Electronic supplementary information for

Proton-coupled electron transfer from a luminescent excited state

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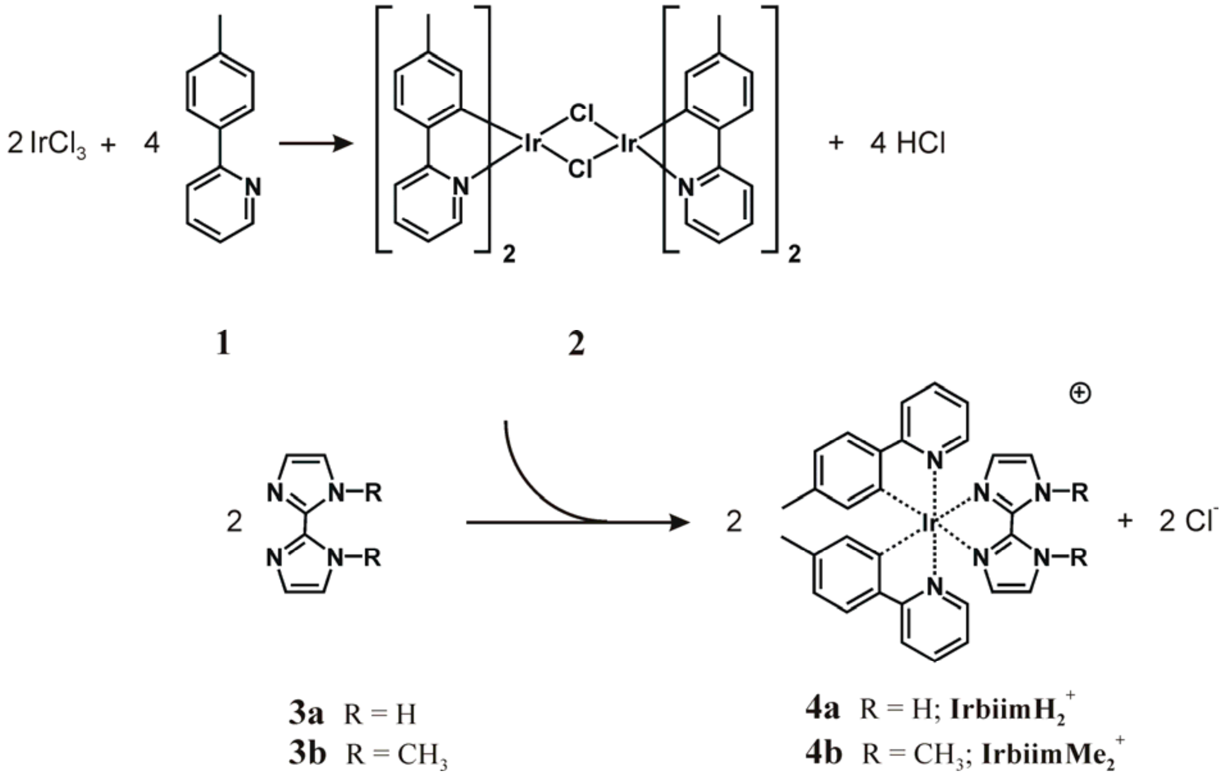
Synthesis and characterization of the iridium complexes

The two cyclometalated iridium(III) complexes $IrbiimH_2^+$ and $IrbiimMe_2^+$ were synthesized according to the generally adopted strategy illustrated in the following scheme.[1-3]



1 **2**

3a R = H
3b R = CH_3

4a R = H; **$IrbiimH_2^+$**
4b R = CH_3; **$IrbiimMe_2^+$**

In a typical procedure, 1 mmol of $IrCl_3$ (Alfa Aeasar, Product No. 12158) was reacted with 2.2 mmol 2-(*p*-tolyl)pyridine **1** (Sigma Aldrich, Product No. 198870) in a solvent mixture comprised of 15 ml 2-ethoxyethanol and 5 ml de-ionized water. After refluxing for 24 hours, the resulting iridium dimer **2** was filtered off using a glass frit (porosity No. 3). It was washed first with de-ionized water, then with diethyl ether. Yields were typically above 60 %. The ^{1}H-NMR spectrum of **2** is consistent with the heterocyclic rings of the cyclometalating ligand being in a *trans* disposition; this is in line with previous studies.

2,2’-biimidazole **3a** and N,N’-dimethyl-2,2’-biimidazole **3b** were synthesized following published protocols.[4, 5] In order to obtain the target complexes **4a** and **4b**, these ligands were reacted with iridium dimer **2** in refluxing ethanol. In a typical procedure, 0.5 mmol of dimer **2** and 1.2 mmol of 2,2’-biimidazole **3a** were suspended in 10 ml ethanol and reacted over night under inert (N_2) atmosphere. After cooling to room temperature, **4a** was precipitated as its hexafluorophosphate salt using saturated aqueous NH_4PF_6. The precipitate was filtered and washed as described above. The yield was 80 %. Only the isomer with the pyridine-rings in *trans*-position is obtained, consistent with the exclusive formation of the *trans* dimer **2**. Mono-deprotonation of complex **4a** was effected using one equivalent of tetrabutylammonium hydroxide (Sigma Aldrich, product No. 230189). Thereby the species **IrbiimH** was obtained.

Iridium[2-(*p*-tolyl)pyridine]$_2$Cl$_2$; compound **2**:
^{1}H-NMR ($CDCl_3$) δ(ppm): 9.16 (ddd, 4H, J=5.8, 1.6, 0.8 Hz, 2-(*p*-tolyl)pyridineH^6), 7.79 (dd, 4H, J=8.2, 1.6 Hz, 2-(*p*-tolyl)pyridineH^3), 7.69 (ddd, 4H, J=8.2, 7.4, 1.6 Hz, 2-(*p*-tolyl)pyridineH^4), 7.36 (d, 4H, J=8.2 Hz, 2-(*p*-tolylH^6)pyridine), 6.71 (dd, J=7.4, 5.8 Hz, 2-(*p*-tolyl)pyridineH^5), 6.55 (dd, 4H, J=8.2, 1.6, 0.8 Hz, 2-(*p*-tolylH^5)pyridine), 5.73 (d, 4H, J=1.6Hz, 2-(*p*-tolylH^3)pyridine), 1.92 (s, 12H, 2-(*p*-tolylCH_3)pyridine). **ESI-MS**: *m/z* calcd for [Ir(2-(*p*-tolyl)pyridine)$_2$]$^+$ fragment: 529.4; found 529.1.

[Iridium[2-(*p*-tolyl)pyridine)]$_2$(2,2’-biimidazole)]$^+$PF$_6^-$; compound **4aPF$_6$** or **IrbiimH$_2^+$PF$_6^-$**:
^{1}H-NMR ($CDCl_3$) δ(ppm): 7.80 (dd, 2H, J=8.3, 1.0 Hz, 2-(*p*-tolyl)pyridineH^3), 7.69 (dd, 2H, J=8.3, 8.3 Hz, 2-(*p*-tolyl)pyridineH^4), 7.66 (d, 2H, J=6.1 Hz, 2-(*p*-tolyl)pyridineH^6), 7.52 (d, 2H, J=8.0 Hz, 2-(*p*-tolylH^6)pyridine), 7.13 (d, 2H, J=1.2 Hz, 2,2’-biimidazoleH^4), 6.95 (ddd, 2H, J=8.3, 6.1, 1.0 Hz, 2-(*p*-tolylH^5)pyridine), 6.77 (d, 2H, J=8.0 Hz, 2-(*p*-tolylH^5)pyridine), 6.53 (d, 2H, J=1.2 Hz, 2,2’-biimidazoleH^5), 6.17 (s, 2H, 2-(*p*-tolylH^3)pyridine), 2.07 (s, 6H, 2-(*p*-tolylCH_3)pyridine). **ESI-MS**: *m/z* calcd for [Ir[2-(*p*-tolyl)pyridine)]$_2$(2,2’-biimidazole)]$^+$ cation: 663.5; found 663.2. **Elemental Analysis**: calcd (%) for $C_{32}H_{32}N_6OF_6IrP\cdot C_2H_5OC_2H_5OH$: C 45.48, H 4.04, N 9.36; found: C 44.61, H 3.83, N 9.82.

[Iridium[2-(*p*-tolyl)pyridine)]$_2$(2,2’-biimidazole)]; mono-deprotonated complex **IrbiimH**:
^{1}H-NMR ($CDCl_3$) δ(ppm): 7.76 (d, 2H, J=7.8 Hz, 2-(*p*-tolyl)pyridineH^3), 7.72 (d, 2H, J=5.9 Hz, 2-(*p*-tolyl)pyridineH^6), 7.63 (dd, 2H, J=7.8, 7.8 Hz, 2-(*p*-tolyl)pyridineH^4), 7.52 (d, 2H,

J=8.1 Hz, 2-(*p*-tolyl*H^6*)pyridine), 7.02 (d, 2H, J=1.0 Hz, 2,2'-biimidazole*H^4*), 6.88 (dd, 2H, J=7.8, 5.9 Hz, 2-(*p*-tolyl)pyridine*H^5*), 6.75 (dd, 2H, J= 8.1, 1.5 Hz, 2-(*p*-tolyl*H^5*)pyridine), 6.43 (d, 2H, J=1.0Hz, 2,2'-biimidazole*H^5*), 6.22 (d, 2H, J=1.5 Hz, 2-(*p*-tolyl*H^3*)pyridine), 1.92 (s, 6H, 2-(*p*-tolyl*CH_3*)pyridine).

[Iridium[2-(*p*-tolyl)pyridine)]$_2$(N,N'-dimethyl-2,2'-biimidazole)]$^+$$PF_6^-$; compound **4bPF$_6$** or **IrbiimMe$_2^+PF_6^-$**:
^{1}H-NMR ($CDCl_3$) δ(ppm): 7.87 (d, 2H, J=6.0Hz, 2-(*p*-tolyl)pyridine*H^3*), 7.74 (dd, 2H, J=6.0, 6.0 Hz, 2-(*p*-tolyl)pyridine*H^4*), 7.67 (d, 2H, J=7.5 Hz, 2-(*p*-tolyl)pyridine*H^6*), 7.50 (d, 2H, J=8.2 Hz, 2-(*p*-tolyl*H^6*)pyridine), 7.13 (d, 2H, J=1.2 Hz, 2,2'-biimidazole*H^4*), 6.84 (dd, 2H, J=7.5, 6.0 Hz, 2-(*p*-tolyl)pyridine*H^5*), 6.71 (d, 2H, J=8.2 Hz, 2-(*p*-tolyl*H^5*)pyridine), 6.47 (d, 2H, J=1.2 Hz, 2,2'-biimidazole*H^5*), 6.21 (s, 2H, 2-(*p*-tolyl*H^3*)pyridine), 4.16 (s, 6H, N*CH_3*), 2.10 (s, 6H, 2-(*p*-tolyl*CH_3*)pyridine). **ESI-MS**: *m/z* calcd for [Ir[2-(*p*-tolyl)pyridine)]$_2$(N,N0-dimethyl-2,2'-biimidazole)]$^+$ cation: 691.0 found 691.2.

Hexafluorophosphate to benzoate **anion exchange** was effected by adding the respective tetrabutylammonium benzoate salts to a solution of IrbiimH$_2^+$PF$_6^-$ or IrbiimMe$_2^+$PF$_6^-$ in dichloromethane. The resulting ion mixtures were stirred at room temperature for 3 hours, then evaporated to dryness. The resulting solid was treated with acetonitrile and filtered. Slow addition of diethyl ether to the filtrate induced precipitation of the pure benzoate salts of the iridium complexes.
The tetrabutylammonium benzoate salts were obtained from the reaction of 3,5-dinitrobenzoic acid (Sigma Aldrich, product No. 121258) or benzoic acid (Sigma Aldrich, product No. 242381) with tetrabutylammonium solution in methanol (Sigma Aldrich, product No. 230189).

Single crystals of IrbiimH$_2^+$(3,5-dinitrobenzoate)$^-$ were grown at room temperature by layering diisopropyl ether above a dichloromethane solution of the iridium complex.

NMR, MS, Elemental analysis, photophysical and electrochemical experiments

^{1}H-NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer. All chemical shifts are reported versus the tetramethylsilane signal. Deuterated solvents were bought from the Sigma Aldrich chemical company.

Electrospray ionization **mass spectrometry** was performed on a Finnigan MAT SSQ 7000 instrument. Methanol (HPLC grade, VWR) was used to solubilise the iridium compounds.

Elemental analysis was conducted by Dr. Hansjörg Eder, School of Pharmaceutical Sciences, University of Geneva, Switzerland.

Optical absorption spectra were measured on a Cary 5000 UV-Vis-NIR spectrophotometer (Varian), and **luminescence** experiments were measured on a Horiba Fluorolog-3. In the luminescence titration experiments, the normalized luminescence intensity was corrected for any occurring changes in absorbance at the excitation wavelength (410 nm). The solvent used for these measurements was dichloromethane of spectrophotometric grade (Sigma Aldrich, product No. 154792). The luminescence lifetimes of $\mathrm{IrbiimH_2^+PF_6^-}$ and $\mathrm{IrbiimMe_2^+PF_6^-}$ were measured on the experimental setup described recently (Group of Professor Andreas Hauser, Department of Physical Chemistry, University of Geneva).[6]

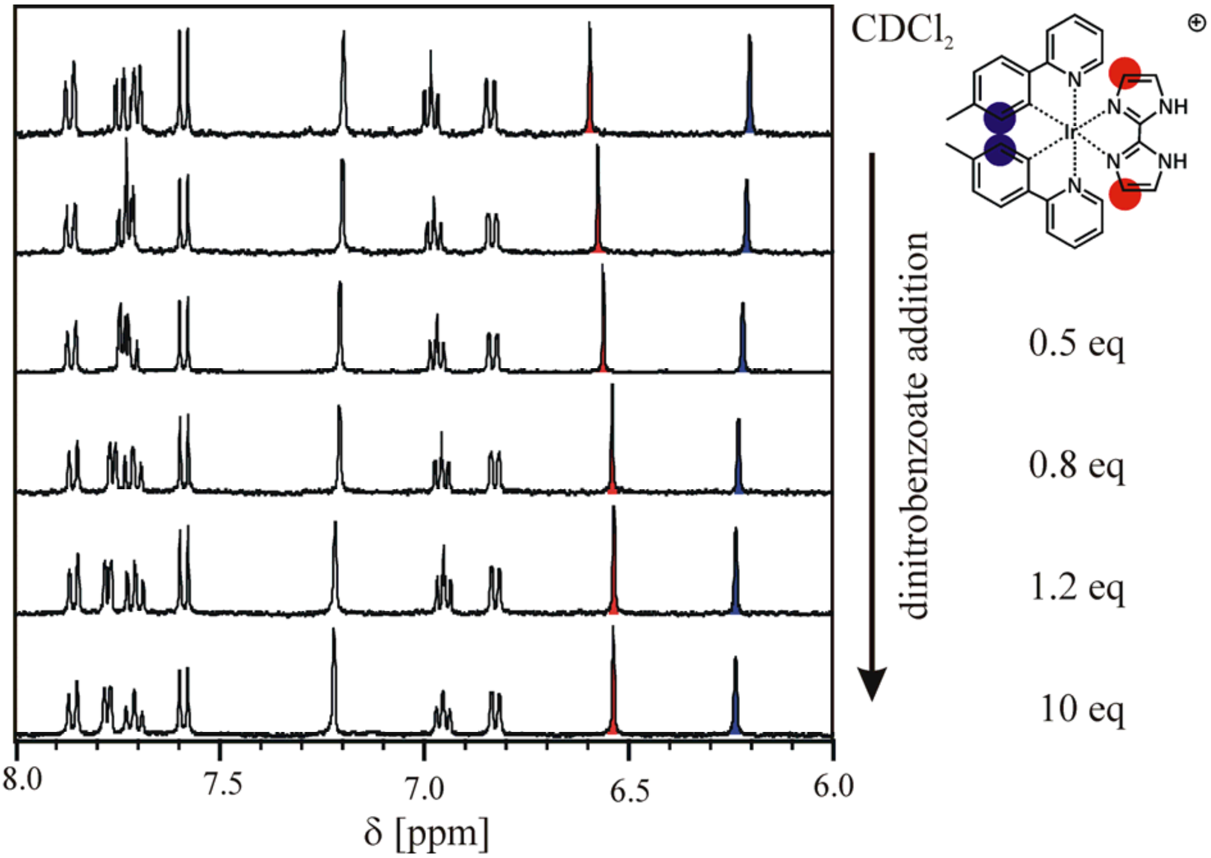
Cyclic voltammetry was performed using a Versastat3-100 Potentiostat equipped with the K0264 Micro-Cell kit from Princeton Applied Research. A silver wire was used as a quasi-reference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Fluka, product No. 86879) in dry acetonitrile (HPLC grade, VWR). The solution was deoxygenated prior to voltammetry sweeps by bubbling nitrogen gas.

Crystallographic details

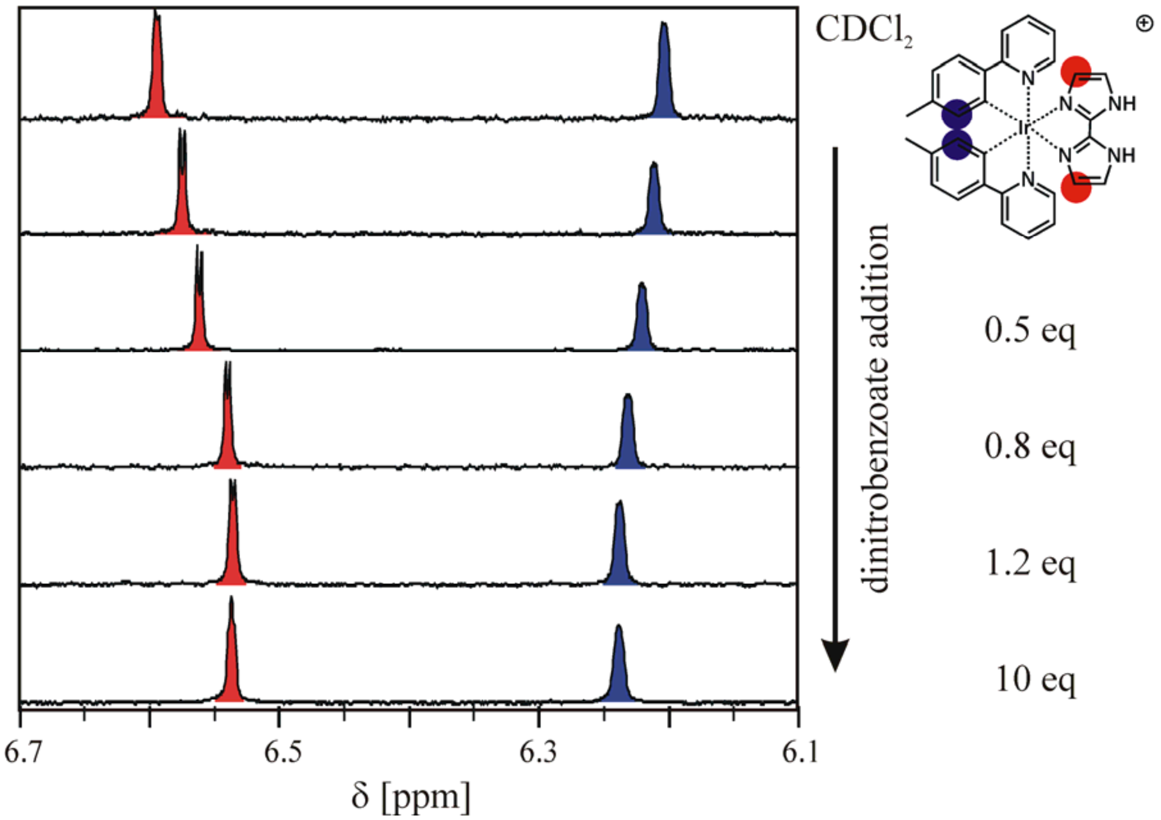
[Ir ($C_{12}H_{10}N)_2$ $(C_6H_6N_4)]^+$ $(C_7H_3N_2O_6)^-$] • $(C_4H_{10}O)$, M = 948.1, triclinic, space group $P\ \bar{1}$, a = 8.4670(5), b= 15.5019(12), c = 16.0030(11) Å, α = 74.619(8), β = 79.968(8), γ = 82.562(8)°, U = 1986.6(3)Å^3, Z = 2, Mo[K_α] radiation (λ = 0.7103 Å), μ = 3.42 mm^{-1}, T = 150K, Stoe IPDS-I diffractometer, 25884 reflections measured, 8873 unique (R_{int} = 0.030) of which 7311 with $|Fo| > 4\ \sigma\ (Fo)$. Final values R = 0.024, ωR = 0.025 and S = 1.19(2).

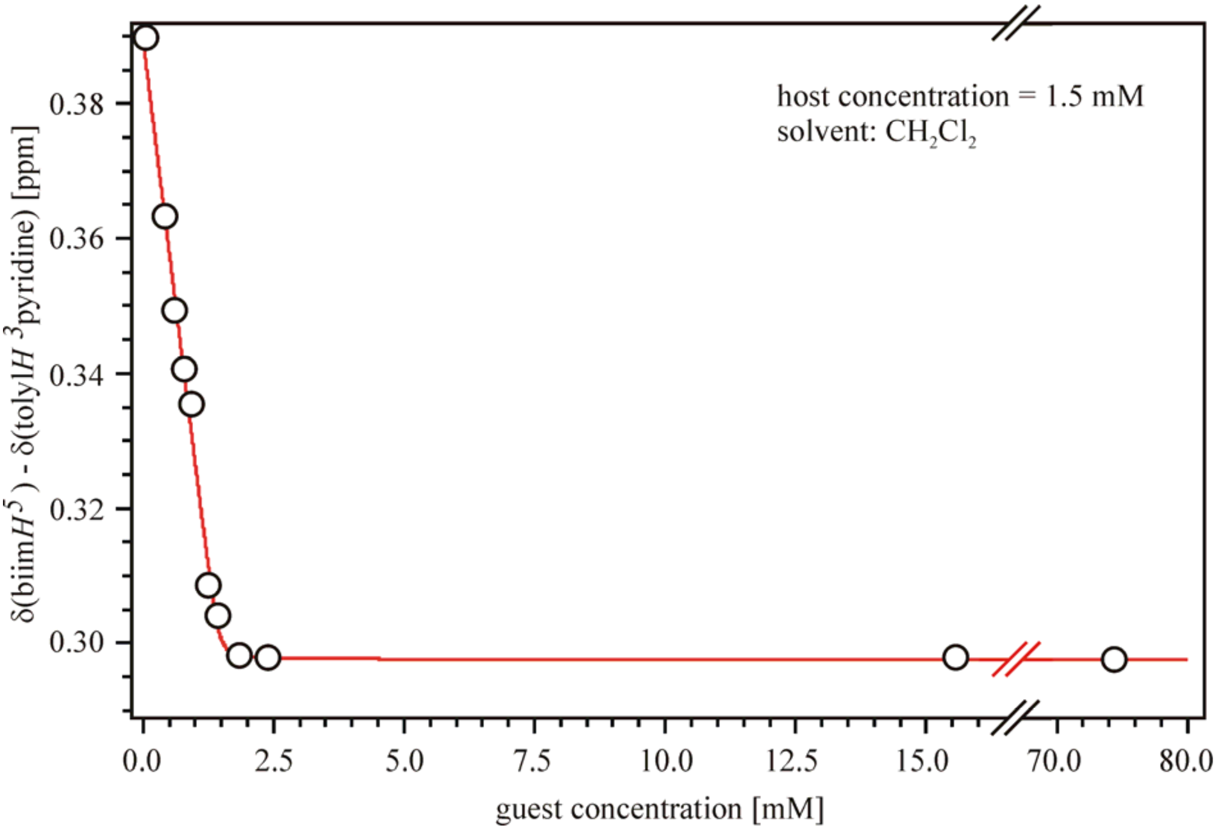
^{1}H-NMR titration data

The ^{1}H-NMR titration of IrbiimH$_2$$^+PF_6$$^-$ with tetrabutylammonium 3,5-dinitrobenzoate was effected in deuterated dichloromethane solution. The concentration of the iridium complex was 1.5 mM.



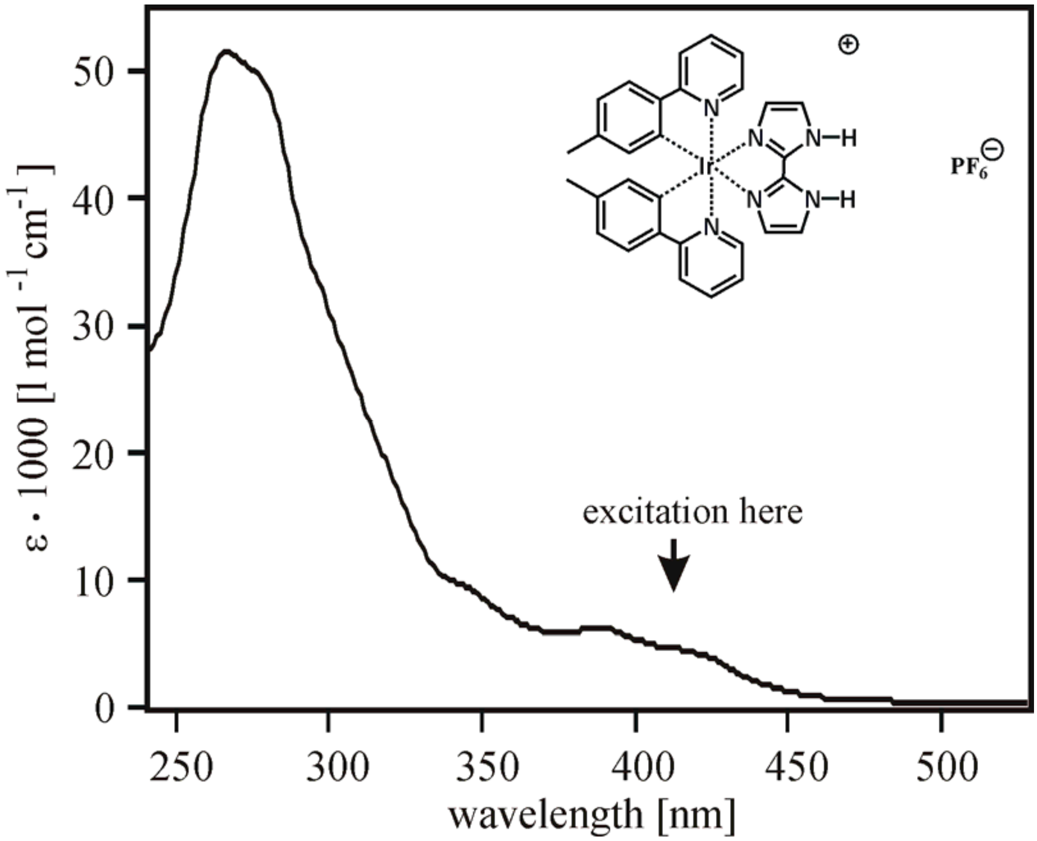
The data was fitted using the appropriate expression derived by Macomber.[7] This was done using the Igor Pro software package, whereby a numerical value for the association constant K$_a$ could be extracted (log(K$_a$) = 5.5).


CDCl₂
⊕
N
N
N
NH
N
NH
Ir
dinitrobenzoate addition
0.5 eq
0.8 eq
1.2 eq
10 eq
6.7
6.5
6.3
6.1
δ [ppm]


host concentration = 1.5 mM
solvent: CH₂Cl₂
δ(biimH^5) - δ(tolyl$H$ ^{3}pyridine) [ppm]
0.38
0.36
0.34
0.32
0.30
0.0
2.5
5.0
7.5
10.0
12.5
15.0
70.0
80.0
guest concentration [mM]

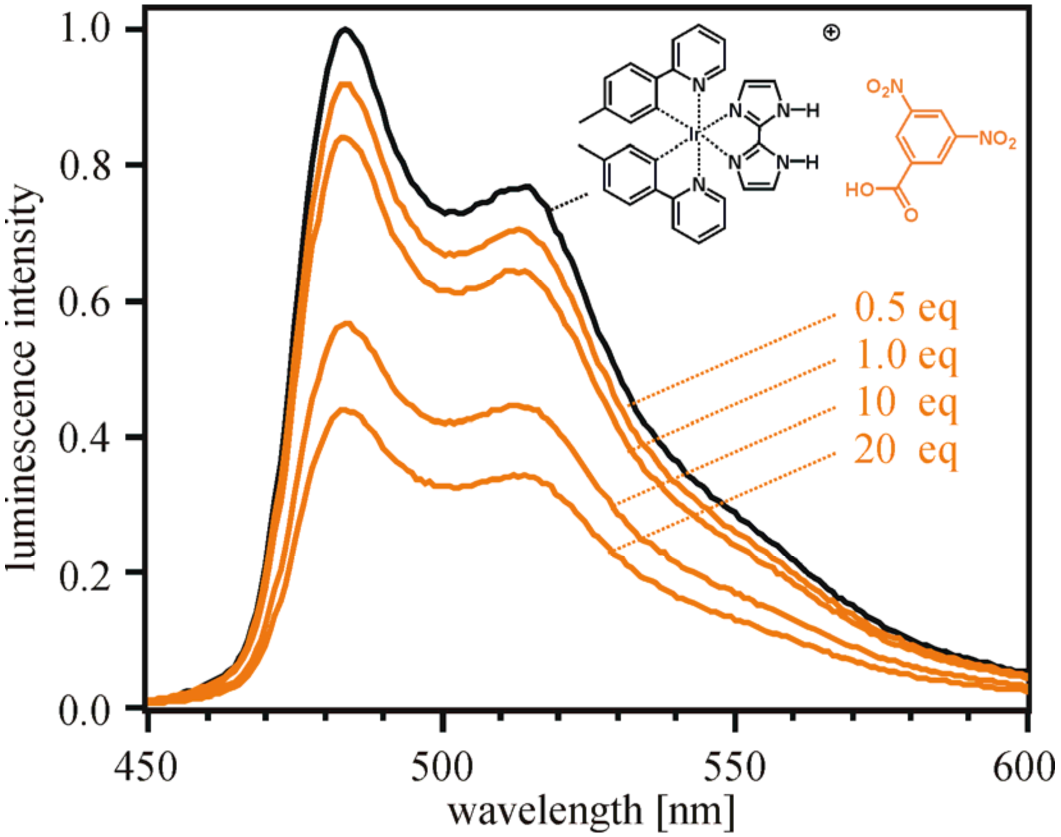
Optical spectroscopic data

The following figure shows the optical absorption spectrum of an IrbiimH$_2^+$PF$_6^-$ solution in dichloromethane.



The excitation wavelength used for all luminescence experiments was 410 nm.

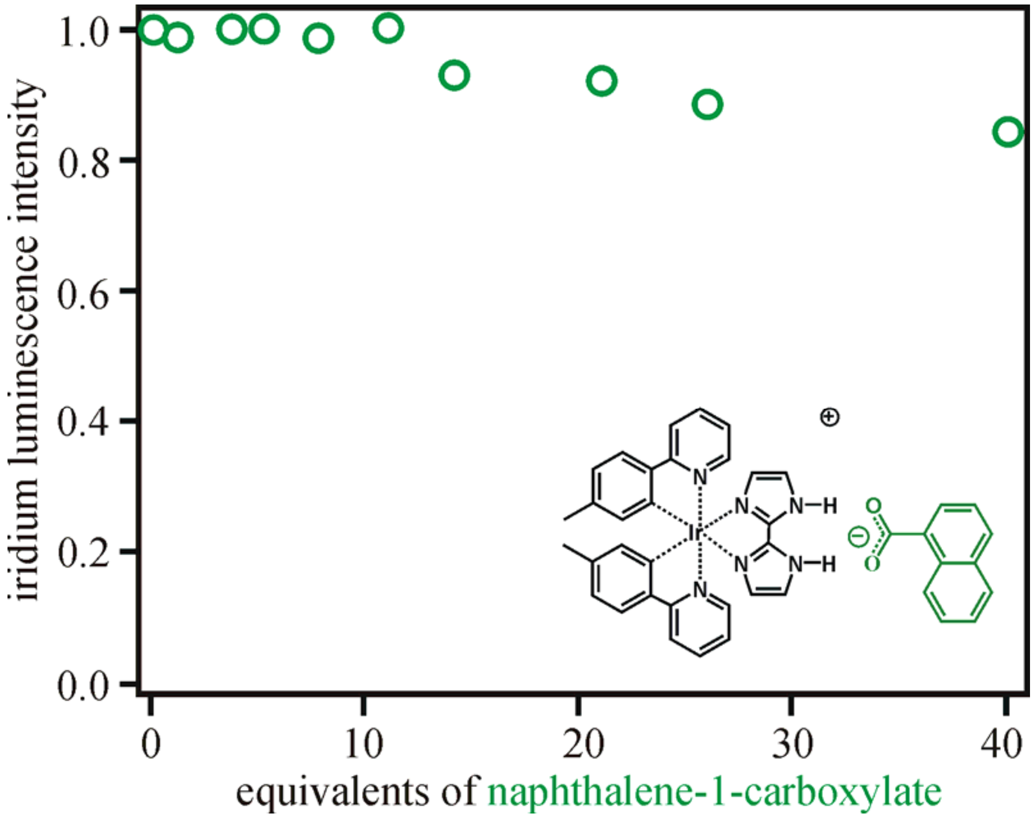
The following figure shows the luminescence spectra of IrbiimH$_2^+$ with various amounts of 3,5-dinitrobenzoic acid (Hdnb) present.



Iridium luminescence quenching *is* observed, electron transfer processes *do* take place. Spectral changes are *not* observed, proton transfer does *not* take place.

These data correspond to the orange squares in Figure 3c.

Result of a luminescence titration of $IrbiimH_2^+PF_6^-$ with tetrabutylammonium naphthalene-1-carboxylate:



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