Electronic Supporting Information

for

Triple-channel lab-on-a-molecule for triple-anion quantification using an iridium(III)-imidazolium conjugate

Kun Chen, Michael Schmittel*

*Center for Micro- and Nanochemistry and Engineering, Organische Chemie, Universität Siegen,
Adolf-Reichwein-Strasse, D-57068, Siegen, Germany.*

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Experimental Section

General information

All commercial reagents were used without further purification unless indicated otherwise. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at 298 K. Electrospray ionisation mass spectra were recorded using a Thermo-Quest LCQ Deca with ion trap. Elemental analyses were conducted with an EA 3000 CHNS. UV−Vis absorption and PL spectra were recorded on Varian Cary 50 Bio UV−Vis and Varian Cary Eclipse fluorescence spectrometers. Infrared spectra were recorded on a Perkin Elmer 1750 FT-IR spectrometer**.** Electrochemical measurements were conducted with a Parstat 2273 at room temperature. A conventional three-electrode set-up was used, with a platinum electrode serving as the working electrode, a platinum wire as an auxiliary electrode and a sliver wire as a quasi-reference. DPV measurements were conducted on samples (0.5 mM) dissolved in MeCN with 0.1 M n-Bu_4NPF_6 as supporting electrolyte. The scan rate was set at 40 mV/s. Decamethylferrocene (Fc*) was used as internal standard to calibrate the redox potential. Precursors **3, 4**,[1] **5**[2] and **6**[3] were prepared according to previous work.

ECL measurements were done on the iridium complexes (10 μM) in MeCN-Tris buffer aqueous solution (9/1, *v*/*v*, 10 mM, pH = 7.2) containing tri-*n*-propylamine (TPrA; 30 mM) as a co-reactant and tetra-*n*-butylammonium hexafluorophosphate (0.05 M) as electrolyte. A standard three-electrode set-up (3.0 mm diameter Pt working electrode, Pt wire auxiliary electrode, and a silver wire as reference electrode) connected to a Princeton Applied Research Model 362 potentialstat was used. To generate the ECL, the potential of the working electrode was swept between 0.7 to 2.0 V (*vs* a silver wire as quasi-reference electrode) at a scan rate v = 100 mV s^{-1}. The resulting emission spectra were obtained with a CCD camera cooled to –50 °C (0.500 m Imagining Triple Grating Monochromator/Spectrograph), which was connected to spectrometer Spectrapro 2500i (Acton Research Corporation). The following mechanism is assumed (M = Ir complex)[4]:

$$\mathrm{M - e^- \rightarrow M^{+\bullet}} \tag{1}$$

$$\mathrm{TPrA - e^- \rightarrow TPrA^{+\bullet}} \tag{2}$$

$$\mathrm{M^{+\bullet} + TPrA \rightarrow M + TPrA^{+\bullet}} \tag{3}$$

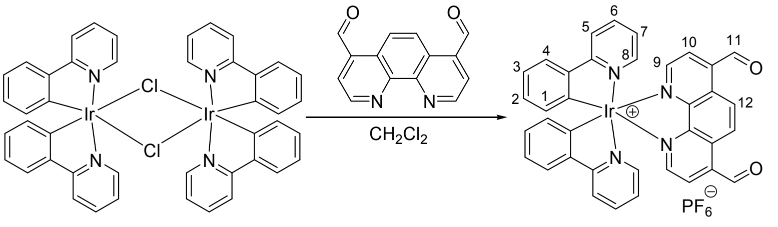
$$\mathrm{TPrA^{+\bullet} \rightarrow TPrA^{\bullet} + H^+} \tag{4}$$

$$\mathrm{M^{+\bullet} + TPrA^{\bullet} \rightarrow M^* + TPrA^+}\ \text{(side product)} \tag{5}$$

$$\mathrm{M + TPrA^{\bullet} \rightarrow M^{-\bullet} + TPrA^+}\ \text{(side product)} \tag{6}$$

$$\mathrm{M^{+\bullet} + M^{-\bullet} \rightarrow M^* + M} \tag{7}$$

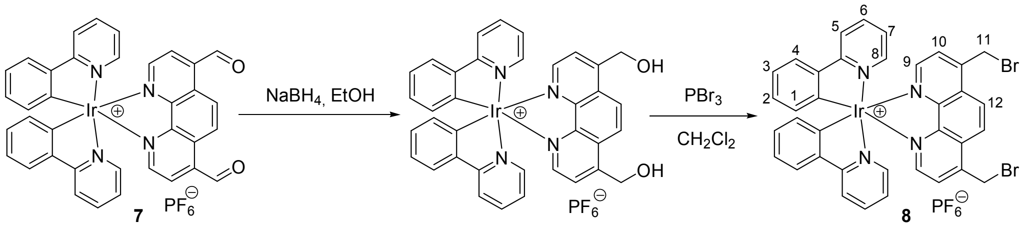
Synthesis of compounds



4 **7**

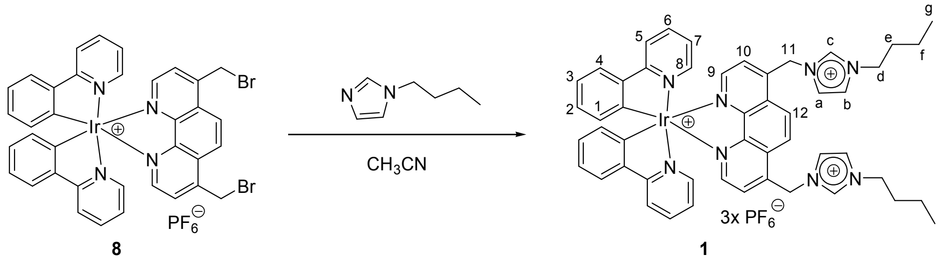
Preparation of **7**. Compound **4** (53.6 mg, 50.0 μmol) and 1,10-phenanthroline-4,7-dicarboxaldehyde (23.6 mg, 100 μmol) were dissolved in dichloromethane (15 mL), and the solution was heated to reflux for 5 hrs. After cooling to rt, KPF$_6$ (55.2 mg, 300 μmol) was added and the mixture stirred for 1 hr. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane. The organic layer was washed with water and dried over Na$_2$SO$_4$. The product was purified by column chromatography with dichloromethane/methanol (19/1, *v*/*v*) as eluent (R_f = 0.22) to afford **7** as a red solid (74.4 mg, 84.5 μmol, 85%). Mp: 204-207 °C (dec.). IR (KBr, cm^{-1}): 3046, 2928, 1705 (C=O), 1608, 1577, 1481, 1419, 1385, 1239, 1114, 1030, 978, 841, 757, 745, 659, 556. ^{1}H NMR (400 MHz, CD$_3$CN): δ = 10.62 (s, 11-H, 2H), 9.33 (s, 12-H, 2H), 8.65 (d, J = 5.1 Hz, 9-H, 2H), 8.26 (d, J = 5.1 Hz, 10-H, 2H), 8.08 (ddd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, J_3 = 0.7 Hz, 5-H, 2H), 7.87 (dd, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 4-H, 2H), 7.81 (ddd, J_1 = 8.2 Hz, J_2 =7.4 Hz, J_3 = 1.5 Hz, 6-H, 2H), 7.41 (ddd, J_1 = 5.9 Hz, J_2 = 1.5 Hz, J_3 = 0.7 Hz, 8-H, 2H), 7.11 (ddd, J_1 = 7.8 Hz, J_2 = 7.6 Hz, J_3 = 1.0 Hz, 3-H, 2H), 7.00 (ddd, J_1 = 7.6 Hz, J_2 = 7.4 Hz, J_3 = 1.3 Hz, 2-H, 2H), 6.86 (ddd, J_1 = 7.4 Hz, J_2 = 5.9 Hz, J_3 = 1.3 Hz, 7-H, 2H), 6.36 (ddd, J_1 = 7.4 Hz, J_2 = 1.0 Hz, J_3 = 0.7 Hz, 1-H, 2H); ^{13}C NMR (100 MHz, CD$_3$CN): δ = 193.0, 168.2, 153.8, 150.6, 150.2, 148.7, 145.1, 139.8, 138.7, 132.6, 131.5, 131.3, 129.1, 127.6, 126.0, 124.5, 124.0, 121.0. ESI-MS $(C_{36}H_{24}IrN_4O_2)^+$: Calcd: *m/z* =

736.8, found: 737.6. Anal. for $C_{36}H_{24}F_6IrN_4O_2P{\bullet}0.2CH_2Cl_2$: Calcd: C, 48.38; H, 2.74; N, 6.23; found: C, 48.31; H, 2.67; N, 6.21.

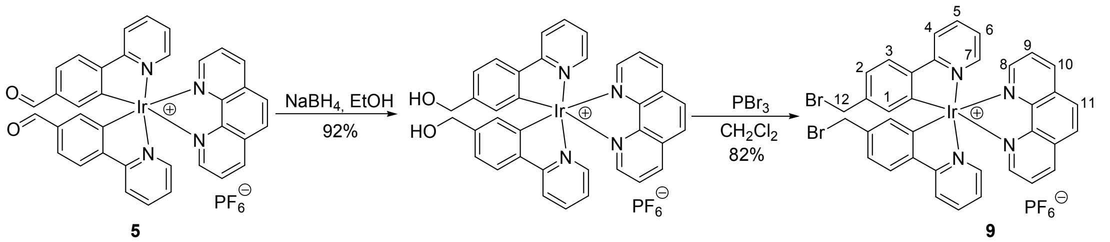


Preparation of **8**. Dicarbaldehyde **7** (44.1 mg, 50.0 μmol) and $NaBH_4$ (7.57 mg, 200 μmol) were mixed in ethanol (25 mL) under N_2. The solution was stirred for 1 h at room temperature and solvent removed under reduced pressure. The residue was quenched by water (50 mL) and extracted by dichloromethane (3×25 mL). The organic layers were combined and dried over Na_2SO_4 for 2 h. After filtering off the salt, the filtrate was evaporated to dryness and residue redissolved in dry dichloromethane (20 mL). PBr_3 (9.49 μL, 100 μmol) was added to the solution under N_2 and the solution was stirred for 4 h at room temperature. Thereafter, the reaction was quenched by water (15 mL) and the aqueous layer extracted by dichloromethane (2 ×15 mL). KPF_6 (55.2 mg, 300 μmol) was added to the combined organic solution and the mixture stirred for 1 h. After filtering off the salt, the filtrate was evaporated and the residue purified by column chromatography with dichloromethane/methanol (19/1, v/v) as eluent (R_f = 0.52) to afford product **8** as yellow solid (38.4 mg, 38.0 μmol, 76%). Mp: 209-213 °C (dec.). IR (KBr, cm^{-1}): 3042, 1606, 1577, 1475, 1442, 1328, 1241, 1149, 1061, 1032, 841, 756, 728, 557. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.53$ (s, 12-H, 2H), 8.32 (d, $J = 5.2$ Hz, 9-H, 2H), 7.96 (ddd, $J_1 = 8.3$ Hz, $J_2 = 1.4$ Hz, $J_3 = 0.8$ Hz, 5-H, 2H), 7.81 (d, $J = 5.2$ Hz, 10-H, 2H), 7.76 (ddd, $J_1 = 8.3$ Hz, $J_2 = 7.6$ Hz, $J_3 = 1.2$ Hz, 6-H, 2H), 7.74 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 4-H, 2H), 7.35 (ddd,

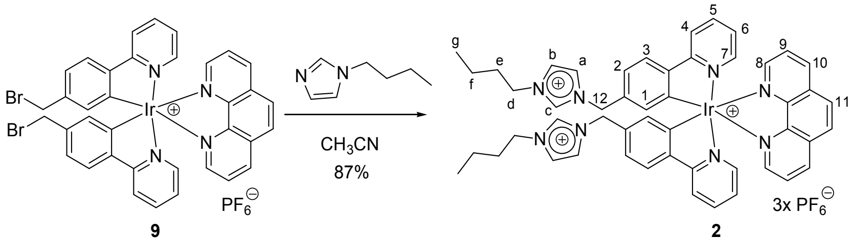
J_1 = 5.9 Hz, J_2 = 1.2 Hz, J_3 = 0.8 Hz, 8-H, 2H), 7.11 (ddd, J_1 = 7.6 Hz, J_2 = 7.4 Hz, J_3 = 1.2 Hz, 3-H, 2H), 6.99 (ddd, J_1 = 7.6 Hz, J_2 = 7.4 Hz, J_3 = 1.2 Hz, 2-H, 2H), 6.90 (ddd, J_1 = 7.6 Hz, J_2 = 5.9 Hz, J_3 = 1.4 Hz, 7-H, 2H), 6.39 (ddd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1-H, 2H), 5.08 (d, J=11.1 Hz, 11-H, 2H), 5.00 (d, J=11.1 Hz, 11-H, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 168.0, 151.8, 149.6, 149.1, 147.8, 146.6, 144.2, 138.7, 132.1, 131.1, 130.1, 127.5, 125.3, 125.1, 123.8, 123.3, 120.2, 27.3. ESI-MS $(C_{36}H_{26}IrN_4)^+$: Calcd: m/z = 866.6, found: 867.2. Anal. for $C_{36}H_{26}Br_2F_6IrN_4P$: Calcd: C, 42.74; H, 2.59; N, 5.54; found: C, 42.80; H, 2.45; N, 5.77.



Preparation of **1**. The dibromide **8** (30.3 mg, 30.0 μmol) and 1-(*n*-butyl)imidazole (15.7 μL, 120 μmol) were dissolved in dry acetonitrile (25 mL) under N_2 and the solution heated to reflux for 12 h. After removal of the solvent, the residue was triturated with diethyl ether (50 mL) and solid collected by filtration. After dissolving the solid in dichloromethane, KPF_6 (27.6 mg, 150 μmol) was added and the mixture stirred for 1 h. The salts were filtered off. Product **1** was obtained as orange solid (36.3 mg, 26.1 μmol, 87%) from the filtrate after evapourating the solvent. Mp: 178-180 °C (dec.). IR (KBr, cm^{-1}): 3444 (C2–H), 3168, 2963, 1610, 1580, 1479, 1422, 1257, 1165, 1032, 843, 760, 628, 558. ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 8.66 (t, J = 1.5 Hz, c-H, 2H), 8.39 (d, J = 5.3 Hz, 9-H, 2H), 8.38 (s, 12-H, 2H), 7.92 (ddd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, J_3 = 0.7 Hz, 5-H, 2H), 7.74 (dd, J_1 = 7.9 Hz, J_2 = 1.1 Hz, 4-H, 2H), 7.71 (ddd, J_1= 8.3 Hz, J_2= 7.6 Hz, J_3 = 1.4 Hz, 6-H, 2H), 7.52 (dd, J_1 = 1.8 Hz, J_2 = 1.5 Hz, a-/b-H, 2H), 7.47 (d, J = 5.3 Hz, 10-H, 2H), 7.40 (ddd, J_1 = 5.9 Hz, J_2 = 1.4 Hz, J_3 = 0.7 Hz, 8-H, 2H), 7.33 (dd, J_1 = 1.8 Hz, J_2 = 1.5 Hz, b/a-H, 2H), 7.08 (ddd, J_1 = 7.9 Hz, J_2 = 7.7 Hz, J_3 = 1.1 Hz, 3-H, 2H), 6.96 (ddd, J_1 = 7.7 Hz, J_2 = 7.6 Hz, J_3 = 1.1 Hz, 2-H, 2H), 6.92 (ddd, J_1= 7.6 Hz. J_2 = 5.9 Hz, J_3 = 1.4 Hz, 7-H, 2H), 6.37 (dd, J_1 = 7.6 Hz, J_2 = 1.1 Hz, 1-H, 2H), 6.11 (d, J = 16.4 Hz, 11-H, 2H), 6.04 (d, J = 16.4 Hz, 11-H, 2H), 4.20-4.11 (m, d-H, 4H), 1.89-1.80 (m, e-H, 4H), 1.35 (m, f-H, 4H), 0.93 (t, J = 7.4 Hz, g-H, 6H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.6, 152.3, 149.8, 149.3, 147.7, 144.3, 141.7, 138.6, 136.5, 132.1, 131.0, 129.7, 126.3, 125.2, 124.9, 124.2, 123.6, 123.3 (2C; C3 and Cb), 120.0, 50.9, 49.9, 32.0, 19.8, 13.4 ppm. ESI-MS $(C_{50}H_{50}IrN_8{\cdot}2PF_6)^+$: Calcd: m/z = 1245.1; found: 1245.3. Anal. for $C_{50}H_{50}F_{18}IrN_8P_3$: Calcd: C, 43.20; H, 3.63; N, 8.06; found: C, 42.82; H, 3.46; N, 7.87.



Preparation of **9**. Dicarbaldehyde **5** (44.1 mg, 50.0 μmol), $NaBH_4$ (7.57 mg, 200 μmol) and ethanol (25 mL) were stirred under N_2 for 1 h at rt, then the solvent was removed under reduced pressure. The residue was quenched by addition of water (50 mL) and extracted by dichloromethane (3×25 mL). The organic layers were dried over Na_2SO_4 for 2 h. The salt was filtered off and the filtrate evapourated to dryness. The resultant solid was dissolved in dry dichloromethane (20 mL). PBr_3 (9.49 μL, 100 μmol) was added to the solution under N_2, then it was stirred for 4 h at rt. Thereafter, the reaction was quenched by water (15 mL) and the aqueous layer was extracted by dichloromethane (2 ×15 mL). KPF_6 (55.2 mg, 300 μmol) was added to the combined organic layers and the mixture stirred for 1 h. The salts were filtered off and the concentrated filtrate was purified by column chromatography with dichloromethane/methanol (19/1, v/v) as eluent (R_f = 0.46) to afford product **9** as yellow solid (38.7 mg, 38.3 μmol, 77%). Mp: 175-178 °C (dec.). IR (KBr, cm^{-1}): 3065, 2924, 1590, 1477, 1425, 1310, 1225, 1010, 842, 779, 723, 640, 556. ^1H NMR (400 MHz, CD_2Cl_2): δ= 8.65 (dd, J_1 = 8.3 Hz, J_2= 1.4 Hz, 10-H, 2H), 8.31 (dd, J_1 = 5.1 Hz, J_2= 1.4, 8-H, 2H), 8.22 (s, 11-H, 2H), 7.98 (ddd, J_1 = 8.5 Hz, J_2= 1.3 Hz, J_3= 0.7 Hz, 4-H, 2H), 7.85 (dd, J_1 = 8.3 Hz, J_2= 5.1 Hz, 9-H, 2H), 7.80-7.74 (m, 3-H, 5-H, 4H), 7.33 (ddd, J_1 = 5.9 Hz, J_2=1.4 Hz, J_3= 0.7 Hz, 7-H, 2H), 7.21 (dd, J_1 = 8.1 Hz, J_2= 1.7 Hz, 2-H, 2H), 6.89 (ddd, J_1 = 7.3 Hz, J_2= 5.9 Hz, J_3= 1.3 Hz, 6-H, 2H), 6.38 (d, J = 1.7 Hz, 1-H, 2H), 4.35 (d, J = 10.2 Hz, 12-H, 2H), 4.32 (d, J = 10.2 Hz, 12-H, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.4, 151.6, 149.6, 149.0, 147.1, 144.5, 140.6, 139.1, 138.9, 132.3, 132.0, 128.9, 127.2, 125.6, 124.5, 124.0, 120.6, 34.3. ESI-MS $(C_{36}H_{26}IrN_4)^+$: Calcd: m/z = 866.6, found: 867.2. Anal. for $C_{36}H_{26}Br_2F_6IrN_4P$•$1.5CH_2Cl_2$: Calcd: C, 39.54; H, 2.57; N, 4.92; found: C, 39.40; H, 2.35; N, 4.63.



Preparation of **2**. Dibromide **9** (30.3 mg, 30.0 μmol) and 1-(*n*-butyl)imidazole (15.7 μL, 120 μmol) in dry acetonitrile (25 mL) were heated to reflux for 12 h under N_2. After removal of the solvent, the residue was triturated by diethyl ether (50 mL) and the solid collected by filtration. After dissolving it in dichloromethane, KPF_6 (27.6 mg, 150 μmol) was added to the solution and the mixture was stirred for 1 h. The salts were filtered off. Product **2** was obtained as orange solid (35.6 mg, 25.6 μmol, 85%) from the filtrate after removing the solvent. Mp: 159-161 °C (dec.). IR (KBr, cm^{-1}): 3438 (C2–H), 3161, 2962, 2870, 1608, 1565, 1478, 1435, 1402, 1339, 1257, 1164, 1064, 843, 752, 632, 558. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.57 (t, J = 1.5 Hz, c-H, 2H), 8.56 (dd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 10-H, 2H), 8.36 (dd, J_1 = 5.1 Hz, J_2 = 1.4 Hz, 8-H, 2H), 8.14 (s, 11-H, 2H), 7.96 (dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 4-H, 2H), 7.90 (dd, J_1 = 8.3 Hz, J_2 = 5.1 Hz, 9-H, 1H), 7.80 (d, J = 8.1 Hz, 3-H, 2H), 7.76 (ddd, J_1 = 8.3 Hz, J_2 =7.9 Hz, J_3 =1.4 Hz, 5-H, 2H), 7.42 (ddd, J_1 = 5.7 Hz, J_2 = 1.4 Hz, J_3 = 0.7 Hz, 7-H, 2H), 7.28 (dd, J_1 = 1.8 Hz, J_2 = 1.5 Hz, a or b-H, 2H), 7.20 (dd, J_1 = 1.8 Hz, J_2 = 1.5 Hz, a or b-H, 2H), 6.98-6.91 (m, 2-H, 6-H, 4H), 6.23 (d, J = 1.7 Hz, 1-H, 2H), 5.22 (d, J = 15.1 Hz, 12-H, 2H), 5.10 (d, J = 15.1 Hz, 12-H, 2H), 4.14 (t, J = 7.4 Hz, d-H, 4H), 1.90-1.79 (m, e-H, 4H), 1.36 (m, f-H, 4H), 0.97 (t, J = 7.4 Hz, g-H, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 166.8, 152.6, 150.6, 149.8, 147.0, 145.5, 138.9, 138.6, 135.9, 135.1, 131.7, 131.4, 128.6, 127.8, 125.7, 124.7, 123.3, 122.9, 122.5, 120.5, 53.8 (partly obscured by solvent signal), 50.5, 32.3, 19.8, 13.5. ESI-MS $(C_{50}H_{50}IrN_8{\bullet}2PF_6)^+$: Calcd: m/z = 1245.1, found: 1245.3. Anal. for $C_{50}H_{50}F_{18}IrN_8P_3{\bullet}0.2CH_2Cl_2$: Calcd.: C, 43.02; H, 3.62; N, 8.01; found: C, 42.74; H, 3.64; N, 7.82.

Figures and Tables

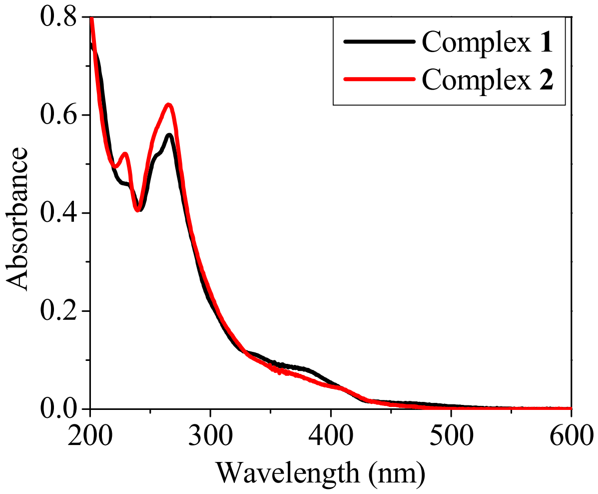


Figure S1 UV-Vis absorption spectra of complexes **1** and **2** in MeCN; [**1**] = [**2**] = 10 µM.

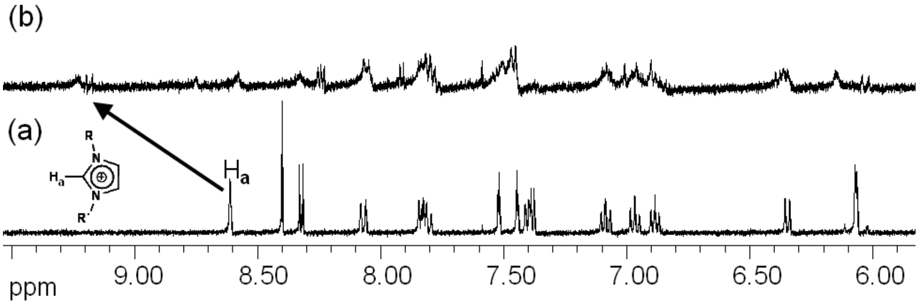


Figure S2 ^{1}H NMR spectra of complex **1** (1 mM) in CD_3CN in (a) absence and (b) presence of 2.8 equiv. of *n*-Bu_4NF.

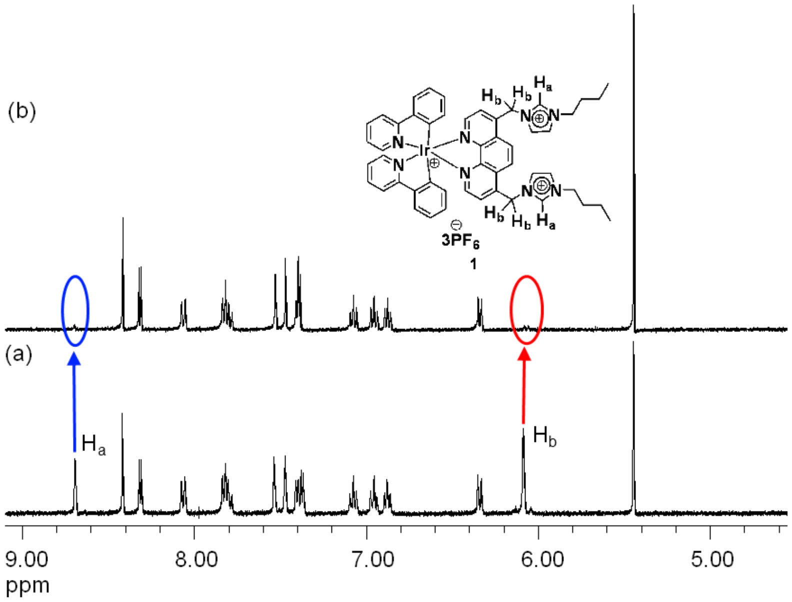


Figure S3 ^{1}H NMR spectrum of complex **1** (1 mM) in CD_3CN/CD_3OD (v/v, 9:1) in (a) absence and (b) presence of 2.0 equiv. of *n*-Bu_4NF.

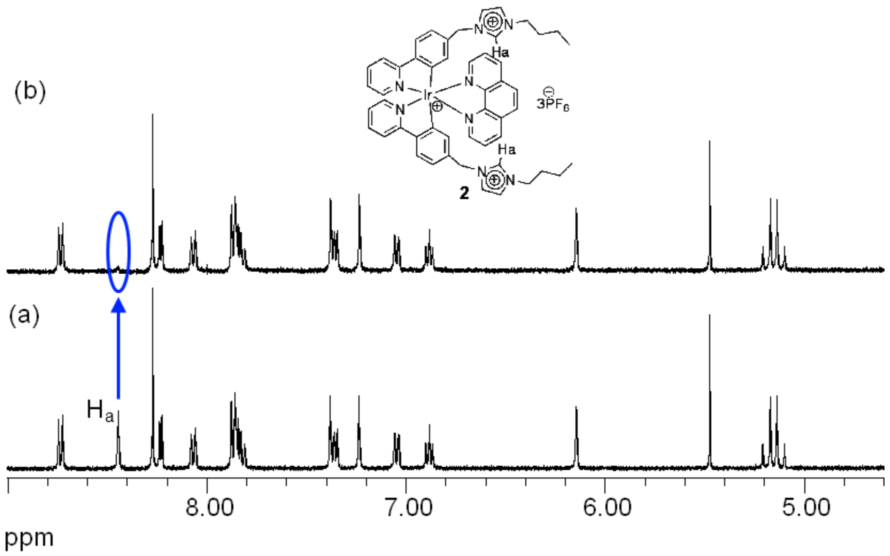


Figure S4 ^{1}H NMR spectrum of complex **2** (1 mM) in CD_3CN/CD_3OD (v/v, 9:1) in (a) absence and (b) presence of 2.0 equiv. of *n*-Bu_4NF.

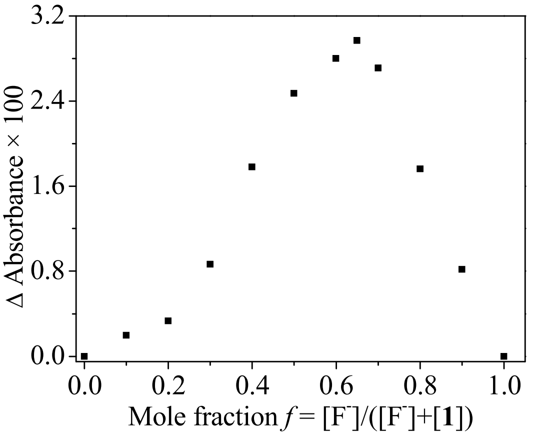


Figure S5 Job plot (ΔAbsorbance at 457 nm) of compound **1** vs. F^- in MeCN. Concentration: $[F^-]$ + [**1**] = 10 μM.

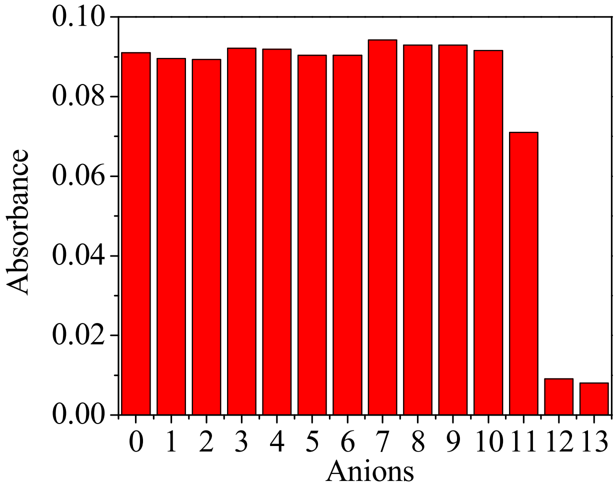


Figure S6 Absorbance (at 457 nm) of complex **1** (10 μM) and 50 μM of F^- in MeCN in presence of various anions at *c* = 50 μM (0: no additive; 1: NO_3^-; 2: PF_6^-; 3: ClO_4^-; 4: BF_4^-; 5: Br^-; 6: $MeSO_3^-$; 7: $CF_3SO_3^-$; 8: Cl^-; 9: TsO^-; 10: $PhCOO^-$; 11: AcO^-; 12: $H_2PO_4^-$; 13: HSO_4^-).

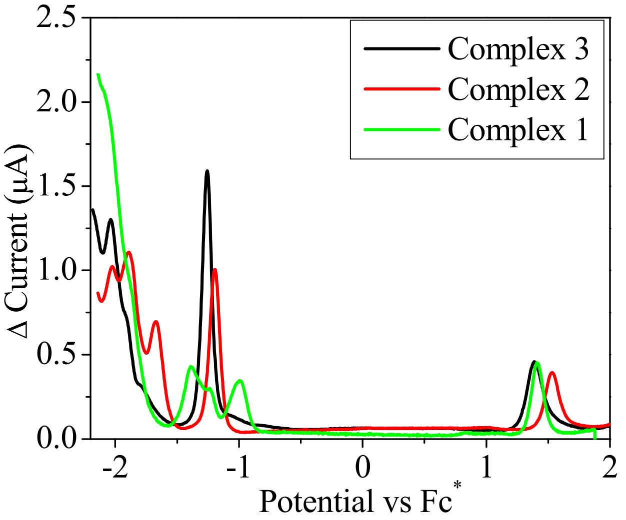


Figure S7 Differential pulse voltammetry (DPV) measurements of complex **1** (green), **2** (red) and **3** (black), all recorded in MeCN with 0.1 M *n*-Bu_4NPF_6 as electrolyte, Fc^* = decamethylferrocene as reference).

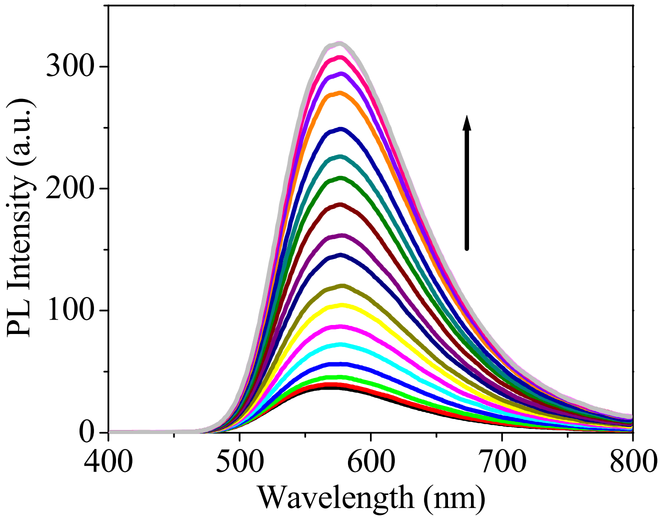


Figure S8 PL spectra (λ_{ex} = 272 nm) of complex **2** (10 μM) in presence of $H_2PO_4^-$ (0 to 36 μM) in MeCN.

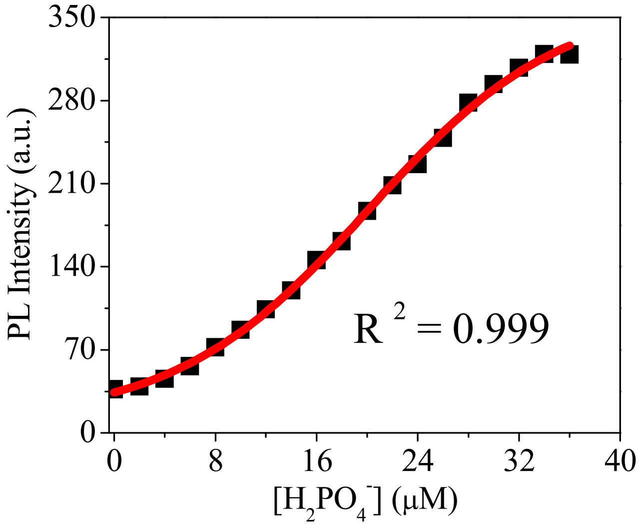


Figure S9 PL titration curve (λ_{ex} = 272 nm, λ_{em} = 566 nm) of **2** (10 μM) in presence of $H_2PO_4^-$ (0 to 36 μM) in MeCN.

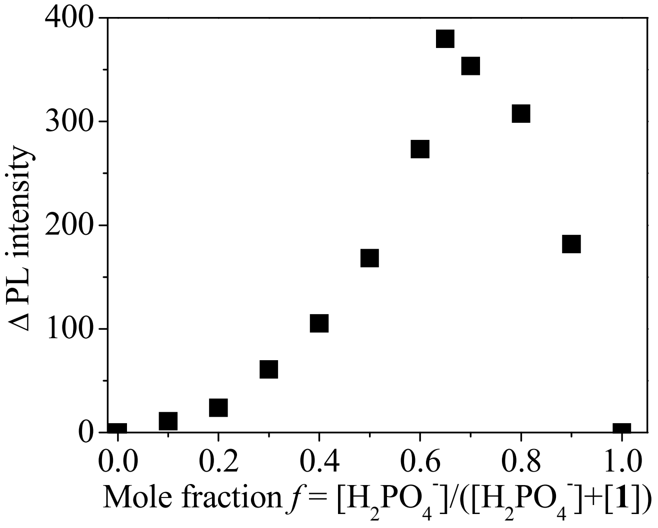


Figure S10 Job plot (ΔPL at 607 nm) of compound **1** vs. $H_2PO_4^-$ in MeCN. Concentrations: $[H_2PO_4^-]$ + [**1**] = 10 μM, λ_{ex} = 272 nm.

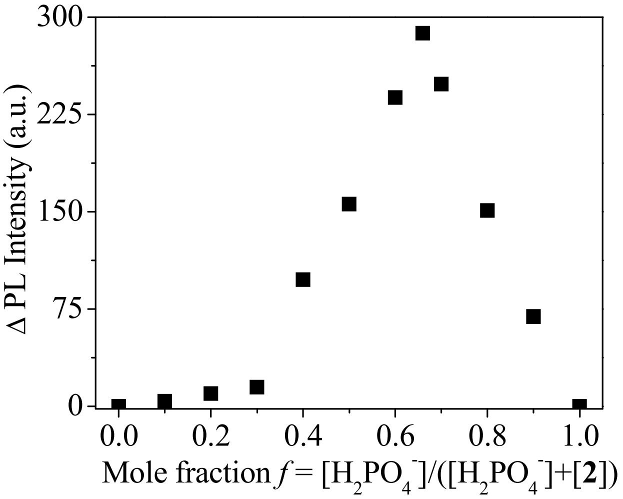


Figure S11 Job plot (ΔPL at 566 nm) of compound **2** vs. $H_2PO_4^-$ in MeCN. Concentrations: $[H_2PO_4^-] + [\mathbf{2}] = 10$ μM, $\lambda_{ex} = 272$ nm.

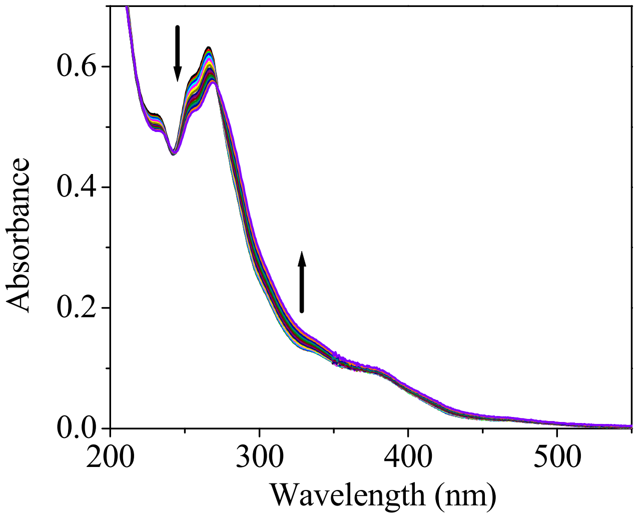


Figure S12 UV-vis absorption spectra of complex **1** (10 μM) in MeCN during a titration with $H_2PO_4^-$ (0 to 30 μM).

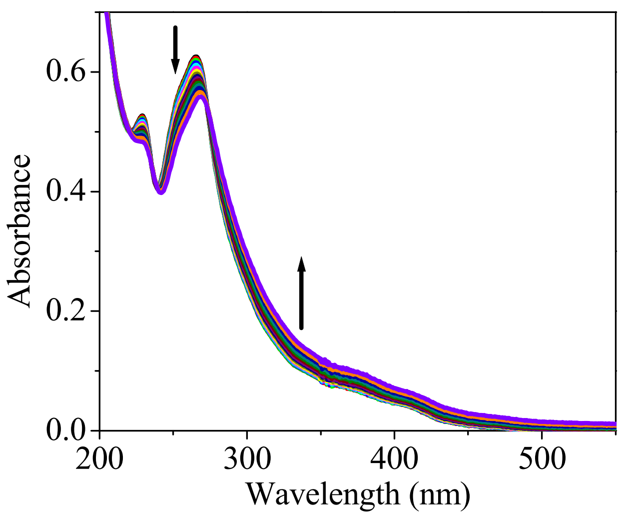


Figure S13 UV-vis absorption spectra of complex **2** (10 μM) in MeCN during a titration with $H_2PO_4^-$ (0 to 30 μM).

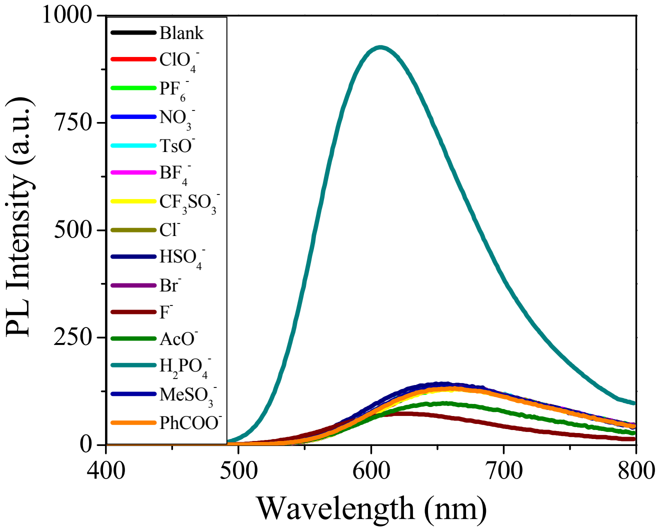


Figure S14 PL spectra (λ_{ex} = 272 nm) of complex **1** (10 μM) in presence of various anions at c = 50 μM ($H_2PO_4^-$, HSO_4^-, F^-, Cl^-, Br^-, BF_4^-, PF_6^-, ClO_4^-, NO_3^-, $CF_3SO_3^-$, $MeSO_3^-$, AcO^-, $PhCOO^-$ and TsO^-).

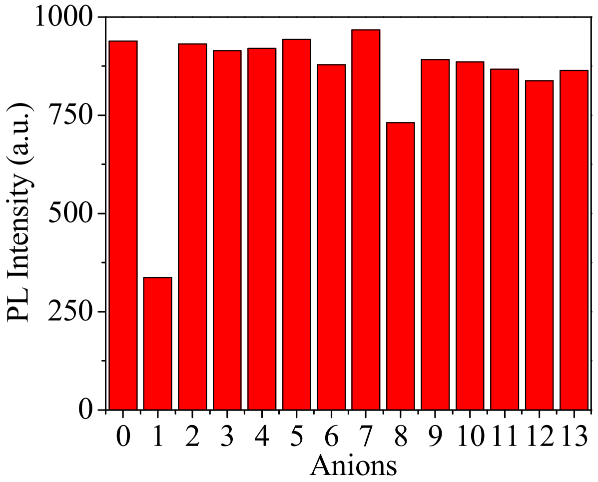


Figure S15 PL intensity (λ_{ex} = 272 nm, λ_{em} = 607 nm) of complex **1** (10 µM) in presence of 50 µM $H_2PO_4^-$ in MeCN and of various anions at *c* = 50 µM (0: no additive; 1: F^-; 2: Cl^-; 3: Br^-; 4: $MeSO_3^-$; 5: ClO_4^-; 6: PF_6^-; 7: BF_4^-; 8: AcO^-; 9: NO_3^-; 10: $PhCOO^-$; 11: TsO^-; 12: $CF_3SO_3^-$; 13: HSO_4^-).

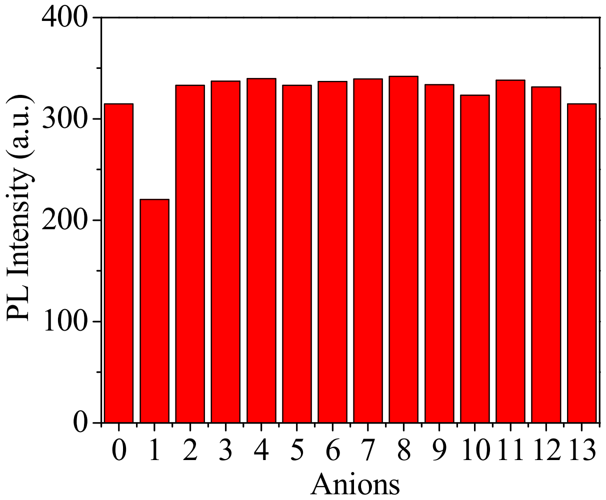


Figure S16 PL intensity (λ_{ex} = 272 nm, λ_{em} = 566 nm) of complex **2** (10 µM) in presence of 50 µM $H_2PO_4^-$ in MeCN and of various anions at *c* = 50 µM (0: no additive; 1: F^-; 2: Cl^-; 3: Br^-; 4: $MeSO_3^-$; 5: ClO_4^-; 6: PF_6^-; 7: BF_4^-; 8: AcO^-; 9: NO_3^-; 10: $PhCOO^-$; 11: TsO^-; 12: $CF_3SO_3^-$; 13: HSO_4^-).

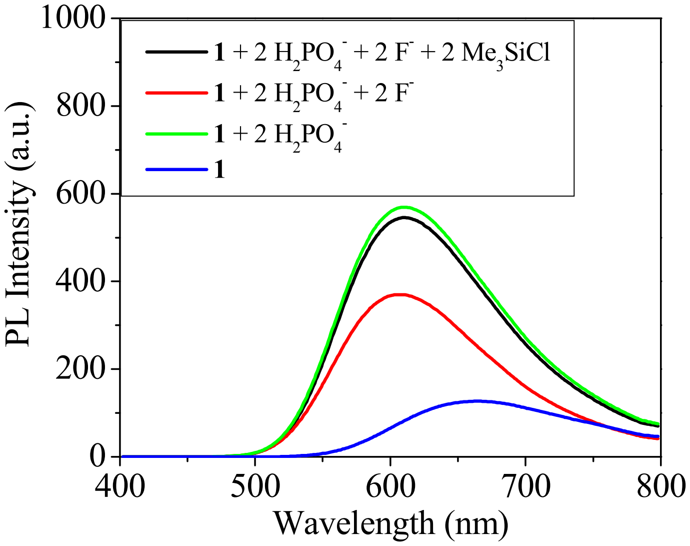


Figure S17 PL spectra (λ_{ex} = 272 nm) of complex **1** (10 μM) (blue), **1** (10 μM) + 2 equiv. of $H_2PO_4^-$ (green), **1** (10 μM) + 2 equiv. of $H_2PO_4^-$ and F^- (red), **1** (10 μM) + 2 equiv. of $H_2PO_4^-$, F^- and Me_3SiCl (black).

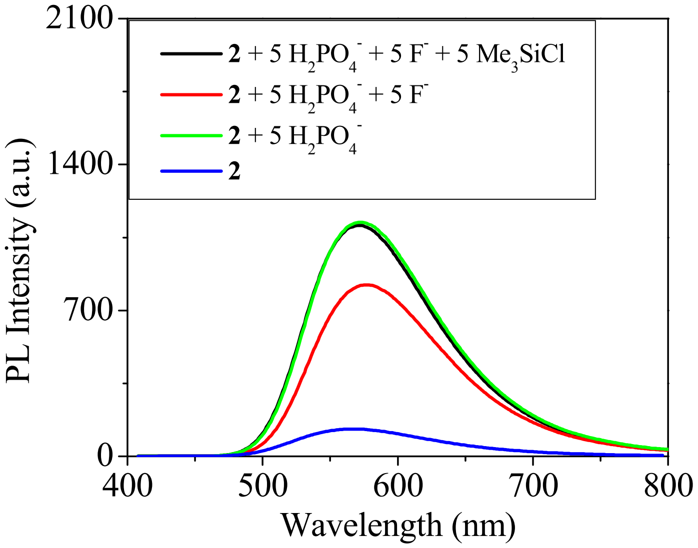


Figure S18 PL spectra (λ_{ex} = 272 nm) of complex **2** (10 μM) (blue), **2** (10 μM) + 2 equiv. of $H_2PO_4^-$ (green), **2** (10 μM) + 5 equiv. of $H_2PO_4^-$ and F^- (red), **2** (10 μM) + 5 equiv. of $H_2PO_4^-$, F^- and Me_3SiCl (black).

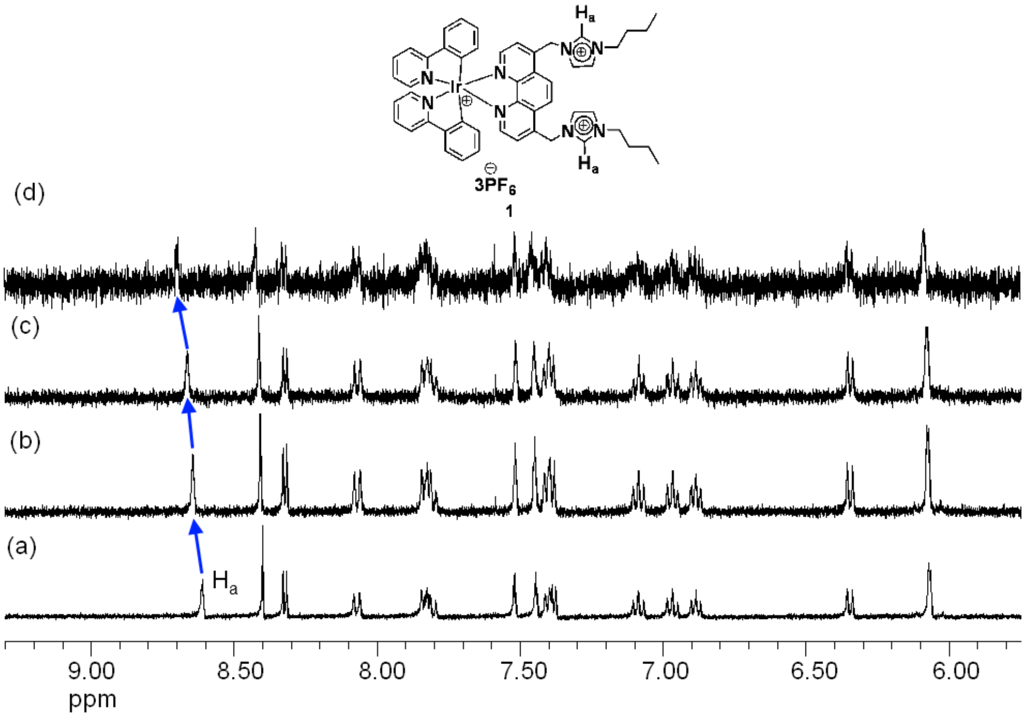


Figure S19 ^{1}H NMR spectrum of complex **1** (1 mM) in CD_3CN: (a) in absence and (b) presence of 0.8 equiv, (c) 1.6 equiv, (d) 2.4 equiv of *n*-$Bu_4NH_2PO_4$.

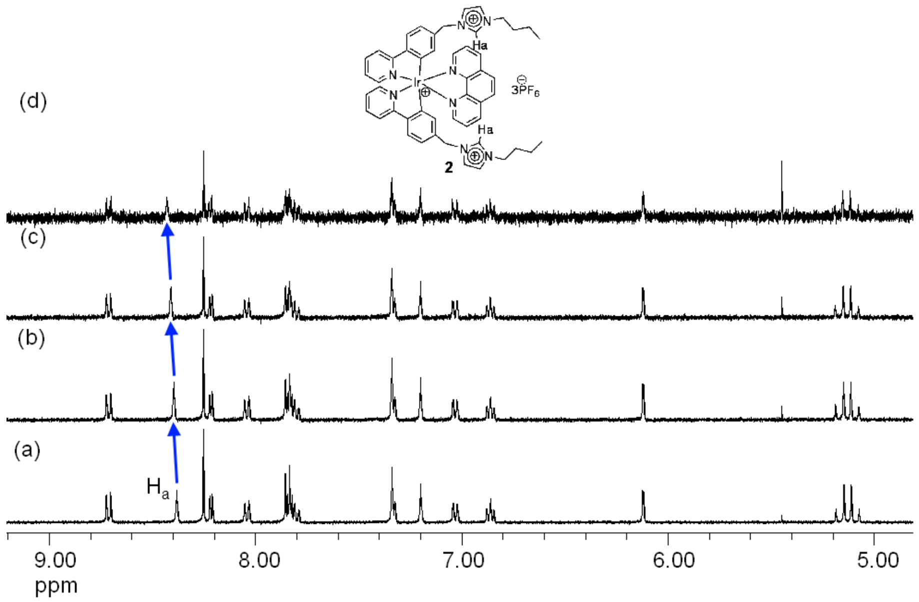


Figure S20 ^{1}H NMR spectrum of complex **2** (1 mM) in CD_3CN: (a) in absence and (b) presence of 0.8 equiv, (c) 1.6 equiv, (d) 2.4 equiv of *n*-$Bu_4NH_2PO_4$.

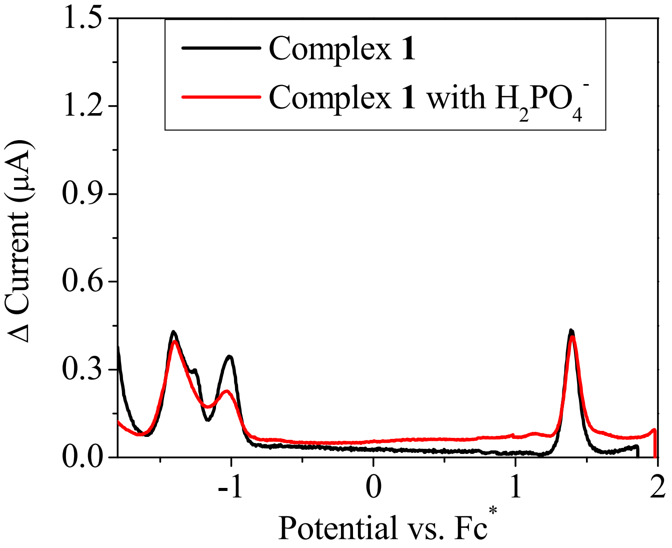


Figure S21 Differential pulse voltammetry (DPV) measurements of complex **1** in the absence (black) and presence (red) of $H_2PO_4^-$ in MeCN (0.1 M *n*-Bu_4NPF_6 as electrolyte, Fc^* = decamethylferrocene as reference).

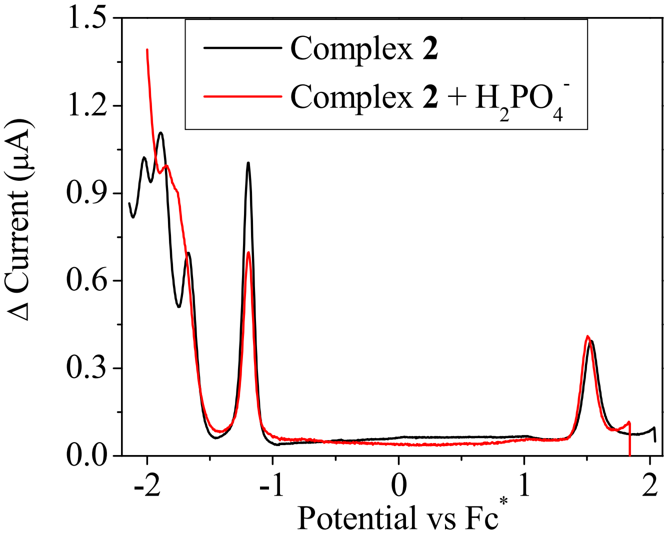


Figure S22 Differential pulse voltammetry (DPV) measurements of complex **2** in the absence (black) and presence (red) of $H_2PO_4^-$ in MeCN (0.1 M *n*-Bu_4NPF_6 as electrolyte, Fc^* = decamethylferrocene as reference).

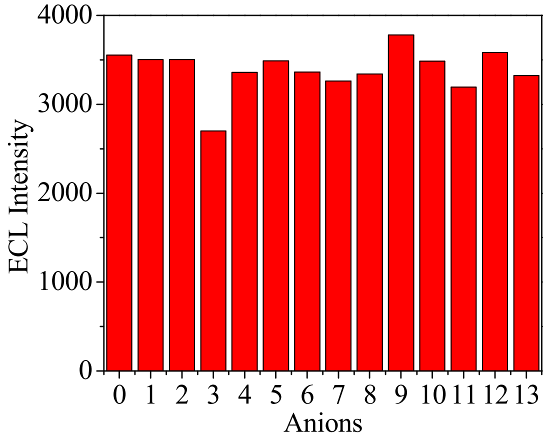


Figure S23 ECL intensity (λ_{em} = 605 nm) of complex **1** (10 μM) in presence of 2 mM AcO⁻ in MeCN-Tris buffered solution (v/v, 9:1, 10 mM, pH = 7.2) and of equimolar amounts of various anions (0: only AcO⁻; 1: F⁻; 2: Cl⁻; 3: Br⁻; 4: $MeSO_3^-$; 5: ClO_4^-; 6: PF_6^-; 7: BF_4^-; 8: $H_2PO_4^-$; 9: NO_3^-; 10: TsO⁻; 11: $CF_3SO_3^-$; 12: HSO_4^-; 13: PhCOO⁻).

General remarks on probe 1

Our triple-channel lab-on-a-molecule for three different anions operates on a very fine balance of deprotonation, electrostatic interaction and hydrogen bonding for sensing. Addition of H^+ will undermine this balance. When the molar ratio of F^- (20 μM) and H^+ (10 μM) reaches 2:1 in a MeCN solution of complex **1** (10 μM), the extra peak at 457 nm in the UV-Vis channel disappears. Similarly, when the molar ratio of $H_2PO_4^-$ (30 μM) and H^+ (60 μM) reaches 1:2 in a solution of complex **1** (10 μM), the enhancement in the PL channel disappears. In case of AcO⁻ (1 mM), H^+ (up to 100 μM) did not affect the response of complex **1** (10 μM) due to the added buffer.

References

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