

## **Electronic Supplementary Information**

### **Lab-on-a-molecule for anions in aqueous solution: Using Kolbe electrolysis and radical methylation at iridium for sensing**

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#### Abbreviations:

ACN: Acetonitrile  
DCM: Dichloromethane  
TPrA: Tri-*n*-propylamine

## General information

**Photoluminescence and UV-Vis measurements.** Using a solution of the iridium complex (10  $\mu\text{M}$ ) in MeCN / aq. buffer = 50 / 50 (v / v; aq. buffer = 0.1 M Tris-ClO<sub>4</sub>, pH 7.24), UV-vis measurements were carried out on a Varian Cary 100 Bio UV-Visible Spectrophotometer and photoluminescence (PL) measurements on a Varian Cary Eclipse Fluorescence Spectrophotometer with excitation and emission slit widths set to 5 nm. For sensing, all PL measurements were done a given time after addition of the anions, in order to allow for completion of the ground state reaction between cyanide and **1**. No or a very slow reaction was registered in case of the other anions.

**Electroanalytical Investigations.** Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) of compounds were measured at a scan rate  $\nu = 100 \text{ mV s}^{-1}$  using a standard three-electrode set-up (1 mm Pt disk working electrode, a Pt auxiliary electrode, a silver wire as a pseudoreference electrode) connected to a PARSTAT 2273 Advanced Electrochemical System. The experiments were carried out on compounds (1 mM) dissolved in acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte, unless stated otherwise. All potentials are referenced to FeCp\*<sub>2</sub> (Cp\* = pentamethylcyclopentadienyl) using FeCp\*<sub>2</sub> as internal standard.

**Electrochemiluminescence (ECL) Investigations.** ECL measurements were done on the iridium complex **1** (10  $\mu\text{M}$ ) in MeCN / aq. buffer = 90 / 10 (v / v; aq. buffer = 0.1 M Tris-ClO<sub>4</sub>, pH 7.24) containing tri-*n*-propylamine (TPrA; 30 mM) as co-reactant and tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as electrolyte. Solutions for sensing the anions were freshly prepared within 2 minutes prior to the ECL measurements. 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 potentiostat was used. To generate the ECL, the potential of the working electrode was swept between 0.5 to 1.8 V (vs a silver wire as quasi-reference electrode) at a scan rate  $\nu = 100 \text{ mV s}^{-1}$ . Potential dependent measurements were carried out at a scan rate of 100  $\text{mV s}^{-1}$  varying the switching potential from 1.3 - 1.8 V. ECL competition experiments were carried with **1** (10  $\mu\text{M}$ ) in presence of 200 equiv. of acetate and of 200 equiv. of the other anion. The resulting emission

spectra were obtained with a CCD camera cooled to  $-50\text{ }^{\circ}\text{C}$  (0.500 m Imaging Triple Grating Monochromator / Spectrograph), which was connected to spectrometer Spectrapro 2500i (Acton Research Corporation).

### Synthesis of iridium compounds 1-3

#### General Information

**NMR spectra.**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker Advance 400 (400 MHz) and Varian DMX 600 (600 MHz). Chemical shifts are reported in ppm. **Mass spectroscopy.** ESI-MS measurements were recorded on a LCQ Deca Thermo Quest instrument. **Elemental analysis.** Elemental analysis was performed on an elemental analyzer from EuroVector

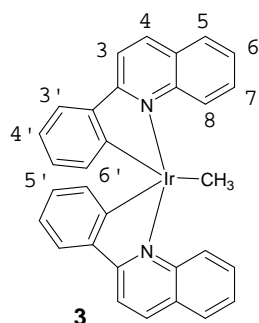
#### Synthesis and characterization of **1**<sup>1</sup>

Iridium trichloride hydrate (145 mg, 403  $\mu\text{mol}$ ) and 2-phenylquinoline (205 mg, 1.00 mmol) were dissolved in a mixture of 2-ethoxyethanol (12 mL) and water (4 mL), then refluxed for 24 h. The solution was cooled to room temp. and the orange-red precipitate was collected by filtration. After washing the precipitate with ethanol (10 mL) and acetone (20 mL), it was dissolved in dichloromethane (15 mL) and filtered. Toluene (10 mL) and hexane (5 mL) were added to the filtrate, which was then reduced in volume to 20 mL by evaporation and cooled to furnish red crystals of  $[\text{Ir}(\text{pq})_2\text{Cl}]_2$ . Yield: 200 mg (157  $\mu\text{mol}$ , 78%).

$^1\text{H}$ -NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 5.80 (d,  $J$  = 7.6 Hz, 1H), 6.37 (dt,  $J_1$  = 1.9 Hz,  $J_2$  = 7.2 Hz,  $J_3$  = 8.0 Hz, 1H), 6.84 (t,  $J$  = 7.4 Hz, 1H), 7.14-7.18 (m, 1H), 7.40-7.41 (m, 1H), 7.63-7.66 (m, 1H), 7.70 (d,  $J$  = 7.8 Hz, 1H), 7.95-7.96 (m, 1H), 8.03-8.06 (m, 1H), 8.53 (d,  $J$  = 8.9 Hz, 1H). ESI-MS for  $(\text{C}_{30}\text{H}_{20}\text{IrN}_2)^+$ : Calcd.:  $m/z$  = 601.7, found:  $m/z$  = 601.7. Elemental analysis for  $\text{C}_{60}\text{H}_{40}\text{Ir}_2\text{N}_4\text{Cl}_2$ : Calcd.: C, 56.93; H, 3.29; N, 4.28. Found: C, 56.64; H, 3.17; N, 4.40.



### Synthesis and characterization of **3**



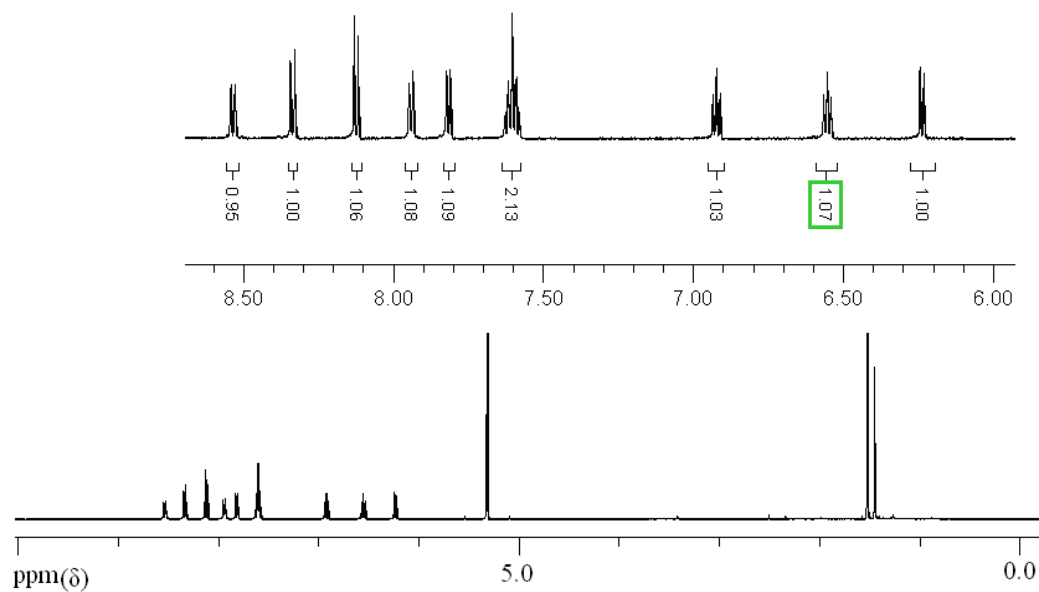
A mixture of **1** (12.7 mg, 10.0  $\mu\text{mol}$ ) and *n*-Bu<sub>4</sub>NOAc (15.0 mg, excess) was dissolved in DCM (15 mL). This solution was put into in the anodic chamber of an electrolytic cell and connected to a Pt wire as working electrode. Likewise, 15 mL of DCM containing 15.0 mg of *n*-Bu<sub>4</sub>NOAc was added into cathodic chamber using a Pt wire as counter electrode. The electrolysis process was controlled by a constant potential set to 1.8 V, while the solutions in both chambers were kept stirring in the dark for 4 h (during electrolysis). Then, the solutions were extracted with water (3 x 20 mL). The organic phase was collected and the solvent amount was reduced to 15 mL in vacuo. Then 15 mL of toluene were added to the solution and left for slow evaporation at room temperature. Recrystallization by this procedure afforded **3** as dark red crystals. *R*<sub>f</sub> of **3** is 0.72 (eluent: 10% methanol in DCM). Yield: 5.41 mg (8.78  $\mu\text{mol}$ , 88%).

<sup>1</sup>H-NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1.45 (s, 3H, Ir-CH<sub>3</sub>), 6.24 (dd,  $J_1$  = 1.1 Hz,  $J_2$  = 7.8 Hz, 2H, 3'-H), 6.55 (ddd,  $J_1$  = 1.3 Hz,  $J_2$  = 7.2 Hz,  $J_3$  = 7.8 Hz, 2H, 4'-H), 6.92 (ddd,  $J_1$  = 1.1 Hz,  $J_2$  = 7.2 Hz,  $J_3$  = 7.8 Hz, 2H, 5'-H), 7.60 (m, 4H, 6-H, 7-H), 7.81 (dd,  $J_1$  = 1.3 Hz,  $J_2$  = 7.2 Hz, 2H, 6'-H), 7.94 (m, 2H, 5-H), 8.12 (d,  $J$  = 8.8 Hz, 2H, 3-H), 8.34 (d,  $J_2$  = 8.8 Hz, 2H, 4-H), 8.54 (ddd,  $J_1$  = 0.8 Hz,  $J_2$  = 1.9 Hz,  $J_3$  = 7.8 Hz, 2H, 8-H).

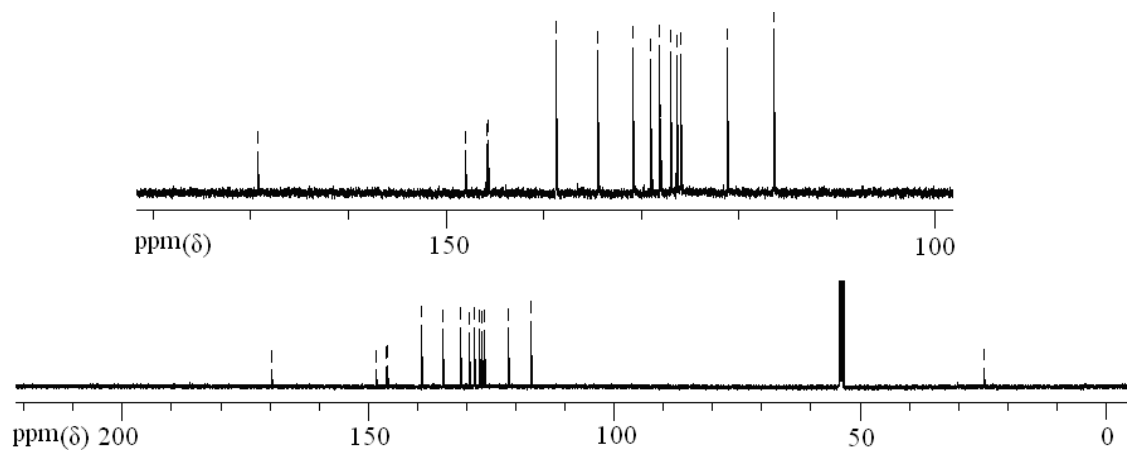
<sup>13</sup>C-NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 24.8 (Ir-CH<sub>3</sub>), 116.8 (C3), 121.6 (C5'), 126.4 (C6'), 126.8 (C6), 127.3 (C8), 128.4 (C5), 128.5, 129.4 (C4'), 131.2 (C7), 134.8 (C3'), 139.2 (C4), 146.1, 146.2, 148.4, 169.6.

ESI-MS: (C<sub>30</sub>H<sub>20</sub>IrN<sub>2</sub>)<sup>+</sup> Calcd.:  $m/z$  = 601.7, found:  $m/z$  = 601.6.

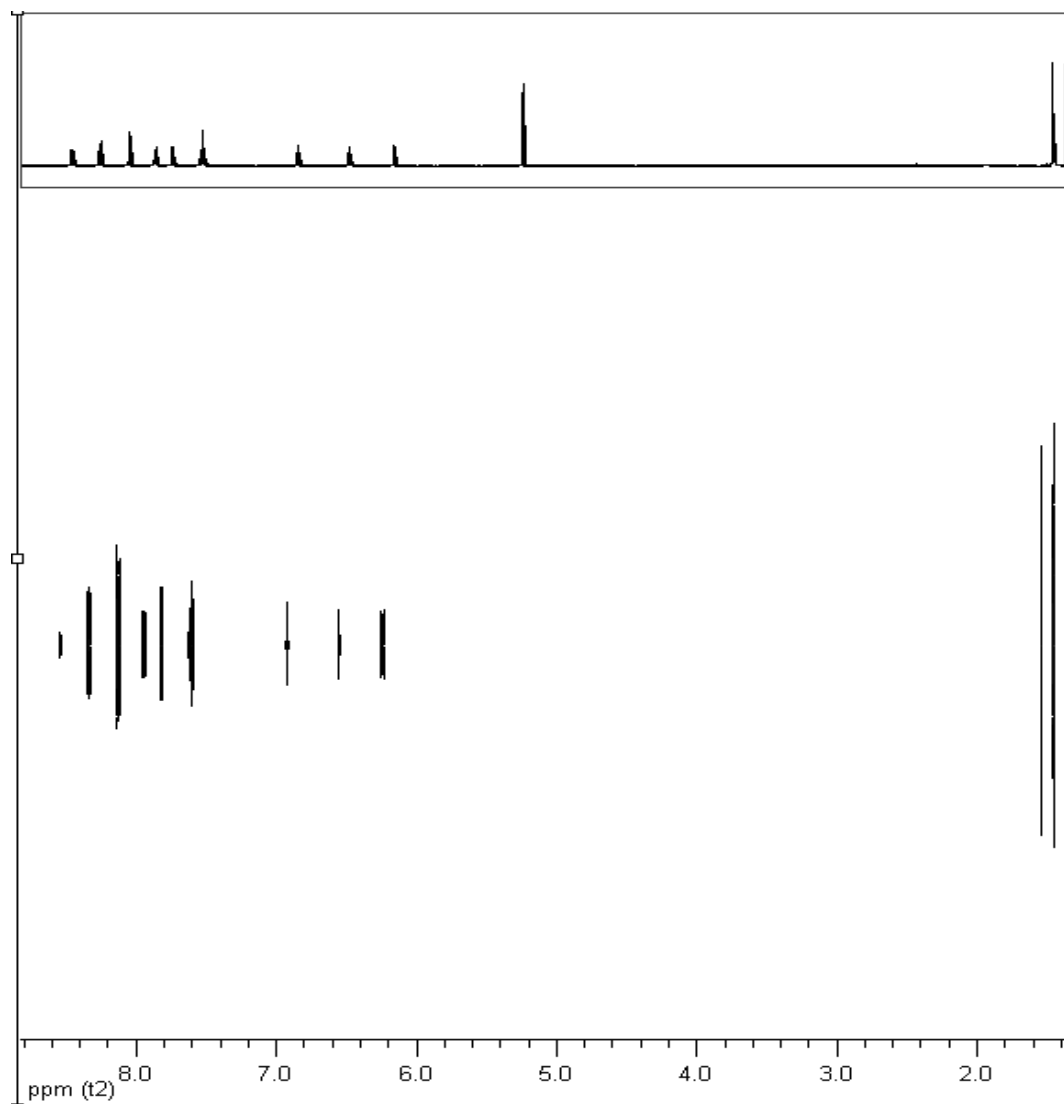
Elemental analysis for C<sub>31</sub>H<sub>23</sub>IrN<sub>2</sub> · 0.5 CH<sub>2</sub>Cl<sub>2</sub>: Calcd.: C, 57.08; H, 3.66; N, 4.22. Found: C, 57.48; H, 3.68; N, 4.26.



**Figure S2.**  $^1\text{H}$  NMR of **3** in  $\text{CD}_2\text{Cl}_2$ . Peak at 1.54 ppm is derived from residual water, as it exchanges with  $\text{CD}_3\text{OD}$ .

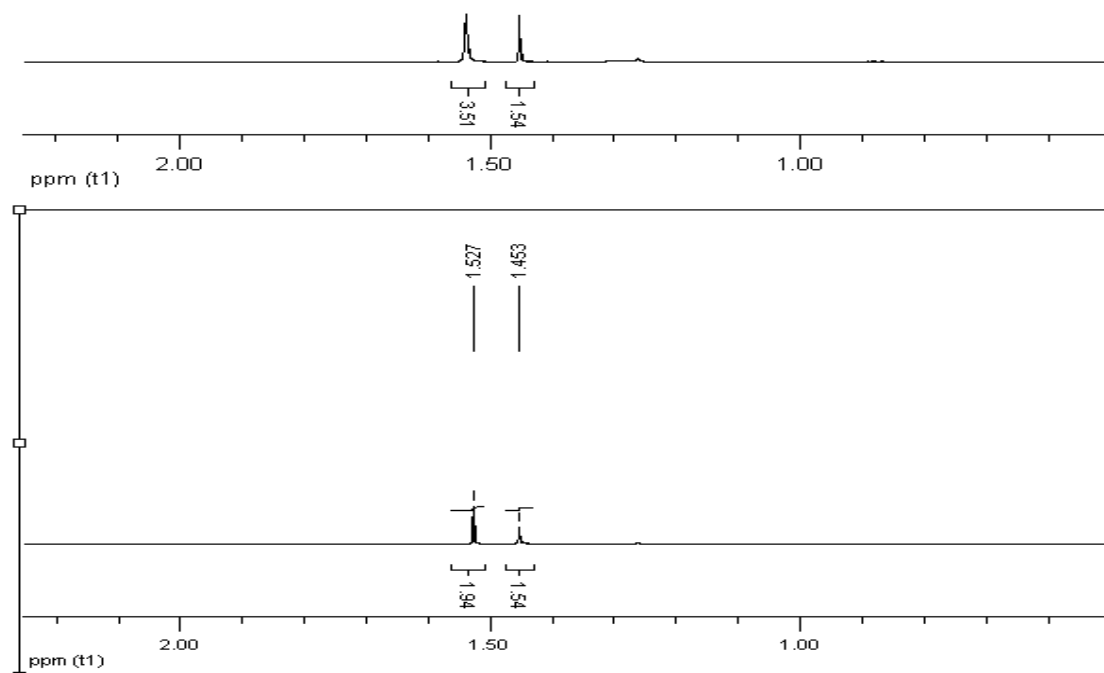


**Figure S3.**  $^{13}\text{C}$  NMR spectra of **3** in  $\text{CD}_2\text{Cl}_2$ . Top: aromatic carbons; bottom: full spectrum.

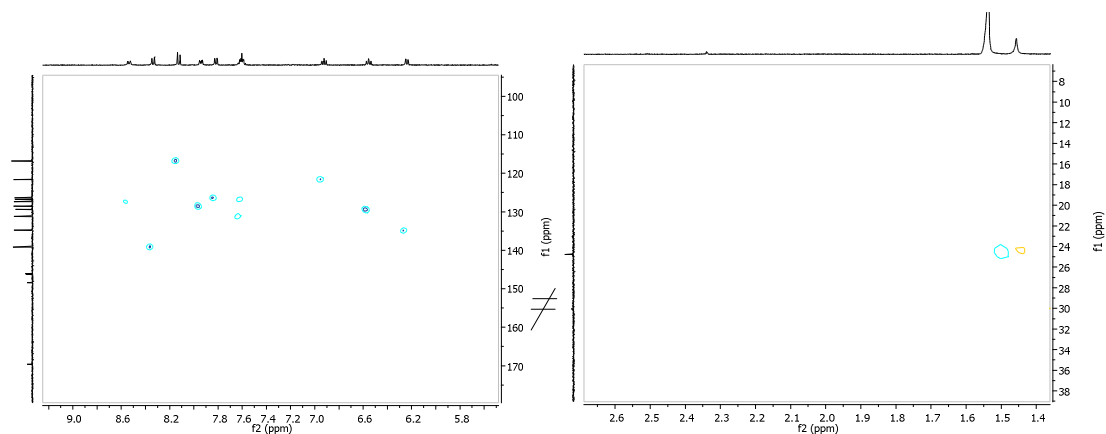


**Figure S4.** DOSY spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .

The DOSY spectrum of **3** indicates that the aromatic and aliphatic protons belong to the same molecule diffusing at  $D(\text{CD}_2\text{Cl}_2) = 10^{-10} \text{ m}^2/\text{s}$ . The signal at 1.53 ppm is assigned to residual water in  $\text{CD}_2\text{Cl}_2$  as it changes its integration relative to other protons upon exposure to  $\text{CD}_3\text{OD}$  (see Figure S5). The DOSY thus confirms that the signal at 1.45 ppm (a methyl group by integration) is part of molecule **3**.



**Figure S5.** Non-aromatic region of  $^1\text{H}$  NMR spectra before (top) and after (bottom) adding one drop of  $\text{CD}_3\text{OD}$  to the NMR sample of **3** in  $\text{CD}_2\text{Cl}_2$

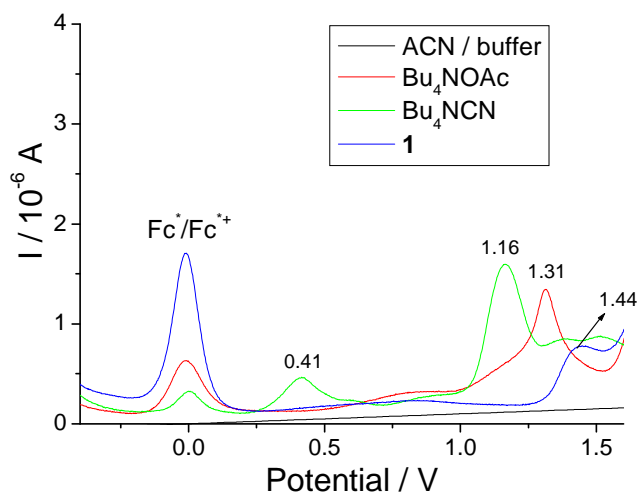


**Figure S6.** HSQC spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  (left: aromatic region, right: aliphatic region, proton at 1.53 ppm from residual water).

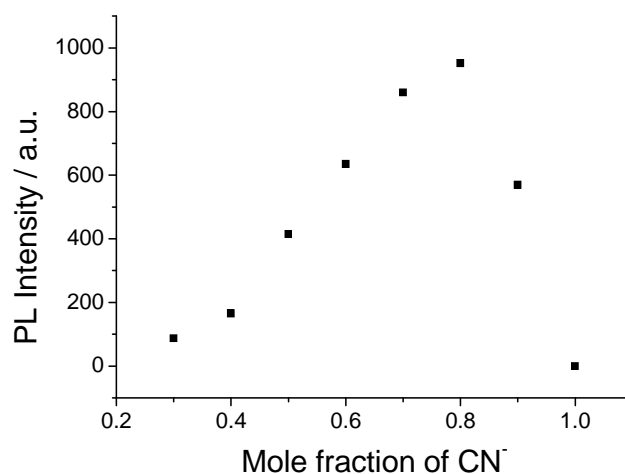
The most important information from the HSQC spectra of **3** indicates that the carbon at 24.8 ppm only correlates with the methyl group at 1.45 ppm and not with signals in the aromatic region. Therefore, it is concluded that the methyl group is connected to the iridium center as  $\text{Ir-CH}_3$ . All the other correlations are used to assign the aromatic carbon signals.



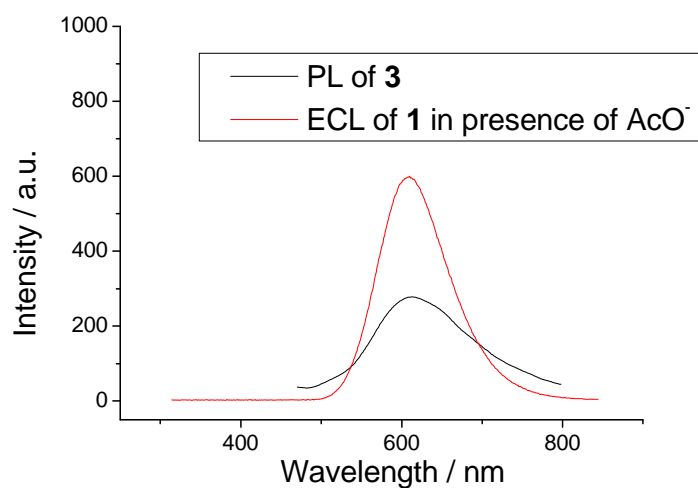
## Electrochemical, photophysical and ECL measurements



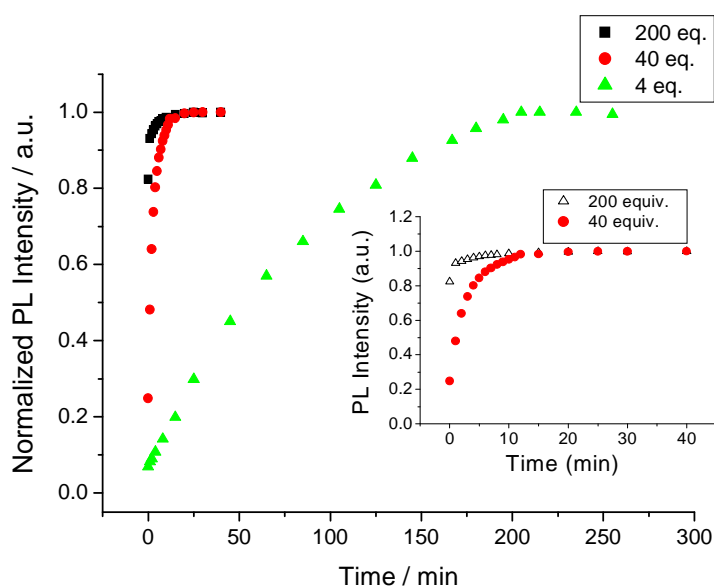
**Figure S7.** DPV of Bu<sub>4</sub>NOAc, Bu<sub>4</sub>NCN, **1** and buffer in MeCN / aq. buffer (0.1 M Tris-ClO<sub>4</sub>, pH 7.24) = 90 : 10 (v/v) vs. FeCp\*<sub>2</sub>. The first oxidation wave in presence of *n*-Bu<sub>4</sub>NCN was assigned to the formation of cyanate from cyanide in aqueous buffer.<sup>4</sup>



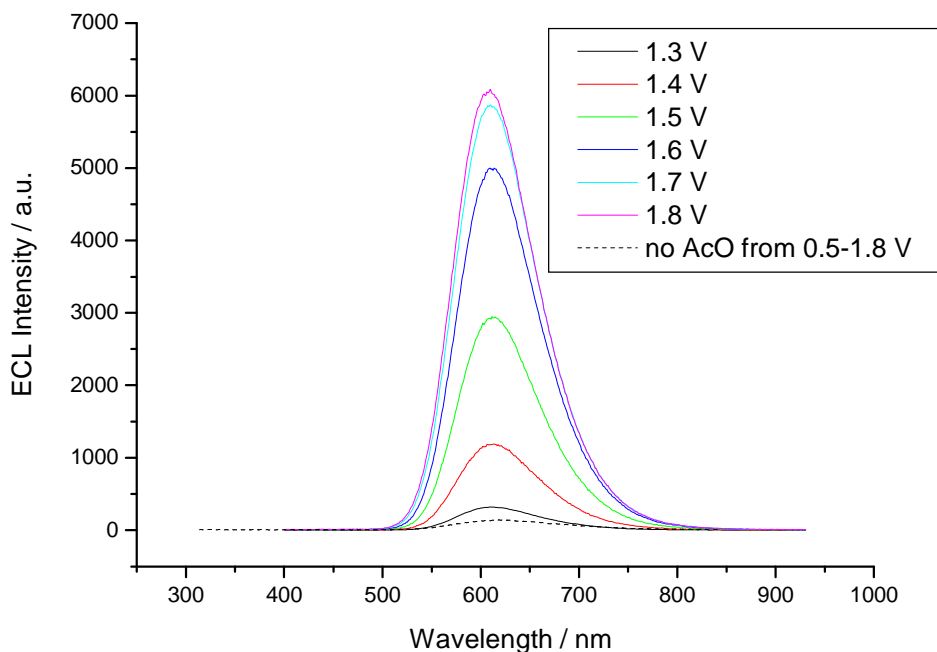
**Figure S8.** Job plot of the PL titration of **1** (10 μM) at λ<sub>em</sub> = 579 nm upon addition of CN<sup>-</sup> in Tris-ClO<sub>4</sub> buffer solution (ACN / aq. buffer = 50 / 50, v / v, pH 7.24), λ<sub>exc</sub> = 336 nm.



**Figure S9.** Comparison of the PL of **3** (prepared from the electrolysis of **1** and Bu<sub>4</sub>NOAc,  $\lambda_{\text{exc}} = 336$  nm) with the ECL emission of **1** [in presence of acetate in aq. Tris-ClO<sub>4</sub> (0.1 M) buffer solution (ACN / aq. buffer = 90 / 10, v / v, pH 7.24)].



**Figure S10.** PL kinetic traces of **1** at  $\lambda_{\text{em}} = 567$  nm upon addition of 4, 40 and 200 equiv. of cyanide. ( $\lambda_{\text{exc}} = 336$  nm; in aq. 0.1 M Tris-ClO<sub>4</sub> buffer solution; ACN / aq. buffer = 50 / 50, v / v, pH 7.24). Inset: PL kinetic trace of **1** at  $\lambda_{\text{em}} = 567$  nm upon addition of 40 and 200 equiv. of cyanide within the first minutes.



**Figure S11.** Potential dependent ECL of **1** (10  $\mu$ M) in presence of acetate in aq. 0.1 M Tris-ClO<sub>4</sub> buffer solution (ACN / aq. buffer = 90 / 10, v / v, pH 7.24). The potential scan was started at 0.5 V and ended at various potentials from 1.3 V to 1.8 V. For comparison the ECL response of **1** without added acetate is provided (dashed line, scanned potential range: 0.5-1.8 V).

## References

- <sup>1</sup> S. Sprouse, K. A. King, P. J. Spellane and R. J. Watts, *J. Am. Chem. Soc.*, 1984, **106**, 6647.
- <sup>2</sup> D. Di Censo, S. Fantacci, F. De Angelis, C. Klein, N. Evans, K. Kalyanasundaram, H. J. Bolink, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2008, **47**, 980.
- <sup>3</sup> Since the presence of TPrA did not influence the formation of **3** in any apparent manner, electrolysis of **1** was carried out in presence of acetate but absence of TPrA to enable a simpler purification.
- <sup>4</sup> F. Kitamura, M. Takahashi and M. Ito, *Chem. Phys. Lett.*, 1986, **130**, 181.