

# An Aldol Reaction-Based Iridium(III) Chemosensor for the Visualization of Proline in Living Cells

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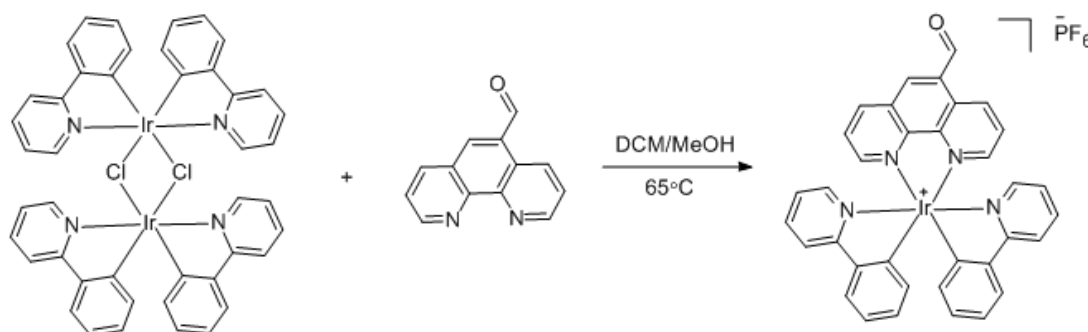
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**General experimental.** Mass spectrometry was performed at the Mass Spectroscopy Unit at the Department of Chemistry, Hong Kong Baptist University, Hong Kong (China). Deuterated solvents for NMR purposes were obtained from Armar and used as received.

$^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were referenced internally to solvent shift (acetone- $d_6$ :  $^1\text{H}$ ,  $\delta$  2.09,  $^{13}\text{C}$   $\delta$  205.87, 30.60; DMSO- $d_6$ :  $^1\text{H}$   $\delta$  2.50,  $^{13}\text{C}$   $\delta$  39.5). Chemical shifts ( $\delta$ ) are quoted in ppm, the downfield direction being defined as positive. Uncertainties in chemical shifts are typically  $\pm 0.01$  ppm for  $^1\text{H}$  and  $\pm 0.05$  for  $^{13}\text{C}$ . Coupling constants are typically  $\pm 0.1$  Hz for  $^1\text{H}$ - $^1\text{H}$  and  $\pm 0.5$  Hz for  $^1\text{H}$ - $^{13}\text{C}$  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.

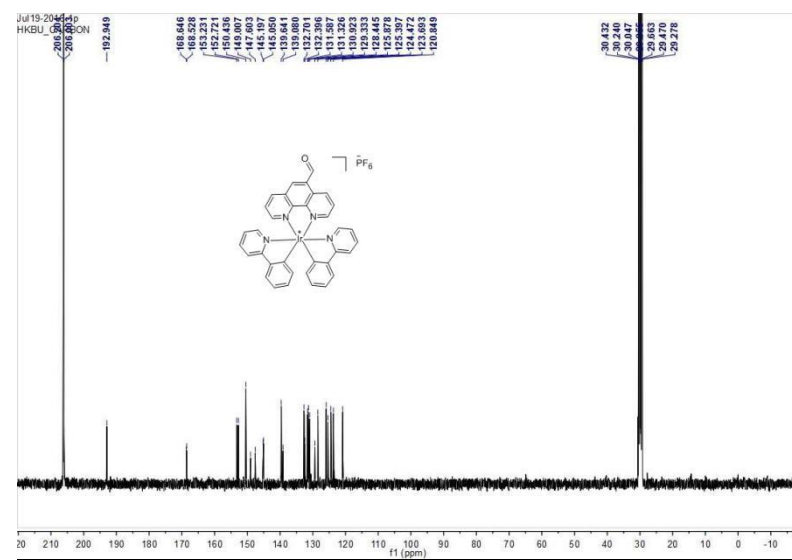
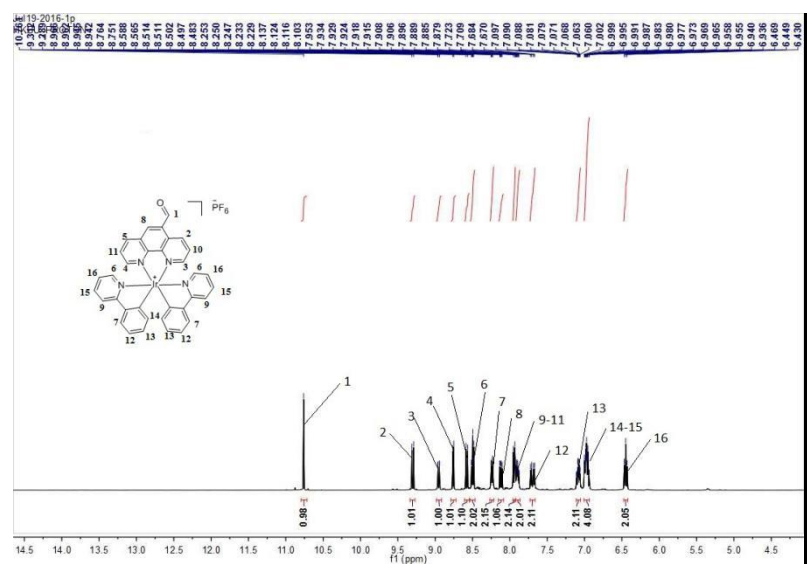
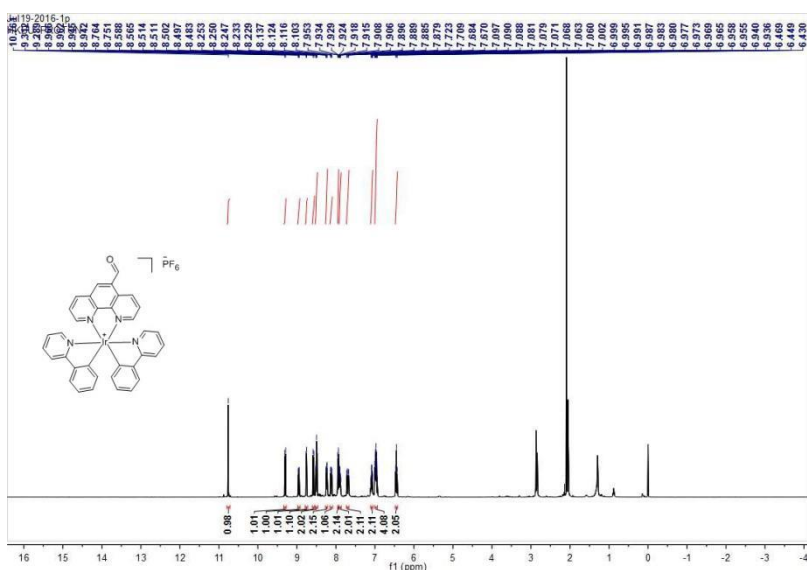
**Materials.** Reagents, unless specified, were purchased from Sigma Aldrich (St. Louis, MO) and used as received. Iridium chloride hydrate ( $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ ) was purchased from Precious Metals Online (Australia).

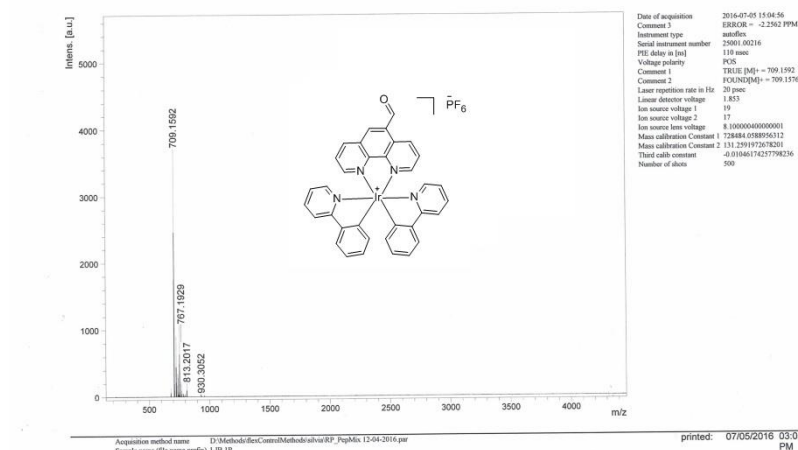


**Scheme S1.** Synthesis of **1**.

Complex **1**. Yield: 64%.  $^1\text{H}$  NMR (400 MHz, acetone)  $\delta$  10.76 (s, 1H), 9.30 (d,  $J = 9.2$  Hz, 1H), 8.95 (dd,  $J = 8.3, 1.3$  Hz, 1H), 8.76 (d,  $J = 5.1$  Hz, 1H), 8.58 (d,  $J = 9.2$  Hz, 1H), 8.50 (dd,  $J = 6.6, 4.5$  Hz, 2H), 8.25 – 8.23 (m, 1H), 8.12 (dd,  $J = 8.3, 5.1$  Hz, 1H), 7.93 (d,  $J = 1.7$  Hz, 2H), 7.92 – 7.87 (m, 2H), 7.70 (dd,  $J = 15.6, 5.5$  Hz, 2H), 7.08 (tdd,  $J = 7.7, 3.5, 1.1$  Hz, 2H), 7.00 – 6.93 (m, 4H), 6.45 (t,  $J = 7.7$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz, acetone)  $\delta$  192.95, 168.65, 168.53, 153.23, 152.72, 150.44, 149.01, 147.60, 145.20, 145.05, 139.64, 139.08, 132.70, 132.40, 131.59, 131.33, 130.92, 129.33, 128.45, 125.88, 125.40, 124.47, 123.69, 120.85. MALDI-TOF-HRMS: Calcd. for  $\text{C}_{38}\text{H}_{32}\text{F}_6\text{IrN}_4\text{OP} [\text{M}-\text{PF}_6]^+$ : 709.1592, found: 709.1576.

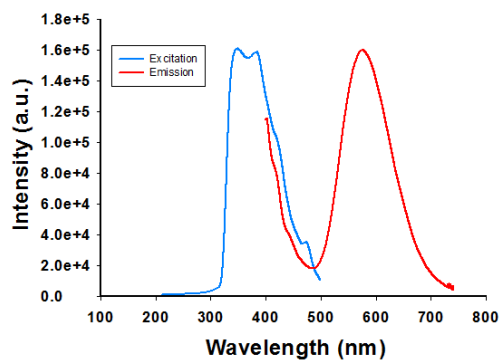
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectrum of **1**.



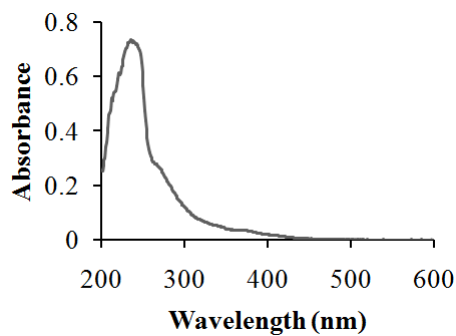


**Table S1.** Photophysical properties of iridium(III) complex **1**.

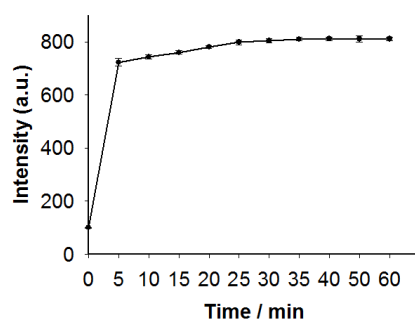
Quantum yield	$\lambda_{em}/\text{nm}$	Lifetime/ $\mu\text{s}$	UV-Vis absorption $\lambda_{abs}/\text{nm}$ ( $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ )
0.718	580	3.750	235 ( $3.6 \times 10^4$ ), 370 ( $1.5 \times 10^3$ )



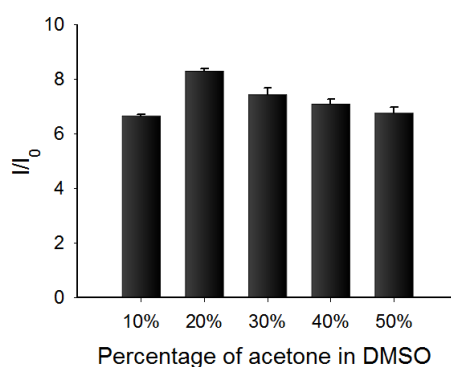
**Figure S1.** Excitation and emission spectra of **1** (10  $\mu\text{M}$ ) in DMSO/acetone (4:1, v/v).



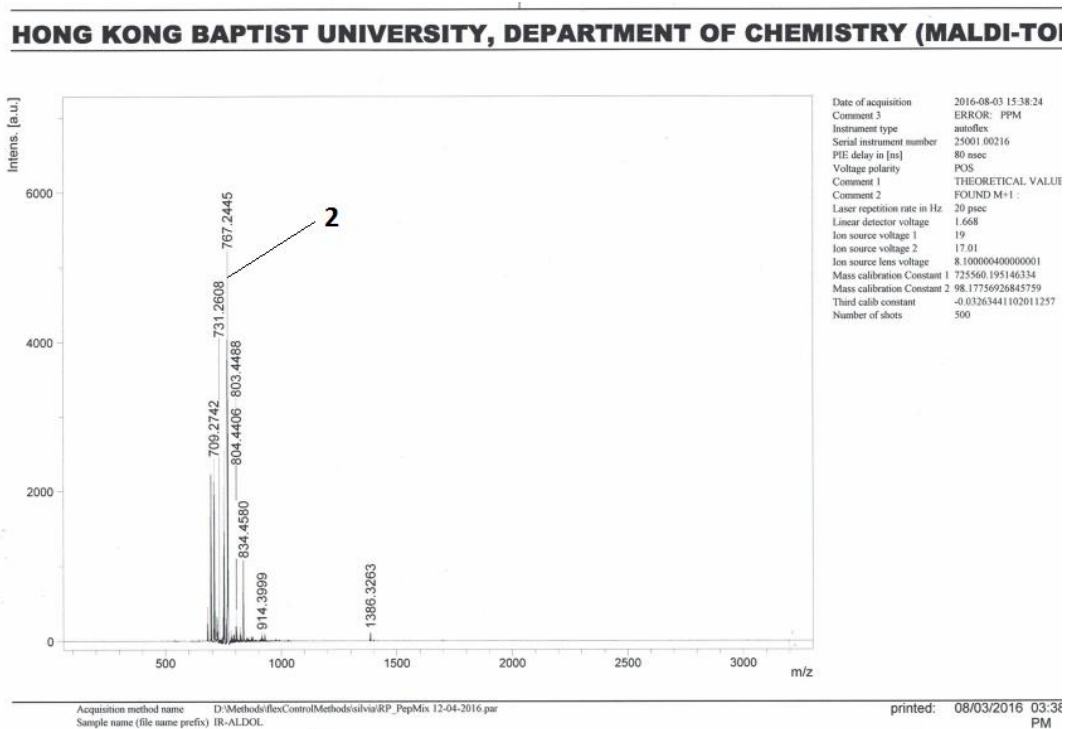
**Figure S2.** UV-Vis absorption spectra of **1** (20  $\mu\text{M}$ ) in DMSO.



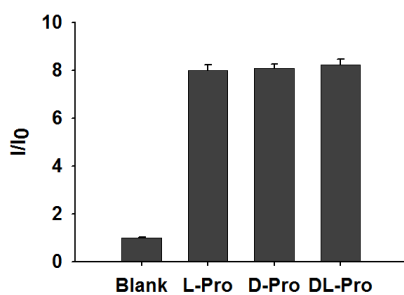
**Figure S3.** Time course of luminescence response of **1** (10  $\mu$ M) in the presence of Pro (80  $\mu$ M) at 25  $^{\circ}$ C.



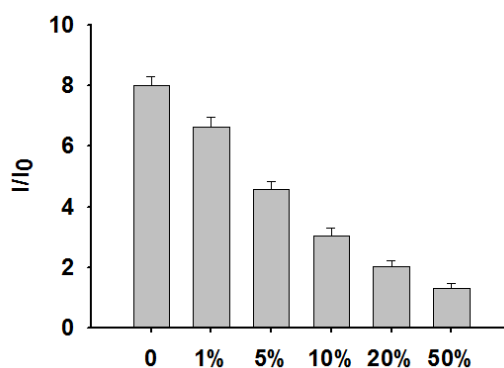
**Figure S4.** Luminescence enhancement of **1** (10  $\mu$ M) with Pro (80  $\mu$ M) in various percentage of acetone in DMSO.



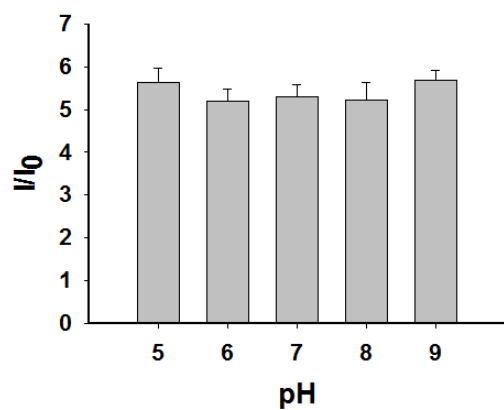
**Figure S5.** High-resolution mass spectrum of the reaction product **2**.



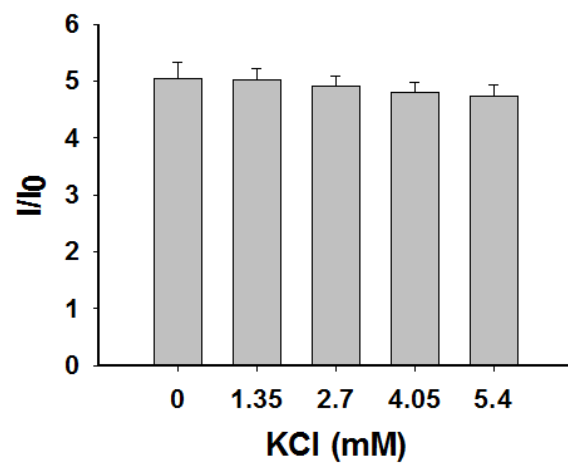
**Figure S6.** Luminescence enhancement of system in response to **1** (10  $\mu$ M) in the absence or presence of L, D, or DL-proline (80  $\mu$ M).



**Figure S7.** Luminescence enhancement of **1** (10  $\mu$ M) with Pro (80  $\mu$ M) in various percentage of PBS buffer in DMSO/acetone (4:1, v/v).



**Figure S8.** Influence of pH (5 to 9) on the luminescence enhancement of **1** (10  $\mu$ M) with Pro (80  $\mu$ M) in DMSO/acetone (4:1, v/v) with 5% PBS medium.



**Figure S9.** Influence of KCl concentration on the luminescence enhancement of **1** (10  $\mu$ M) with Pro (80  $\mu$ M) in DMSO/acetone (4:1, v/v) with 5% PBS medium.