Electronic supplementary information for

Proton-coupled electron transfer from a luminescent excited state

Jonathan C. Freys, Gérald Bernardinelli, Oliver S. Wenger*

Department of Inorganic, Analytical and Applied Chemistry
University of Geneva
30 Quai Ernest-Ansermet
1211 Geneva 4, Switzerland
oliver.wenger@unige.ch

and

Laboratory of X-ray Crystallography
University of Geneva
24 Quai Ernest-Ansermet
1211 Geneva 4, Switzerland

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**Synthesis and characterization of the iridium complexes**

The two cyclometalated iridium(III) complexes IrbiimH₂⁺ and IrbiimMe₂⁺ were synthesized according to the generally adopted strategy illustrated in the following scheme.[1-3]

![Scheme](image)

In a typical procedure, 1 mmol of IrCl₃ (Alfa Aesar, 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 ¹H-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 (N₂) atmosphere. After cooling to room temperature, 4a was precipitated as its hexafluorophosphate salt using saturated aqueous NH₄PF₆. 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)₂Cl₂; compound 2:

**H-NMR (CDCl₃) δ(ppm):** 9.16 (ddd, 4H, J=5.8, 1.6, 0.8 Hz, 2-(p-tolyl)pyridineH₃), 7.79 (dd, 4H, J=8.2, 1.6 Hz, 2-(p-tolyl)pyridineH₄), 7.69 (ddd, 4H, J=8.2, 7.4, 1.6 Hz, 2-(p-tolyl)pyridineH₅), 7.36 (d, 4H, J=8.2 Hz, 2-(p-tolylH₆)pyridine), 6.71 (dd, J=7.4, 5.8 Hz, 2-(p-tolyl)pyridineH₆), 6.55 (dd, 4H, J=8.2, 1.6, 0.8 Hz, 2-(p-tolylH₅)pyridine), 5.73 (d, 4H, J=1.6Hz, 2-(p-tolylH₃)pyridine), 1.92 (s, 12H, 2-(p-tolylCH₃)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)]⁺PF₆⁻; compound 4aPF₆ or IrbiimH₂⁺PF₆⁻:

**H-NMR (CDCl₃) δ(ppm):** 7.80 (dd, 2H, J=8.3, 1.0 Hz, 2-(p-tolyl)pyridineH₃), 7.69 (dd, 2H, J=8.3, 8.3 Hz, 2-(p-tolyl)pyridineH₄), 7.66 (d, 2H, J=6.1 Hz, 2-(p-tolyl)pyridineH₅), 7.52 (d, 2H, J=8.0 Hz, 2-(p-tolylH₆)pyridine), 7.13 (d, 2H, J=1.2 Hz, 2,2’-biimidazoleH₃), 6.95 (ddd, 2H, J=8.3, 6.1, 1.0 Hz, 2-(p-tolylH₅)pyridine), 6.77 (d, 2H, J=8.0 Hz, 2-(p-tolylH₃)pyridine), 6.53 (d, 2H, J=1.2 Hz, 2,2’-biimidazoleH₃), 6.17 (s, 2H, 2-(p-tolylH₇)pyridine), 2.07 (s, 6H, 2-(p-tolylCH₃)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 C₃₂H₃₂N₆O₆IrP·C₃H₇OC₂H₅OH: 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:

**H-NMR (CDCl₃) δ(ppm):** 7.76 (d, 2H, J=7.8 Hz, 2-(p-tolyl)pyridineH₃), 7.72 (d, 2H, J=5.9 Hz, 2-(p-tolyl)pyridineH₄), 7.63 (dd, 2H, J=7.8, 7.8 Hz, 2-(p-tolyl)pyridineH₅), 7.52 (d, 2H,
J=8.1 Hz, 2-(p-tolyH₆)pyridine, 7.02 (d, 2H, J=1.0 Hz, 2,2’-biimidazoleH₄), 6.88 (dd, 2H, J=7.8, 5.9 Hz, 2-(p-tolyl)pyridineH₄), 6.75 (dd, 2H, J= 8.1, 1.5 Hz, 2-(p-tolylH₆)pyridine), 6.43 (d, 2H, J=1.0Hz, 2,2’-biimidazoleH₄), 6.22 (d, 2H, J=1.5 Hz, 2-(p-tolylH₆)pyridine), 1.92 (s, 6H, 2-(p-tolylCH₃)pyridine).

[Iridium[2-(p-tolyl)pyridine]₂(N,N’-dimethyl-2,2’-biimidazole)]⁺PF₆⁻; compound 4bPF₆ or IrbiimMe₂⁺PF₆⁻:

$^{1}$H-NMR (CDCl₃) δ (ppm): 7.87 (d, 2H, J=6.0Hz, 2-(p-tolyl)pyridineH₃), 7.74 (dd, 2H, J=6.0, 6.0 Hz, 2-(p-tolyl)pyridineH₃), 7.67 (d, 2H, J=7.5 Hz, 2-(p-tolyl)pyridineH₅), 7.50 (d, 2H, J=8.2 Hz, 2-(p-tolylH₆)pyridine), 7.13 (d, 2H, J=1.2 Hz, 2,2’-biimidazoleH₄), 6.84 (dd, 2H, J=7.5, 6.0 Hz, 2-(p-tolyl)pyridineH₅), 6.71 (d, 2H, J=8.2 Hz, 2-(p-tolylH₆)pyridine), 6.47 (d, 2H, J=1.2 Hz, 2,2’-biimidazoleH₄), 6.21 (s, 2H, 2-(p-tolylH₆)pyridine), 4.16 (s, 6H, NCH₃), 2.10 (s, 6H, 2-(p-tolylCH₃)pyridine). ESI-MS: m/z calcd for [Ir[2-(p-tolyl)pyridine]₂(N,N’-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 IrbiimH₂⁺PF₆⁻ or IrbiimMe₂⁺PF₆⁻ 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 IrbiimH₂⁺(3,5-dinitrobenzoate) were grown at room temperature by layering diisopropyl ether above a dichloromethane solution of the iridium complex.

S4
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 IrbiimH$_2$PF$_6$ and 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

\[ \text{Ir} (\text{C}_{12}\text{H}_{10}\text{N})_2 (\text{C}_6\text{H}_5\text{N}_4) \]^{+} (\text{C}_7\text{H}_3\text{N}_2\text{O}_6)^{-} \cdot (\text{C}_4\text{H}_{10}\text{O}), \text{ } M = 948.1, \text{ triclinic, space group } P \bar{1}, \text{ } a = 8.4670(5), b = 15.5019(12), c = 16.0030(11) \text{ Å}, \alpha = 74.619(8), \beta = 79.968(8), \gamma = 82.562(8)^\circ, \text{ } U = 1986.6(3) \text{Å}^3, \text{ } Z = 2, \text{ Mo}[K\alpha] \text{ radiation (}\lambda = 0.7103 \text{ Å)}, \mu = 3.42 \text{ mm}^{-1}, \text{ } T = 150\text{K}, \text{ Stoe IPDS-I diffractometer, 25884 reflections measured, 8873 unique (}R_{\text{int}} = 0.030) \text{ of which 7311 with } |F_o| > 4 \sigma (F_o). \text{ Final values } R = 0.024, \omega R = 0.025 \text{ and } S = 1.19(2).
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 ($\log(K_a) = 5.5$).
Supplementary Material (ESI) for Chemical Communications

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CDCl$_3$

0.5 eq
0.8 eq
1.2 eq
10 eq

$\delta$ (ppm)

host concentration = 1.5 mM
solvent: CH$_2$Cl$_2$
Optical spectroscopic data

The following figure shows the optical absorption spectrum of an IrbiimH₂⁺PF₆⁻ solution in dichloromethane.

![Optical absorption spectrum of IrbiimH₂⁺PF₆⁻ solution](image)

The excitation wavelength used for all luminescence experiments was 410 nm.
The following figure shows the luminescence spectra of IrbiimH₂⁺ 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:
References


