Electronic Supporting Information

An Iridium Caged Complex with Low Oxygen Quenching.

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General

Oxygen- or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware, using Schlenk techniques. Unless otherwise stated, commercial grade reagents (Aldrich) were used without further purification. The purity of the final compounds was determined by NMR and MS spectrometry. Due to the low amount of final compound, it was not possible to perform elemental analysis. The NMR experiments were performed on a Bruker Avance II NMR spectrometer operating at 600.35 MHz for ^{1}H and 150.09 MHz for ^{13}C or on a Varian Unity 300 spectrometer operating at 300 MHz for ^{1}H. Chemicals shifts are given in ppm using the residual solvent signal as reference. Mass spectra were acquired on a Micromass LCT (ESI-MS) or Voyager-DE RP (MALDI-MS) spectrometer. IR spectra were measured on a Thermo Scientific Nicolet^{TM} 6700 FT-IR spectrometer equipped with a Smart Orbit diamond ATR accessory. Main bands are reported and assigned to functional groups by using the following abbreviations: br. = broad band; str. = stretching band; def. = deformation band. UV-Vis spectra were measured on a Perkin Elmer Lambda 850 UV-Vis spectrophotometer. Steady-state luminescence spectra were measured using an Edinburgh FS900 fluorospectrometer. A 450 W xenon arc lamp was used as excitation source. Luminescence quantum yields at room temperature (Φ and Φ_{air})

were evaluated by comparing wavelength-integrated intensities (I) of isoabsorptive optically diluted solutions (Abs<0.1) with reference to [Ru(bpy)$_3$]Cl$_2$ (Φ_R =0.028 in air-equilibrated water), and perylene (Φ_R=0.92 in EtOH) standards and by using the equation (1)

$$\Phi = \Phi_R \frac{n^2 I}{n_R^2 I_R} \tag{1}$$

where n and n_R are the refractive index of the sample and reference solvent, respectively.[1]

Fluorescence lifetimes were determined using a FluoroMax4, Horiba Jobin Yvon spectrophotometer, equipped with a TCSPC extension and a pulsed 462 nm NanoLED for excitation (all Horiba Jobin Yvon). The recorded data were analyzed using the DAS6 software package of Horiba Jobin Yvon.

Degassed solutions were prepared by four freeze-pump-thaw cycles. Solutions with different oxygen concentration, suitable for the Stern-Volmer quenching studies, were prepared by using N_2/O_2 mixtures prepared with a Brooks 5850S Mass Flow control and by purging the fluorophore solutions for 40 minutes. Ir(ppy)$_3$ (sublimed grade) was purchased from Sigma Aldrich and its purity was checked by NMR prior to use.

Synthetic and Analytical Details

Methyl 6-bromonicotinate. 5.73g (28.4 mmol) of 6-bromonicotinic acid were dissolved in 100ml of Methanol/Ether 1:1. 23ml (46 mmol) of trimethylsilyldiazomethane (2M in hexane) were added dropwise during 5 hours till the reaction mixture showed a permanent yellow colour. The reaction was quenched by addition of acetic acid (5ml) and the solvent was evaporated. The mixture was then dissolved in ether and washed three times with saturated $NaHCO_3$ and eventually with brine. The solution was dried over Na_2SO_4 and the solvent removed under vacuum. Yielded 5.5g (26 mmol; 90%) of compound. ^{1}H-NMR and ESI-MS are compatible with the data reported in literature.[2]

4-(5-(methoxycarbonyl)pyridin-2-yl)benzoic acid (1). 2.504 g (11.575 mmol) of methyl 6-bromonicotinate, 2.132 g (12.79 mmol) of 4-carboxybenzylboronic acid, 4.206 g (27.7 mmol) of CsF and 627 mg (0.54 mmol) of $Pd(PPh_3)_4$ were dissolved in 100ml of methanol and oxygen was removed by Ar/vacuum cycles. The mixture was refluxed overnight. The crude mixture was filtered and the solvent evaporated. The crude was dissolved in saturated solution of Na_2CO_3 and washed 4 times with $CHCl_3$. The pH of the aqueous phase was then adjusted to pH=2 (conc. HCl) and the resulting precipitate filtrated and dried under vacuum over P_2O_5 overnight. Obtained 912 mg (3.55 mmol; 31%).

^{1}H-NMR (300 MHz, *d*$_6$-DMSO): δ 3.91 (s, 3H); 8.06 (d, 2H, $^3J_{HH}$ = 4.5); 8.21 (d, 1H, $^3J_{HH}$ = 3), 8.26 (d, 2H, $^3J_{HH}$ = 4.5), 8.39 (d, 1H, $^3J_{HH}$ = 3), 9.19 (s, 1H). ^{13}C-NMR (150 MHz, *d*$_6$-DMSO): δ 52.97, 121.28, 125.14, 127.75, 130.35, 138.65, 150.70, 158.99, 165. 52, 167.42. FT-IR(neat): cm^{-1} 3000 br (OH str.), 1725 (C=O str. ester), 1720 (C=O str. acid), 1678 (C=O str. acid), 1427 (OH def, acid) 1286 (C-O str. ester), 1115 (OCH_2 ester), 939 (OH def. acid). ESI-MS calcd. for $C_{14}H_{11}NO4$ [M^+] 257.07, found 257.1.

Tripodal ligand (2). 912mg (3,55 mmol) of **1**, 143 µl (0.95 mmol) of tris(2-aminoethyl)amine , 745 mg (3.6 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) and 482 mg (3.57 mmol) of 1-Hydroxybenzotriazole (HOBt) were dissolved in 50ml of anhydrous dimethylacetamide and were stirred at 60°C overnight. The reaction mixture was filtrated and the solid dissolved in conc. HCl. After filtration of this solution (in order to remove the side product of the DCC coupling) the product was precipitated by addition of conc. NaOH and was dried over P_2O_5 overnight giving a 699 mg of pure compound (0.8 mmol; 84%). ^{1}H-NMR (300 MHz, D_2O, TFA): δ 2.23 (s-br, 2H); 2.44 (s-br, 2H); 2.51 (s, 3H); 6.40 (d, 2H, $^3J_{HH}$ = 4); 6.46 (d, 2H, $^3J_{HH}$ = 4); 6.79 (d, 1H, $^3J_{HH}$ = 3); 7.53 (d, 1H, $^3J_{HH}$ = 3); 7.79 (s, 1H). Due to the extremely low solubility, it was not possible to acquire the ^{13}C-NMR. MALDI-MS calcd. for $C_{48}H_{46}N_7O_9$ [$M+H^+$] 864.34, found 864.34. FT-IR(neat): cm^{-1} 3323 (NH str.), 2928 (CH_2 and OCH_3 str.), 2849 (N-CH_2 and CH_2 str.) 1725 (C=O str. ester), 1625 (C=O str. amide), 1536 (N-H str.), 1475 (CH_2-N st.), 1292 (C-O str. ester), 1120 (OCH_2 ester), 751 (N-C-O str. amide).

Ir(III) hemicaged methylester derivative (3). 619 mg (0.72 mmol) of **2**, 217 mg (0.73 mmol) of iridium(III) chloride hydrate and 477 mg (2.16 mmol) of silver trifluoroacetate are dissolved in 25 ml of nitrogen purged ethylene glycol and refluxed overnight. After cooling to room temperature, the mixture was precipitated with brine, filtered and the solid dissolved in MeOH. The solvent was removed and the solid dissolved in THF:H_2O (1:1) and 601 mg (25 mmol) of LiOH was added and the solution stirred overnight at 60°C. The aqueous phase was treated with dil. HCl (1M) to pH=5 and the orange precipitate collected, suspended in CH_2Cl_2:MeOH (9:1) and esterified with an excess of trimethylsilyldiazomethane (2M in hexane). The reaction mixture was filtered, the solvent removed and the crude product purified by column chromatography (SiO_2, CH_2Cl_2:MeOH 94:6) and recrystallized from CH_2Cl_2/Hexane. Obtained 151 mg (0.14 mmol; 20%).

^{1}H-NMR (600 MHz, *d*$_7$-DMF): δ 8.52 (1H, d, $^3J_{HH}$ = 6 Hz); 8.41 (1H, d, $^3J_{HH}$ = 6 Hz); 8.19 (1H, s); 8.05 (1H, d, $^3J_{HH}$ = 6 Hz), 7.53 (1H, s); 7.32 (1H, d, $^3J_{HH}$ = 6 Hz); 6.97 (1H, s broad); 3.80 (3H, s); 3.66 (1H, s broad); 3.26 (1H, t, $^2J_{HH}$ = 12); 2.93 (1H, s broad); 2.32 (1H, d, $^2J_{HH}$ = 6 Hz) (see Figure 1 for peak assignment). MALDI-MS calcd. for $C_{48}H_{42}IrN_7O_9$ [M+H$^+$] 1054.27, found 1054.28. . FT-IR(neat): cm^{-1} 3422 (N-H str.), 2952 (OCH_3 str.), 2895 (CH_2 str.), 2841 (N-CH_2 str.), 1721 (C=O str. ester), 1650 (C=O str. amide), 1601 (N-H str.), 1548 (CNH str.), 1473 (N-CH_2 str.), 1292 (C-O str. ester), 1126 (OCH_2 ester), 757 (N-C-O str. amide).

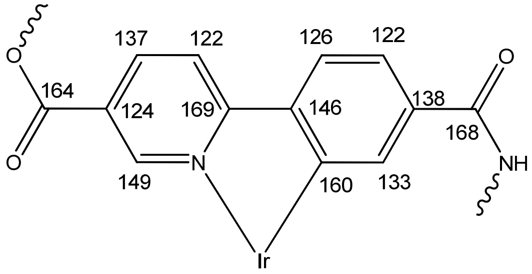

Figure S1. ^{13}C assignment of aromatic protons of hemicaged complex **3**.

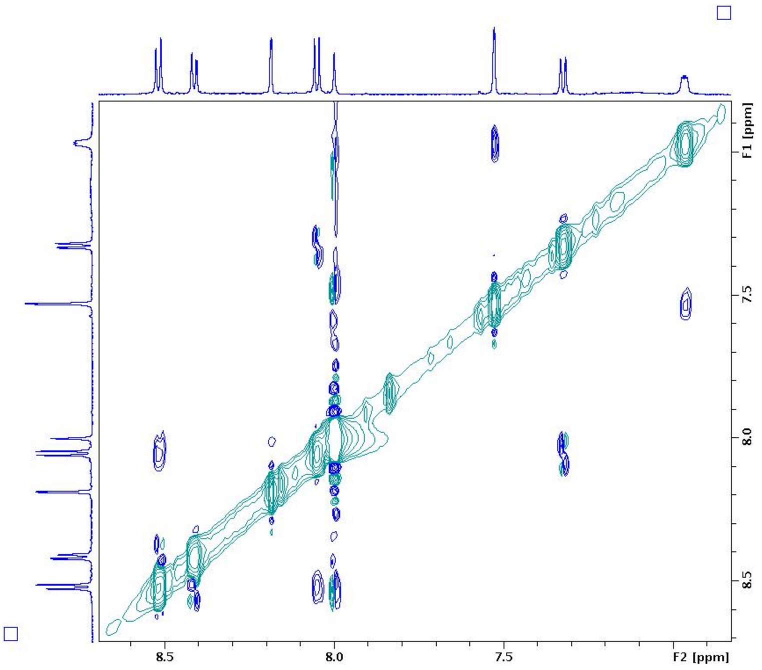

Figure S2. 2D-ROESY spectrum of Ir(III)-hemicaged complex (**3**). Region of the aromatic protons.

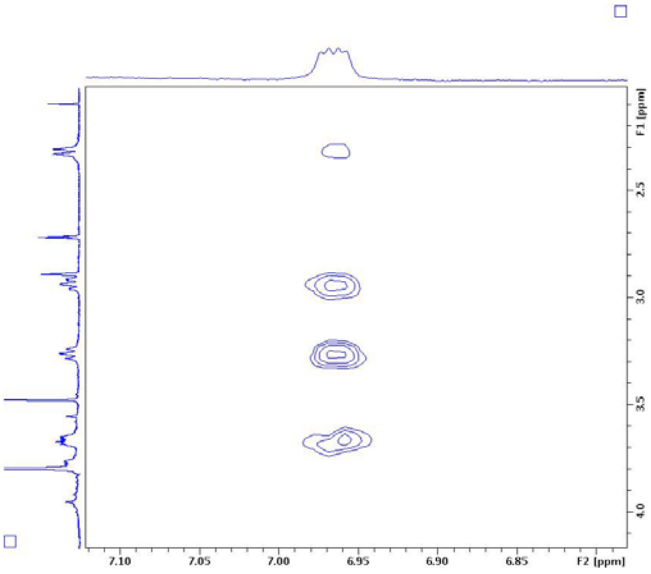

Figure S3. 2D-ROESY spectrum of Ir(III)-hemicaged complex (**3**). Long range coupling of amide proton with aliphatic protons.

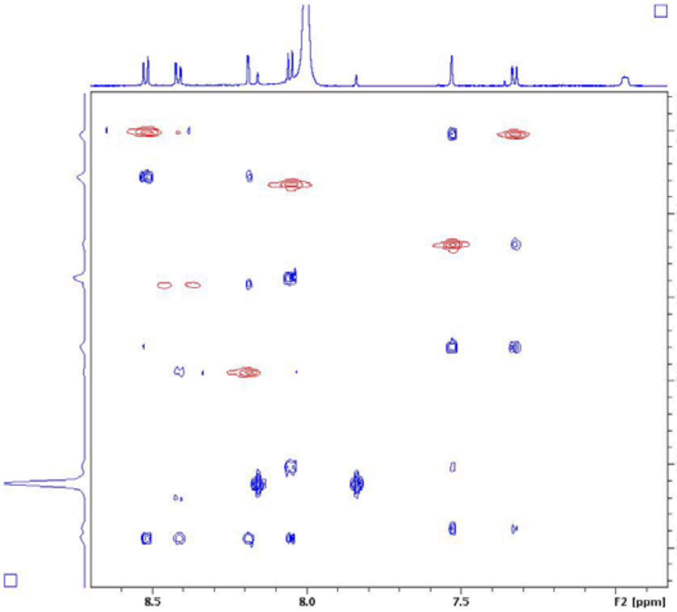

Figure S4. HC-HMQC (red) and HC-HMBC (blue) of hemicaged complex (**3**). Aromatic protons.

Ir(III) caged complex 4. 22mg of **3** (0.02 mmol) were dissolved in THF:H_2O (1:1) and hydrolized with LiOH 10 mg (0.4 mmol) overnight. The THF was then removed under vacuum and the acid precipitated with HCl (1 M). The solid was dried overnight over P_2O_5 and dissolved in 10ml of anhydrous dimethylacetamide. 19 mg (92.1 µmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) and 12 mg (88.8 µmol) of 1-Hydroxybenzotriazole (HOBt) were added to this mixture and subsequenthly a solution of 2.96 µl (mmol) of tris(2-aminoethyl)amine in anhydrous dimethylacetamide was added dropwise. The reaction mixture was heated at 50°C overnight under inert atmosphere and then cooled down to room temperature. The mixture was filtrated and precipitated with diethylether. The compound was purified by preparative TLC (CH_2Cl_2:MeOH 9:1). Obtained 5mg (4.5 µmol; 22%).

^{1}H-NMR (600 MHz, d_7-DMF): δ 8.38 (1H, d, $^3J_{HH}$ = 3 Hz); 8.25 (1H, d, $^3J_{HH}$ = 3 Hz); 7.93 (1H, d, $^3J_{HH}$ = 6 Hz); 7.82 (1H, s); 7.81 (1H, t broad); 7.76 (1H, s); 7.33 (1H, d, $^3J_{HH}$ = 6 Hz); 7.15 (1H, s broad); 3.70 (1H, d broad); 3.56 (1H, d broad); 3.39 (1H, d broad); 3.30 (1H, d, $^2J_{HH}$ = 12 Hz); 3.07-2.98 (2H, multiplet); 2.34 (1H, d, $^2J_{HH}$ = 6 Hz); 2.22 (1H, d, $^2J_{HH}$ = 6 Hz). (see Figure 1 for peak assignment). MALDI-MS calcd. for $C_{51}H_{48}IrN_{11}O_6$ [M+H$^+$] 1104.34, found 1104.34. UV-Vis (DMF) $\lambda_{max.}$ = 402 nm ($\varepsilon = 2.25{\cdot}10^6$ L·mol^{-1}cm^{-1}).

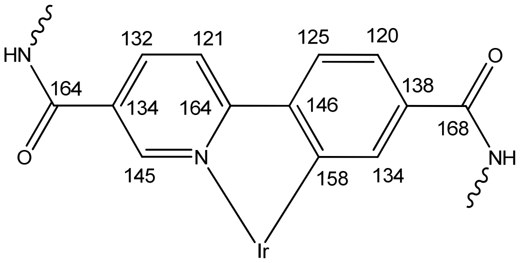

Figure S5. ^{13}C assignment of aromatic protons of caged complex **4**.

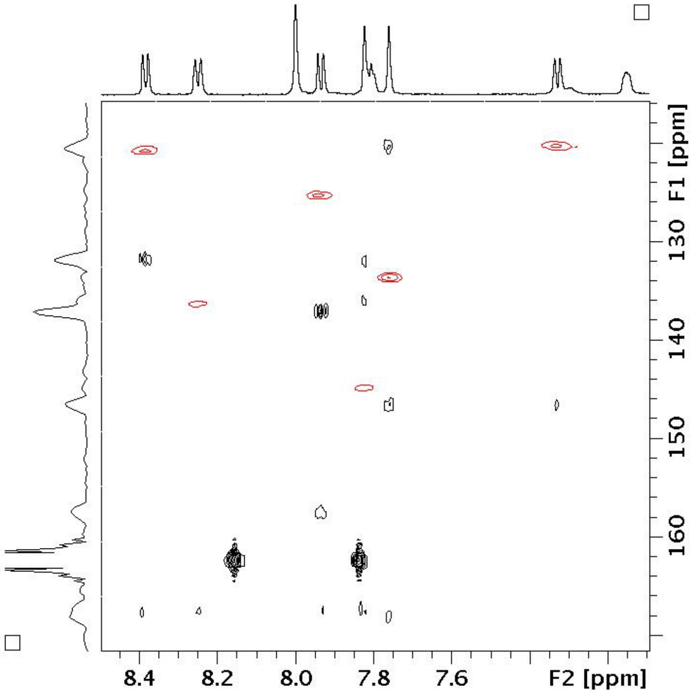

Figure S6. HC-HMQC (red) and HC-HMBC (black) spectra of Ir(III).caged (**4**). Aromatic protons.

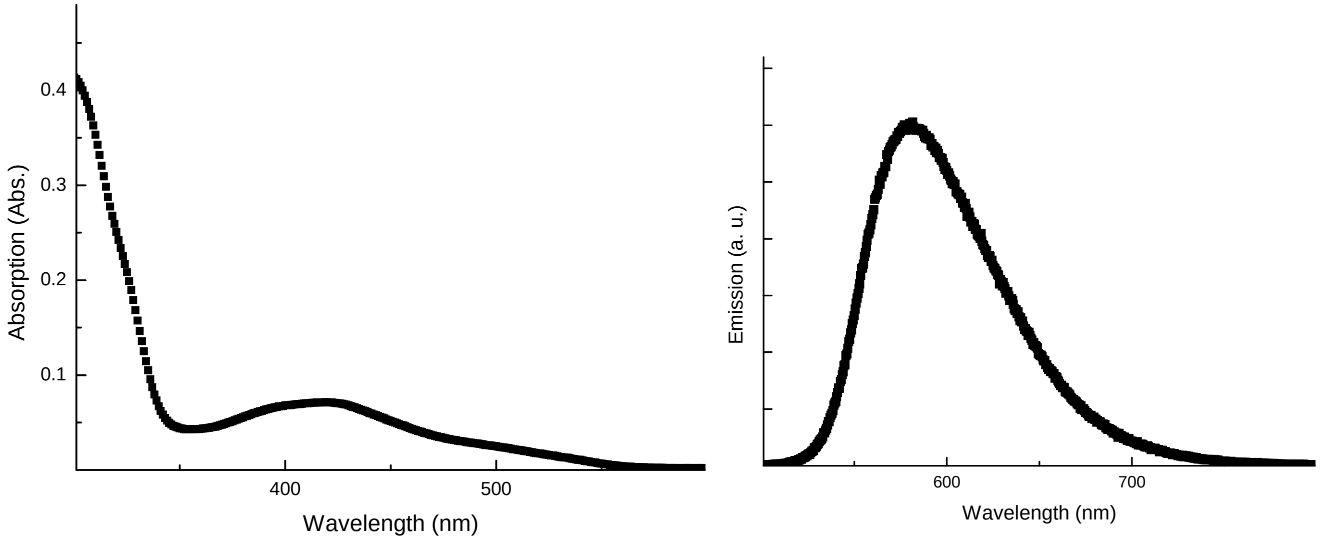

Figure S7. UV-Vis absorption (left) and fluorescence emission (right) of Ir(III)-hemicaged complex **3** in DMF.

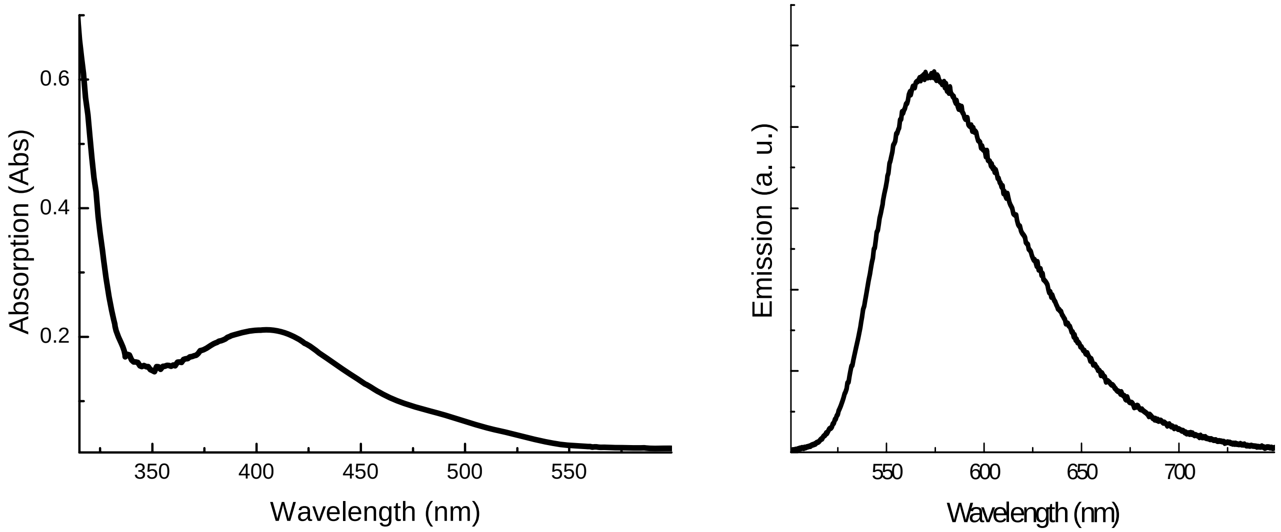

Figure S8. UV-Vis absorption (left) and fluorescence emission (right) of Ir(III)-caged complex **4** in DMF.

1. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T., *Handbook of Photochemistry*. CRC Press: Boca Raton, 2006.
2. Hashizume, H.; Ito, H.; Kanaya, N.; Nagashima, H.; Usui, H.; Oshima, R.; Kanao, M.; Tomoda, H.; Sunazuka, T.; Nagamitsu, T.; Kumagai, H.; Omura, S., *Heterocycles* **1994,** *38*.