

Supporting Information

A long-lived iridium(III) chemosensor for the real-time detection of GHB

Wanhe Wang,^a Zhen-Zhen Dong,^a Guanjun Yang,^b Chung-Hang Leung,^b Sheng Lin^{a,*} and Dik-Lung Ma^{a,*}

^a Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China.

^b State Key Laboratory of Quality Research in Chinese Medicine, Institute of Chinese Medical Sciences, University of Macau, Macao, China.

* Corresponding author:

Dr. Dik-Lung Ma, E-mail: edmondma@hkbu.edu.hk, Tel: (+852) 3411-7075, Fax: (+852) 3411-7348.

Sheng Lin, E-mail: linsentst@life.hkbu.edu.hk.

Materials. Reagents, unless specified, were purchased from Sigma Aldrich (St. Louis, MO), J&K Scientific or Dieckmann (Hong Kong, China), and used as received. Iridium chloride hydrate ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$) was purchased from Precious Metals Online (Australia). Gamma-hydroxybutyric acid (sodium salt) was purchased from TCM Healthcare Ltd. (London, UK). All the beverages used are available in Hong Kong local supermarkets.

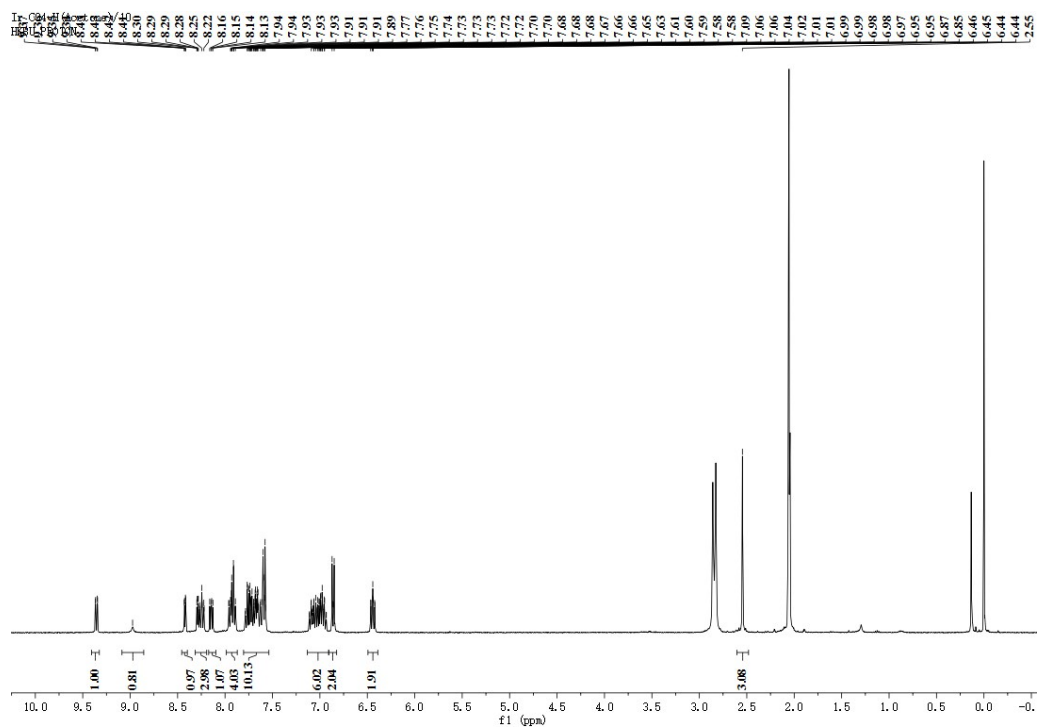
General experimental. Mass spectrometry was performed at the Mass Spectroscopy Unit at the Department of Chemistry, Hong Kong Baptist University, Hong Kong (China). Deuterated solvents for NMR purposes were obtained from Armar and used as received. ^1H and ^{13}C NMR were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C). ^1H and ^{13}C chemical shifts were referenced internally to solvent shift (acetone- d_6 : ^1H , δ 2.09, ^{13}C δ 205.87, 30.60; DMSO- d_6 : ^1H δ 2.50, ^{13}C δ 39.5). Chemical shifts (δ) are quoted in ppm, the downfield direction being defined as positive. Uncertainties in chemical shifts are typically ± 0.01 ppm for ^1H and ± 0.05 for ^{13}C . Coupling constants are typically ± 0.1 Hz for ^1H - ^1H and ± 0.5 Hz for ^1H - ^{13}C couplings. The following abbreviations are used for convenience in reporting the multiplicity of NMR resonances: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

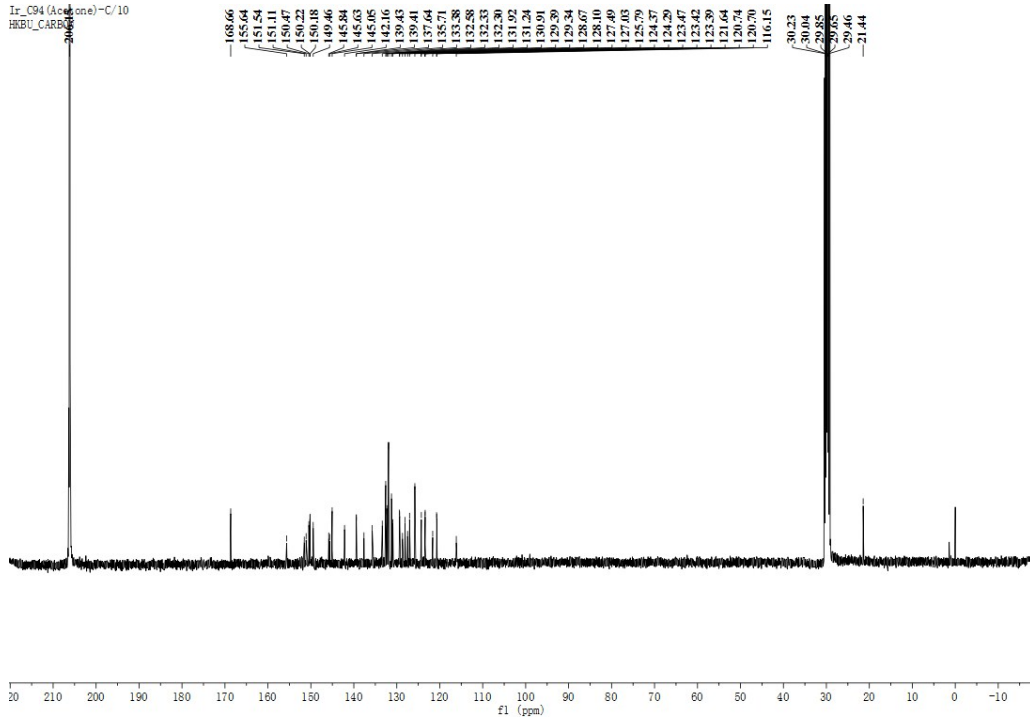
Synthesis. The complex was prepared according to (modified) literature methods.^{1, 2} All complexes are characterized by ^1H -NMR, ^{13}C -NMR, high resolution mass spectrometry (HRMS) and elemental analysis. The precursor iridium(III) complex

dimer $[\text{Ir}_2(\text{C}^{\wedge}\text{N})_4\text{Cl}_2]$ was prepared as reported method.³ Then, a suspension of $[\text{Ir}_2(\text{C}^{\wedge}\text{N})_4\text{Cl}_2]$ (0.2 mmol) and corresponding N^N ligands (0.44 mmol) in a mixture of DCM:methanol (1:1, 20 mL) was refluxed overnight under a nitrogen atmosphere. The resulting solution was then allowed to cool to room temperature, and filtered to remove the unreacted cyclometallated dimer. To the filtrate, an aqueous solution of ammonium hexafluorophosphate (excess) was added and the filtrate was reduced in volume by rotary evaporation until precipitation of crude product occurred. The precipitate was then filtered and washed with several portions of water (2×50 mL) followed by diethyl ether (2×50 mL). The product was recrystallized by acetonitrile:diethyl ether vapor diffusion to yield the titled compound.

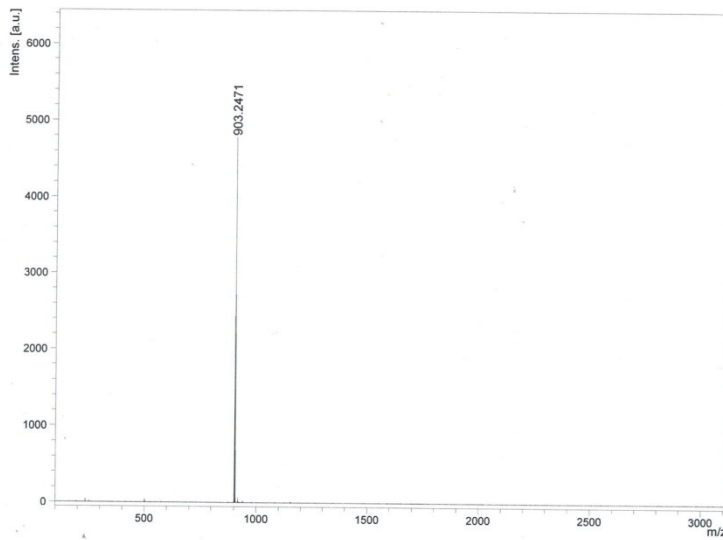
Complex **1**. Yield: 63%. ^1H NMR (400 MHz, Acetone- d_6) δ 9.36 (dd, $J = 8.3, 1.5$ Hz, 1H), 8.97 (s, 1H), 8.42 (dd, $J = 5.1, 1.5$ Hz, 1H), 8.31–8.19 (m, 3H), 8.14 (dd, $J = 8.3, 5.1$ Hz, 1H), 7.99–7.87 (m, 4H), 7.80–7.54 (m, 10H), 7.13–6.91 (m, 6H), 6.91–6.82 (m, 2H), 6.44 (t, $J = 8.9$ Hz, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, Acetone- d_6) δ 168.66, 155.64, 151.54, 151.11, 150.47, 150.22, 150.18, 149.46, 145.84, 145.63, 145.05, 142.16, 139.43, 139.41, 137.64, 135.71, 133.38, 132.58, 132.33, 132.30, 131.92, 131.24, 130.91, 129.39, 129.34, 128.67, 128.10, 127.49, 127.03, 125.79, 124.37, 124.29, 123.47, 123.42, 123.39, 121.64, 120.74, 120.70, 116.15, 21.44. HRMS: Calcd. for $\text{C}_{48}\text{H}_{34}\text{N}_6\text{OIr} [\text{M}-\text{PF}_6]^+$: 903.2423, found: 903.2471. Anal. ($\text{C}_{48}\text{H}_{34}\text{N}_6\text{OIrPF}_6 \cdot 2\text{H}_2\text{O}$) C, H, N: calcd: 53.18, 3.53, 7.75; found: 52.92, 3.46, 7.80.

^1H NMR, ^{13}C NMR and mass spectrum of **1**.





HONG KONG BAPTIST UNIVERSITY, DEPARTMENT OF CHEMISTRY (MALDI-TOF)



Date of acquisition 2016-10-19 14:28:49
 Comment 3 ERROR = 5.5367 PPM
 Instrument type autoflex
 Serial instrument number 25001.00216
 PIE delay in [ns] 120 msec
 Voltage polarity POS
 Comment 1 TRUE [M+] = 903.242999
 Comment 2 FOUND [M+] = 903.2471
 Laser repetition rate in Hz 20 psec
 Linear detector voltage 0
 Ion source voltage 1 19.030001
 Ion source voltage 2 17.18
 Ion source lens voltage 8.100000400000001
 Mass calibration Constant 1 728037.3334613412
 Mass calibration Constant 2 141.6215904696922
 Third calib constant -0.007393332146550379
 Number of shots 71

Acquisition method name D:\Method\flexControl\Methods\20140609_john\RP_PepMix\RP_PepMix 1-4-2014_from David_LOM.par
 Sample name (file name prefix) Ir C94-W-DCTB0_M211

printed: 10/19/2016 02:29:05 PM

Photophysical measurement. Emission spectra and lifetime measurements for complex **1** was performed on a PTI TimeMaster C720 Spectrometer (Nitrogen laser: pulse output 337 nm) fitted with a 395 nm filter. Error limits were estimated: λ (± 1 nm); τ ($\pm 10\%$); ϕ ($\pm 10\%$). All solvents used for the lifetime measurements were degassed using three cycles of freeze-vac-thaw.

Luminescence quantum yields were determined using the method of Demas and Crosby,⁴ $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ in degassed acetonitrile as a standard reference solution ($\Phi_r = 0.062$) and calculated according to the following equation:

$$\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r) \quad (1)$$

where the subscripts s and r refer to sample and reference standard solution respectively, n is the refractive index of the solvents, D is the integrated intensity, and Φ is the luminescence quantum yield. The quantity B was calculated by $B = 1 - 10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length.

Table S1. Photophysical properties of iridium(III) complex **1**.

Quantum yield	λ_{em} / nm	Lifetime / μs
0.086	570	$4.834 \pm 5.032 \times 10^{-3}$

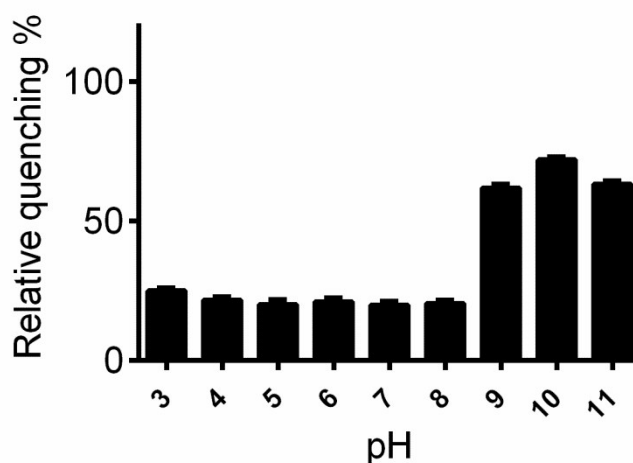


Figure S1. Influence of pH (3 to 11) on the quenching efficiency of **1** ($0.5 \mu\text{M}$) without or with GHB (0.15 mg mL^{-1}) in Tris buffer (10 mM) prepared with deionized water. Error bars represent the standard deviations (SD) of the results from three independent experiments.

References

1. D.-L. Ma, L.-J. Liu, K.-H. Leung, Y.-T. Chen, H.-J. Zhong, D. S.-H. Chan, H.-M. D. Wang and C.-H. Leung, *Angew. Chem. Int. Ed.*, 2014, **53**, 9178-9182.
2. L. Li, T. Wu, J. Wang and R. Wang, *ChemPlusChem*, 2014, **79**, 257-265.
3. Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, F. Li, T. Yi and C. Huang, *Inorg. Chem.*, 2006, **45**, 6152-6160.
4. G. A. Crosby and J. N. Demas, *J. Phy. Chem.*, 1971, **75**, 991-1024.