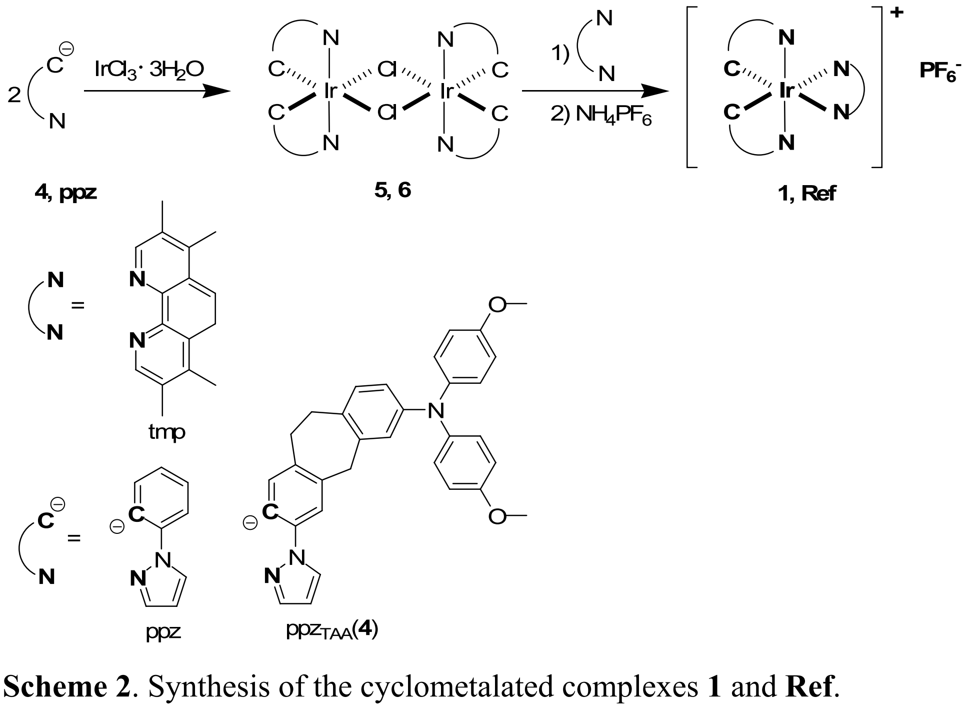
Fluorescent lifetime measurements. Time-dependent fluorescence measurements were performed with an Edinburgh LP 920 Laser Flash spectrometer. The analysis of the decay curves was performed in the same manner as those of the transient absorption measurements.



a: 1*H*-pyrazole, CuI, *trans*-1,2-cyclohexanediamine, potassium phosphate; dioxane, 110 °C, 24 h.

b: 4,4'-dimethoxydiphenylamine, $Pd_2(dba)_3 \cdot CHCl_3$, sodium *tert*-butoxide, P^tBu_3; toluene, 80 °C, 12 h.

Scheme 1. Synthesis of the triarylamine-substituted ligand.



Scheme 2. Synthesis of the cyclometalated complexes **1** and **Ref**.

Methods and Materials. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE 400 FT spectrometer and a Bruker AVANCE 600 DMX FT spectrometer at 25 °C. Mass spectra were recorded with a Finnigan MAT 90 spectrometer and with a Bruker Daltonic micrOTOF focus (ESI), respectively.

All chemicals were of standard quality and were used without further purification. All experiments were carried out under inert-gas conditions (nitrogen, dried with Sicapent from Merck, oxygen was removed by copper oxide catalyst R3-11 from BASF) in flame-dried Schlenk tubes. If necessary, the solvents were purified and dried by standard procedures and kept under inert gas atmosphere. Flash column chromatography was carried out using silica gel (32 – 63 μm) from MP Biomedicals. $IrCl_3 \cdot 3H_2O$ was purchased from Heraeus, 3,4,7,8-tetramethyl-1,10-phenanthroline from ALDRICH organics, 2-phenylpyrazole from ALDRICH and *N*,*N*'-dimethylamino-*m*-nitrobenzene (*N*,*N*'-DMANB) from ACROS organics.

General procedure for the synthesis of cyclometalated Ir(III) dichloro-bridged dimers $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2$ (GP1).[5] $IrCl_3 \cdot 3H_2O$ was mixed together with 2 – 2.5 equiv of the cyclometalating ligand in a 3 : 1 mixture of 2-ethoxyethanol and deionised water. The solution was heated to 110 °C under inert gas atmosphere. After cooling to room temperature the dimers were precipitated by pouring into water. The precipitate was filtered, washed twice with water, and dried. The dimers were used for the following reaction without further purification.

General procedure for the synthesis of $(C^\wedge N)_2Ir(N^\wedge N)^+PF_6^-$ complexes (GP2).[6-8,] The dichloro-bridged iridium dimer and 2.0 equiv of the diimine ligand were mixed together in dichlormethane. The solution was then refluxed for 12 h under inert gas atmosphere. After cooling to room temperature the solvent was evaporated and the resulting solid was dissolved in methanol. After filtration of the solution, counterion exchange from Cl^- to PF_6^- was accomplished via metathesis reaction in which the complexes were precipitated from the filtered methanol solution with an ammonium hexafluorophosphate salt solution in methanol. The resulting precipitate was filtered, washed twice with water and methanol, and dried.

3-Pyrazolyl-7-bromo-10,11-dihydro-5*H*-dibenzo[a,d]-cycloheptene (3).[9] 3,7-Dibromo-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene[2] **2** (1.00 g; 2.84 mmol), 1*H*-pyrazole (193 mg; 2.84 mmol), CuI (54.1 mg; 0.28 mmol), *trans*-1,2-cyclohexanediamine (13.7 μl; 1.14 mmol) and potassium phosphate (1.27 g; 5.97 mmol) were suspended in dry dioxane (2 ml) under nitrogen atmosphere. The solution was then refluxed for 20 h. The solvent was evaporated, the resulting solid was suspended in dichloromethane and washed with water. The crude product was purified by flash chromatography (CH_2Cl_2 : PE = 1:1); yield: 307 mg (0.91 mmol; 64 %) of a colourless solid. M. p. 145 °C.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.86 (d, $^3J_{HH}$ = 2.5 Hz, 1H); 7.68 (d, $^3J_{HH}$ = 1.4 Hz, 1H); 7.53 (d, $^3J_{HH}$ = 2.2 Hz, 1H); 7.40 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.4 Hz, 1H); 7.32 (d, $^3J_{HH}$ = 2.0 Hz, 1H); 7.24 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.2 Hz, 1H); 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 1H); 6.97 (d, $^3J_{HH}$ = 8.1 Hz, 1H); 6.42 (dd, $^3J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 1.9 Hz, 1H); 4.09 (s, 2H); 3.18 – 3.09 (-, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 141.0 (tert.); 140.6 (quart.); 139.6 (quart.); 138.5 (quart.); 138.1 (quart.); 137.3 (quart.); 131.9 (tert.); 131.4 (tert.); 130.8 (tert.); 129.9 (tert.); 126.8 (tert.); 120.1 (tert.); 119.6 (quart.); 117.6 (tert.); 107.5 (tert.); 40.7 (sec.); 32.0 (sec.); 31.9 (sec.). HRMS (70 eV, EI): *m/z* calcd for [M^+] = $C_{18}H_{15}BrN_2^{\cdot+}$: 338.04136; found: 338.04081 (Δ = 1.49 ppm).

3-Pyrazolyl-7-(4,4'-dimethoxydiphenylamino)-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (4).[10, 11] A solution of 3-pyrazolyl-7-bromo-10,11-dihydro-5*H*-dibenzo[a,d]-cycloheptene (**3**) (690 mg, 2.03 mmol), 4,4'-dimethoxydiphenylamine (513 mg, 2.24 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (168 mg, 0.16 mmol), sodium *tert*-butoxide (489 mg, 5.09 mmol) P^tBu_3 (0.24 ml, 0.24 mmol) in dry toluene (5 ml) was stirred under nitrogen atmosphere at 80 °C for 12 h. The solvent was evaporated and the resulting solid was diluted with dichloromethane. The aqueous phase was extracted with dichloromethane. The crude product was purified by flash chromatography (CH_2Cl_2 : PE = 1:1); yield: 836 mg (1.71 mmol; 84 %) of a colourless solid. M. p. 165 °C.

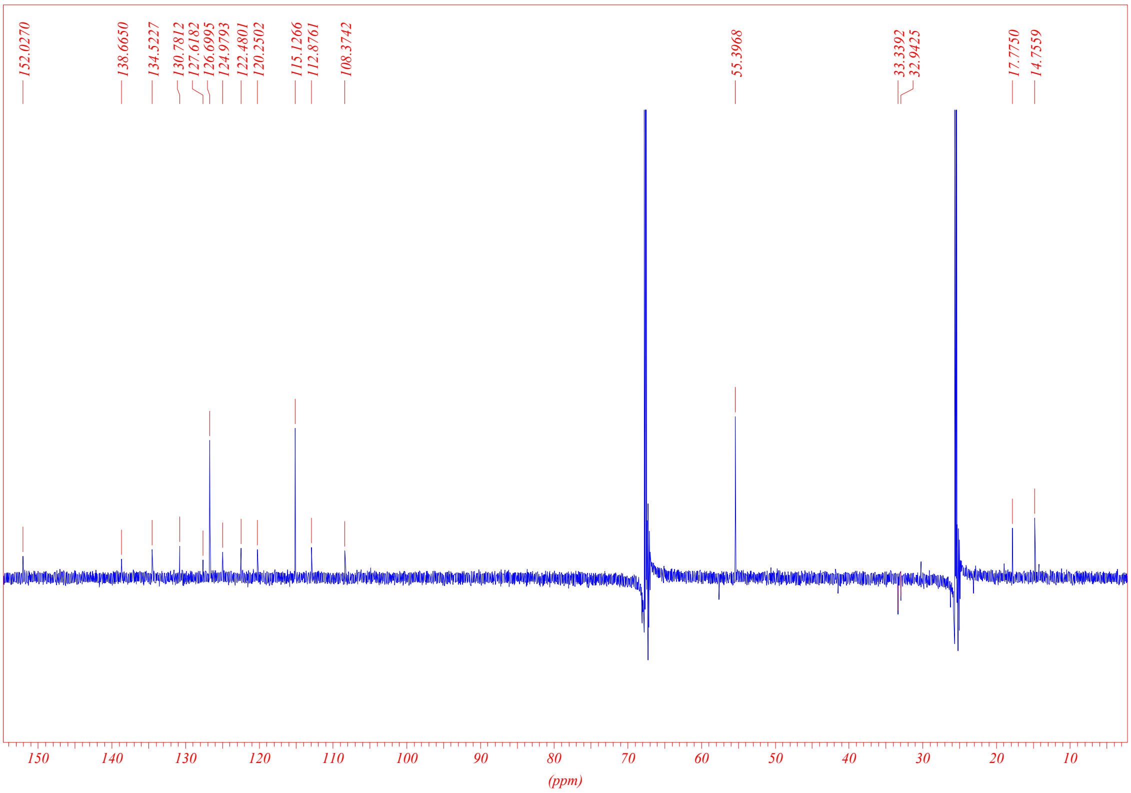
^{1}H NMR (601 MHz, d_8-THF): δ 7.91(-, 1H); 7.65 (-, 1H); 7.47 (-, 1H); 7.44 (-, 1H); 7.20 (-, 1H); 6.97 (AA', 4H); 6.94 (-, 1H); 6.80 (BB', 4H); 6.78 (-, 1H); 6.70 (-, 1H); 6.43 (-, 1H); 4.00 (s, 2H); 3.77 (s, 6H), 3.18 – 3.09 (-, 4H). ^{13}C NMR (150.9 MHz, d_8-THF): δ 156.0 (quart.); 147.2 (quart.); 141.6 (quart.); 140.9 (tert.); 140.8 (quart.); 139.4 (quart.); 138.5 (quart.); 138.1 (quart.); 131.8 (quart.); 130.8 (tert.); 130.6 (tert.); 126.9 (tert.); 126.4 (tert.); 122.0 (tert.); 120.0 (tert.); 119.8 (tert.); 117.3 (tert.); 114.8 (tert.); 107.5 (tert.); 55.7 (prim.); 41.2 (sec.); 32.5 (sec.); 32.0 (sec.). HRMS (70 eV, EI): *m/z* calcd for [M^+] = $C_{32}H_{29}N_3O_2^{\cdot+}$: 487.22543; found: 487.22532 (Δ = 0.22 ppm).

Dimer (5). Following GP1**:** 3-Pyrazolyl-7-(4,4'-dimethoxydiphenylamino)-10,11-dihydro-5*H*-dibenzo[a,d]-cycloheptene (**6**) (231 mg, 0.47 mmol), $IrCl_3\cdot 3H_2O$ (80.0 mg, 0.23 mmol), ethoxyethanol : water = 3 : 1 (3 ml), 14 h at 80 °C, yield: 267 mg (0.11 mmol, 49 %) of a bright yellow solid.

Dimer (6). Following GP1**:** 2-Phenylpyrazole (114 mg, 0.79 mmol), $IrCl_3 \cdot 3H_2O$ (112 mg, 0.32 mmol), ethoxyethanol : water = 3 : 1 (3 ml), 14 h at 80 °C, yield: 71.0 mg (0.11 mmol, 44 %) of a yellow solid.

Complex (1): Following GP2: Dimer (**5**) (75.0 mg, 31.2 μmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (14.8 mg, 62.5 μmol), dichloromethane (2 ml), 14 h at 50 °C, yield: 40.0 mg (25.9 μmol, 41 %) of a green solid. M. p. 214 °C.

^{1}H NMR (601 MHz, d_8-THF): δ 8.58 (-, 2H); 8.55 (-, 2H); 8.34 (s, 2H); 7.45 (s, 2H); 7.09 (AA', 8H); 7.00 (-, 4H); 6,93 (BB', 8H); 6.89 (-, 2H); 6.80 (-, 2H); 6.59 (-, 2H); 6.31 (s, 2H); 3.98 – 4.15 (-, 4H); 3.88 (s, 12H); 3.00 – 3.19 (-, 14H); 2.52 (s, 6H). ^{13}C NMR (150.9 MHz, d_8-THF): δ 156.6 (quart.); 152.1 (tert.); 147.7 (quart.); 147.2 (quart.); 147.1 (quart.); 142.5 (quart.); 142.2 (tert.); 140.2 (quart.); 138.9 (tert.); 138.7 (quart.); 135.6 (quart.); 134.6 (quart.); 134.5 (quart.); 132.6 (quart.); 130.9 (tert.); 130.6 (quart.); 130.5 (quart.); 127.7 (tert.); 126.7 (tert.); 125.0 (tert.); 122.5 (tert.); 120.3 (tert.); 115.2 (tert.); 112.9 (tert.); 108.4 (tert.); 55.4 (prim.); 41.5 (sec.); 33.4 (sec.); 33.0 (sec.); 17.8 (prim.); 14.8 (prim.). ESI pos. (high resolution): calcd for $[M^+] = C_{80}H_{72}IrN_8O_4^+$: 1399.5272; found: 1399.5277 (Δ = 0.33 ppm).



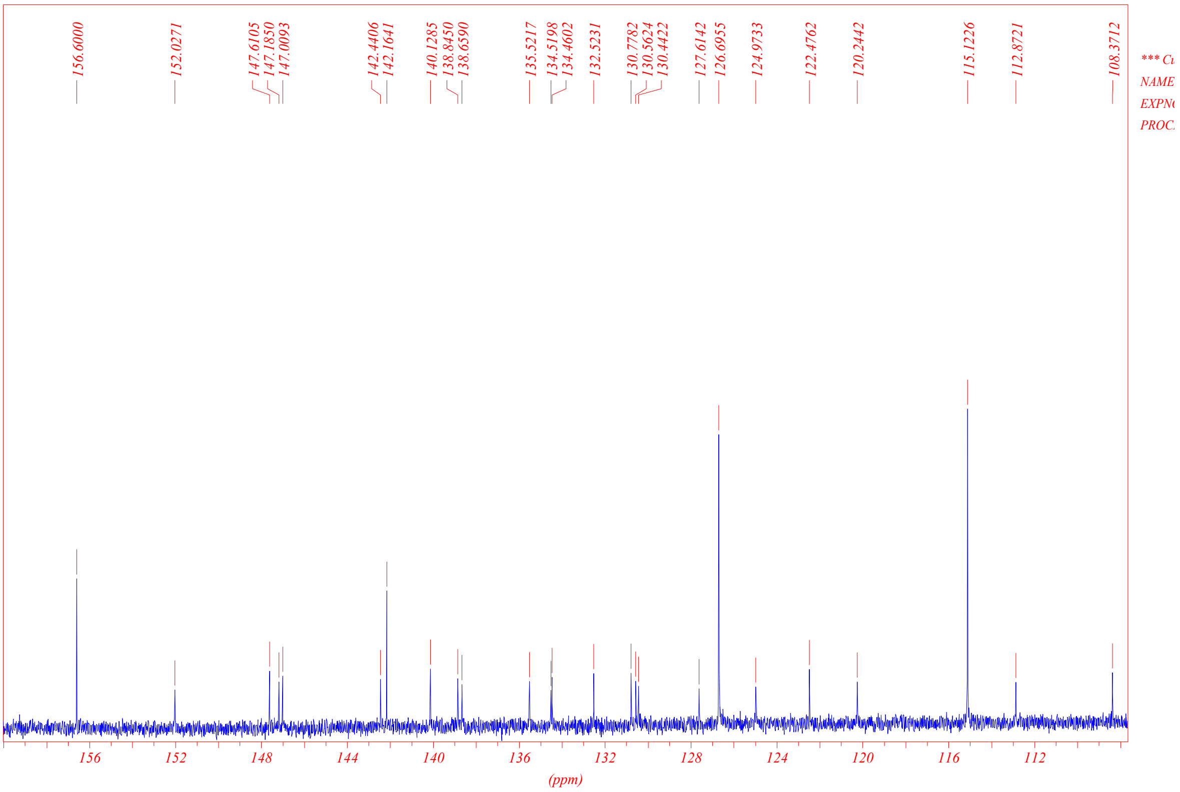


Fig. 2 ^{13}C – NMR of **1** in d$_8$-THF

Complex (Ref): Following GP2: Dimer (**6**) (100 mg, 97.3 μmol), 3,4,7,8-tetramethyl-1,10-phenanthroline (46.0 mg, 0.19 mmol), dichloromethane (2 ml), 14 h at 50 °C, yield: 62.0 mg (72.1 μmol, 37%) of green solid. M. p. 251 °C.

^{1}H NMR (601 MHz, d$_6$-Acetone): δ 8.68 (-, 2H); 8.52 (-, 2H); 8.30 (-, 2H); 7.65 (-, 2H); 7.08 (-, 4H); 6.91 (-, 2H); 6.58 (-, 2H); 6.44 (-, 2H); 2.91 (s, 6H); 2.43 (2, 6H). ^{13}C NMR (150.9 MHz, d$_6$-Acetone): δ 152.7 (tert.); 147.6 (quart.); 147.3 (quart.); 144.6 (quart.); 139.6 (tert.); 136.0 (quart.); 134.3 (tert.); 133.5 (quart.); 130.9 (quart.); 128.9 (tert.); 127.6 (tert.); 125.4 (tert.); 124.2 (tert.); 112.9 (tert.); 109.1 (tert.); 18.2 (prim.); 15.3 (prim.). ESI pos. (high resolution calcd for [M$^+$] = $C_{34}H_{30}IrN_6^+$: 713.2142; found: 713.2132 (Δ = 1.36 ppm).

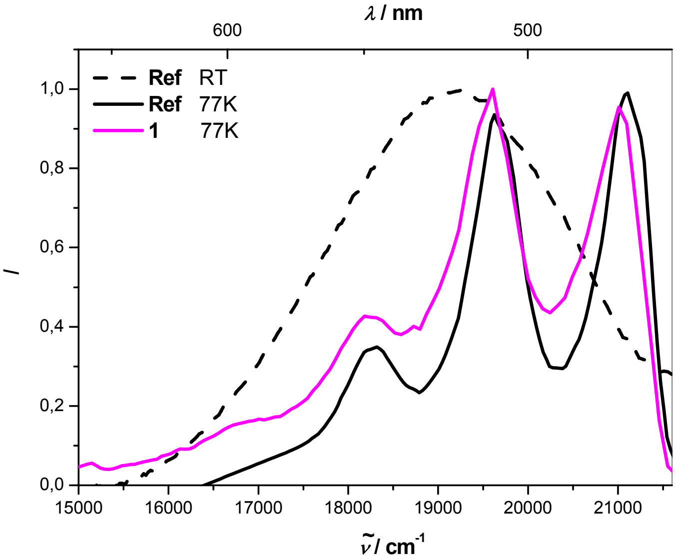


Fig 3 Corrected Emission spectra of **1** and **Ref** at RT and at 77 K.

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