

# **Supporting Information**

## **A Bisferrocenylphenanthroline Iridium(III) Complex as a Lab-on-a-Molecule for Cyanide and Fluoride in Aqueous Solution**

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### **Abbreviations:**

MeCN: Acetonitrile  
DCM: Dichloromethane  
DMFc: Decamethylferrocene

## Synthesis of known precursors following literature procedures

### 3,8-Bis(2-(trimethylsilyl)ethynyl)-1,10-phenanthroline.<sup>1</sup>

3,8-Dibromo-1,10-phenanthroline (1.59 g, 4.70 mmol), trimethylsilanyl-ethyne (3.72 g, 37.6 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (165 mg, 0.24 mmol), CuI (137 mg, 0.470 mmol), DMF (40 mL) and dry triethylamine (10 mL) were placed in a Schlenk tube under an atmosphere of dry nitrogen. In a tightly closed tube the mixture was heated to reflux for three days. After removal of the solvent, the black residue was dissolved in dichloromethane (200 mL), washed with aqueous potassium cyanide (2%, 150 mL) and with water (150 mL). The organic layer was dried over MgSO<sub>4</sub> and then purified by column chromatography (SiO<sub>2</sub>, 1. hexane, 2. 10% CH<sub>2</sub>Cl<sub>2</sub> in hexane) to furnish the title compound as colorless solid. Yield: 1.49 g (4.00 mmol, 85%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 0.31 (s, 18H, Si-H), 7.78 (s, 2H, 5-H, 6-H), 8.32 (d, *J* = 2.0 Hz, 2H, 4-H, 7-H), 9.12 (d, *J* = 2.0 Hz, 2H, 2-H, 9-H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -0.14, 100.0, 101.9, 119.9, 127.3, 128.5, 138.9, 145.0, 152.8. ESI-MS (C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>Si<sub>2</sub>)<sup>+</sup>: Calcd.: *m/z* = 373.6, Found: *m/z* = 373.5.

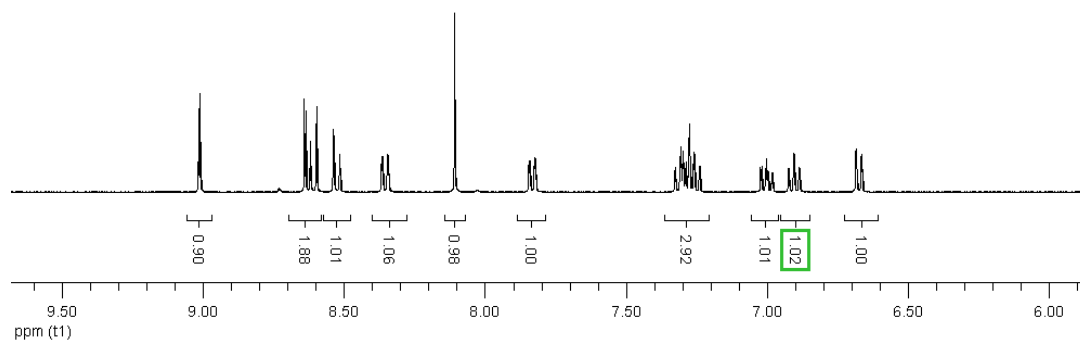
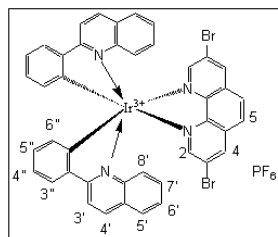
*3,8-Diethynyl-1,10-phenanthroline.*<sup>1</sup> 3,8-Bis(2-trimethyl-silylethynyl)-1,10-phenanthroline (1.49 g, 4.00 mmol) was dissolved in a mixture of methanol (20 mL) and THF (20 mL) in a 100 mL round-bottomed flask, and KOH (1 N, 20 mL) was added slowly. After stirring for 14 h at room temperature, the solution was filtered and the precipitate was washed with water and diethylether to furnish a white solid as product. Yield: 0.82 g (3.60 mmol, 90%) of a white solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 3.31 (s, 2H, ethynyl-H), 7.91 (s, 2H, 5-H, 6-H), 8.52 (d, *J* = 2.0 Hz, 2H, 4-H, 7-H), 9.06 (d, *J* = 2.0 Hz, 2H, 2-H, 9-H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 84.1, 111.1, 120.7, 128.3, 129.7, 140.7, 145.1, 153.2. ESI-MS (C<sub>16</sub>H<sub>9</sub>N<sub>2</sub>)<sup>+</sup>: Calcd.: *m/z* = 230.3, Found: *m/z* = 231.2.

*Iodoferrocene.*<sup>2</sup> To a solution of ferroceneboronic acid (1.15 g, 5.00 mmol) in dry acetonitrile (75 mL) was added *N*-iodosuccinimide (1.35 g, 6.00 mmol). After stirring for 20 h at room temperature, the mixture was extracted with hexane (3×100 mL). The combined extract was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (3×30 mL) and water (2×50 mL)

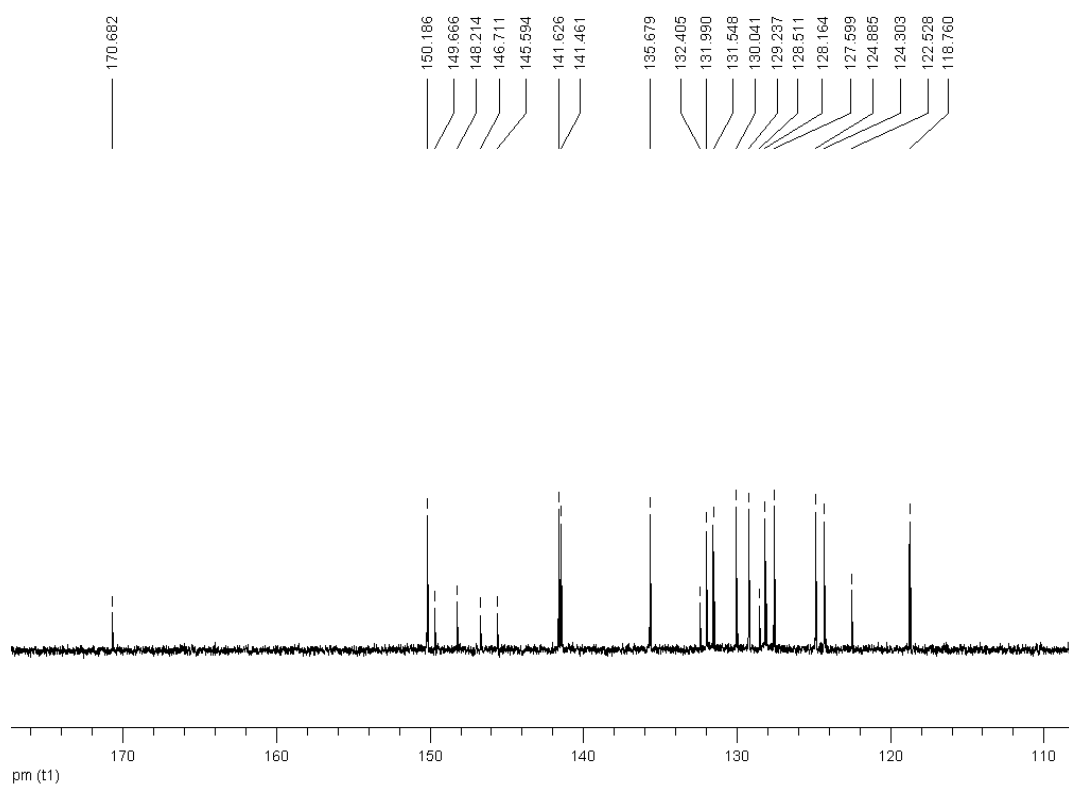
and finally dried over MgSO<sub>4</sub>. Concentration *in vacuo* furnished an orange-brown oil that was purified by flash-chromatography on silica gel 60 (0.040-0.063 mm) with hexane to afford pure iodoferrocene (0.97 g, 62% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.40 (m, 2 H), 4.18 (s, 5 H) and 4.14 (m, 2 H). ESI-MS (C<sub>10</sub>H<sub>9</sub>FeI)<sup>+</sup>: Calcd.: *m/z* = 311.9, Found: *m/z* = 311.9.

*Bis(2-phenylquinoline-C<sup>2</sup>;N<sup>I</sup>)(3,8-dibromo-1,10-phenanthroline) iridium hexafluorophosphate*<sup>3</sup> (**4**). [Ir(pq)<sub>2</sub>Cl]<sub>2</sub><sup>4</sup> (60.2 mg, 47.2  $\mu$ mol) and 3,8-dibromophenanthroline<sup>5</sup> (40.1 mg, 120  $\mu$ mol) were dissolved in DCM (10 mL) and the solution was refluxed for 6 h. NH<sub>4</sub>PF<sub>6</sub> (100 mg, excess) was added and the resulting solution was stirred for 1 h. The precipitate was filtered off and washed with excess of DCM. The filtrate was purified by chromatography on a silica column using DCM and methanol for elution. The solvent was removed on a rotary evaporator to yield an orange-red powder (yield: 82%). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>):  $\delta$  = 6.69 (dd, *J*<sub>1</sub> = 1.0, *J*<sub>2</sub> = 7.5 Hz, 1H, 3''-H), 6.92 (ddd, *J*<sub>1</sub> = 1.3, *J*<sub>2</sub> = 7.0 Hz, *J*<sub>3</sub> = 7.5 Hz, 1H, 4''-H), 7.01 (ddd, *J*<sub>1</sub> = 1.0, *J*<sub>2</sub> = 7.0, *J*<sub>3</sub> = 8.8 Hz, 1H, 5''-H), 7.30 (m, 3H, 6''-, 6'-, 7'-H), 7.84 (dd, *J*<sub>1</sub> = 1.0, *J*<sub>2</sub> = 8.0 Hz, 1H, 5'-H), 8.12 (s, 1H, 5-H), 8.37 (dd, *J*<sub>1</sub> = 1.0, *J*<sub>2</sub> = 8.0 Hz, 1H, 8'-H), 8.54 (d, *J* = 8.8 Hz, 1H, 3'-H), 8.62 (d, *J* = 8.8 Hz, 1H, 4'-H), 8.65 (d, *J* = 2.0 Hz, 1H, 2-H), 9.02 (d, *J* = 2.0 Hz, 1H, 4-H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>):  $\delta$  = 118.8, 122.5, 124.3, 124.9, 127.6, 128.2, 128.5, 129.2, 130.0, 131.5, 132.0, 132.4, 135.7, 141.5, 141.6, 145.6, 146.7, 148.2, 149.7, 150.2, 170.7. Elemental analysis: (C<sub>42</sub>H<sub>26</sub>Br<sub>2</sub>F<sub>6</sub>IrN<sub>4</sub>P), Calcd.: C, 46.55; H, 2.42; N, 5.17, Found: C, 46.47; H, 2.15; N, 5.30. ESI-MS (C<sub>42</sub>H<sub>26</sub>Br<sub>2</sub>IrN<sub>4</sub>)<sup>+</sup>: Calcd.: *m/z* = 939.0, Found: *m/z* = 939.2.

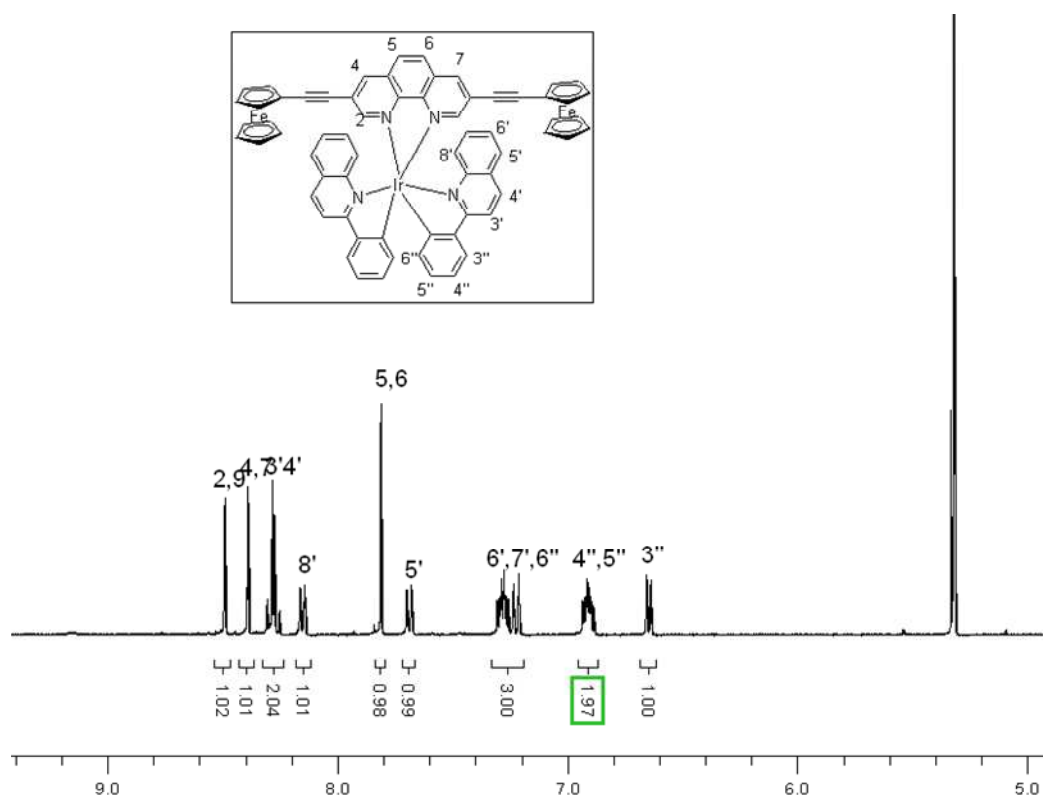
## NMR



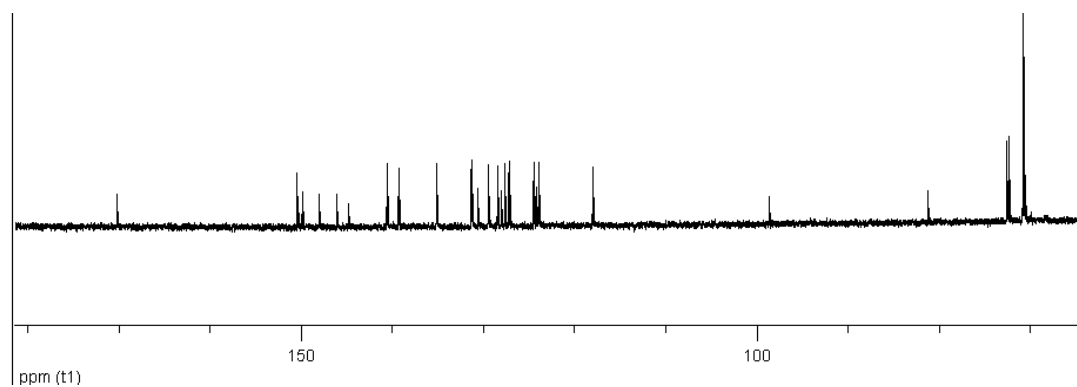
$^1\text{H}$  NMR spectrum of **4** in  $(\text{CD}_3)_2\text{CO}$ .



$^{13}\text{C}$  NMR spectrum of **4** in  $(\text{CD}_3)_2\text{CO}$ .

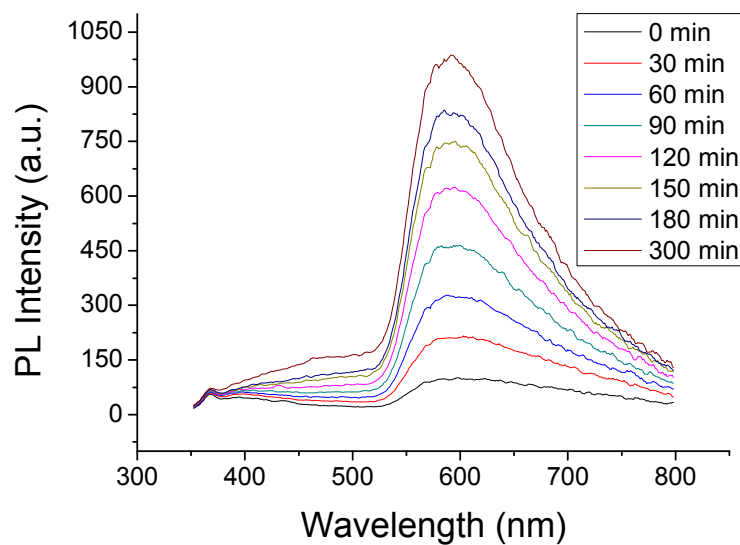


Aromatic region of  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$ .

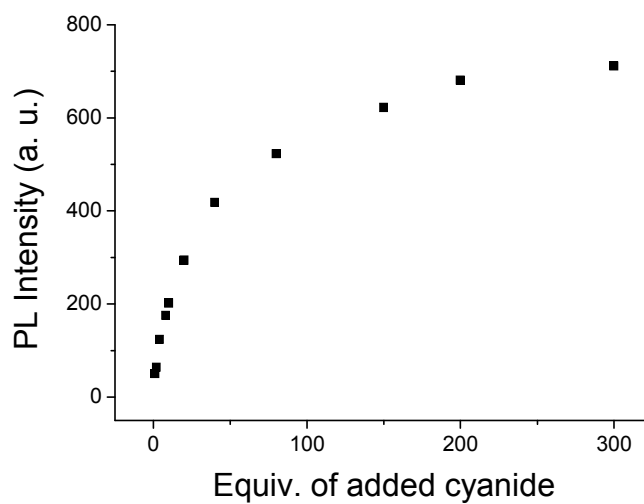


$^{13}\text{C}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2$ .

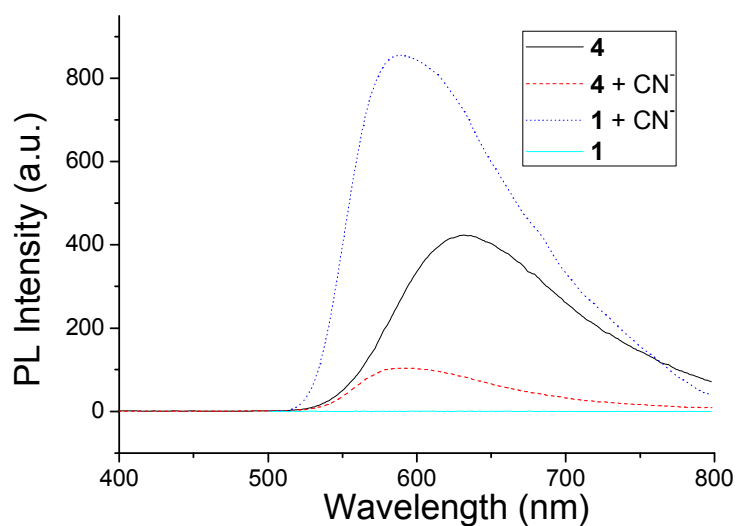
## Photophysical measurements and NMR study



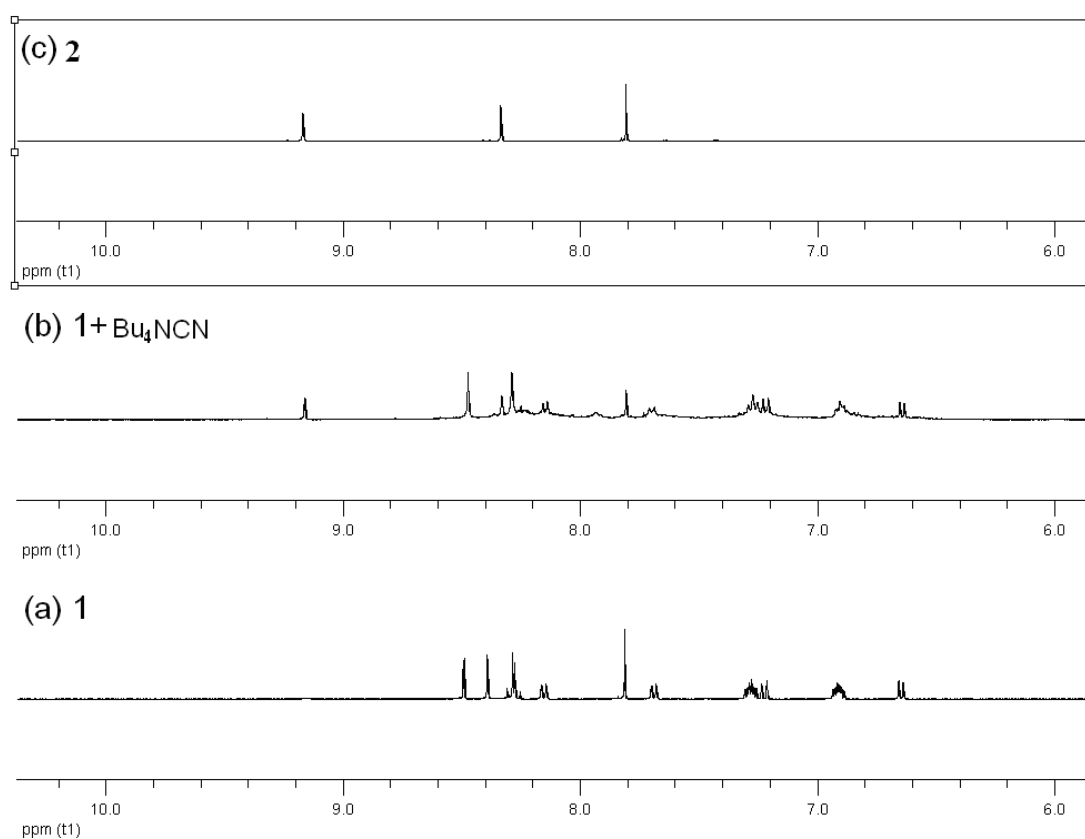
**Figure S1.** PL spectra of **1** (10  $\mu\text{M}$ ) in the presence of 200 equiv  $\text{CN}^-$  as function of time in 0.1 M Tris- $\text{ClO}_4$  buffer solution (MeCN / buffer = 90 / 10, v / v, pH 7.24),  $\lambda_{\text{exc}} = 330$  nm.



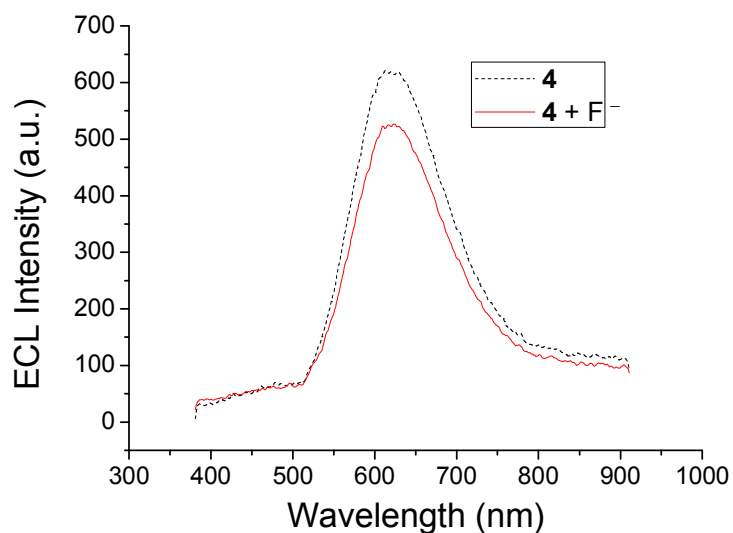
**Figure S2.** PL titration of **1** (10  $\mu\text{M}$ ) with  $\text{CN}^-$  in 0.1 M Tris- $\text{ClO}_4$  buffer solution (MeCN / buffer = 90 / 10, v / v, pH 7.24) at  $\lambda_{\text{em}} = 580$  nm ( $\lambda_{\text{exc}} = 330$  nm, all samples were measured after  $180 \pm 1$  min of reaction).



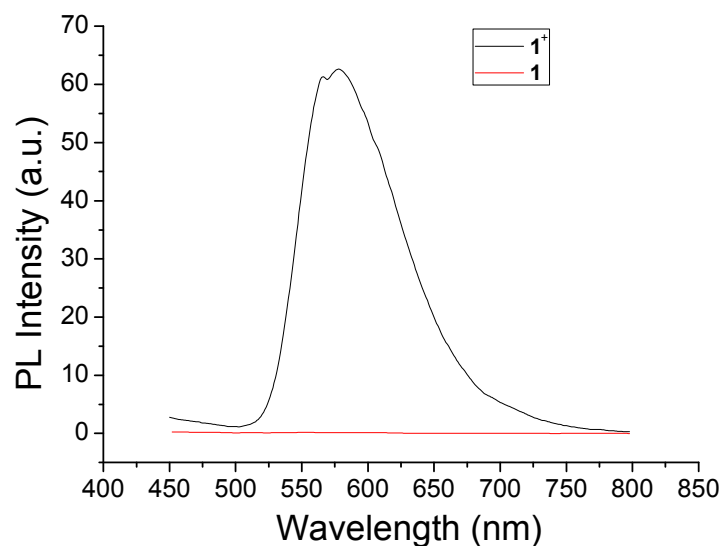
**Figure S3.** PL spectra of **1** (10  $\mu\text{M}$ ), **1** (10  $\mu\text{M}$ ) +  $\text{CN}^-$  and **4** (conc. unknown), **4** (conc. unknown) +  $\text{CN}^-$  in MeCN for comparison ( $\lambda_{\text{exc}} = 330 \text{ nm}$ , all samples were measured after  $180 \pm 1 \text{ min}$  reaction).



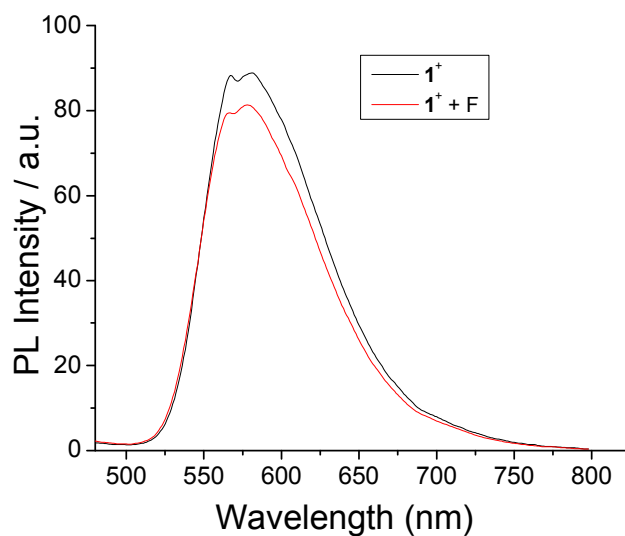
**Figure S4.**  $^1\text{H}$  NMR spectra of (a) **1**, (b) **1** +  $\text{Bu}_4\text{NCN}$  and (c) **2** in  $\text{CD}_2\text{Cl}_2$ . **3** is not visible in spectrum (b) as it is highly insoluble at NMR concentrations.



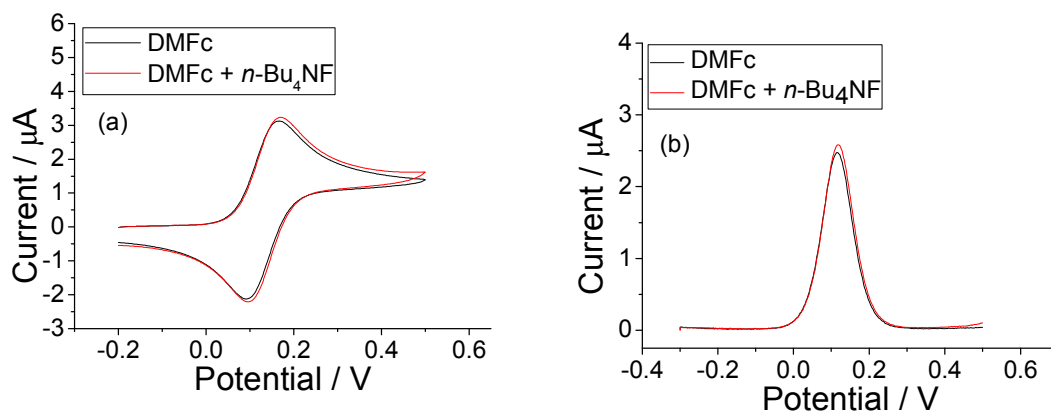
**Figure S5.** ECL spectra of **4** (10  $\mu$ M) in the presence of 200 equiv. of  $n$ -Bu<sub>4</sub>NF $\cdot$ 3H<sub>2</sub>O in 0.1 M  $n$ -Bu<sub>4</sub>NPF<sub>6</sub> Tris-ClO<sub>4</sub> buffer (MeCN / water = 90 / 10, v / v, pH 7.24) using the sweep range of 0.5-1.8 V at a scan rate  $\nu$  = 100 mV s<sup>-1</sup>, 50 mM TPrA as co-reactant. Samples were measured within 2 min after mixing.



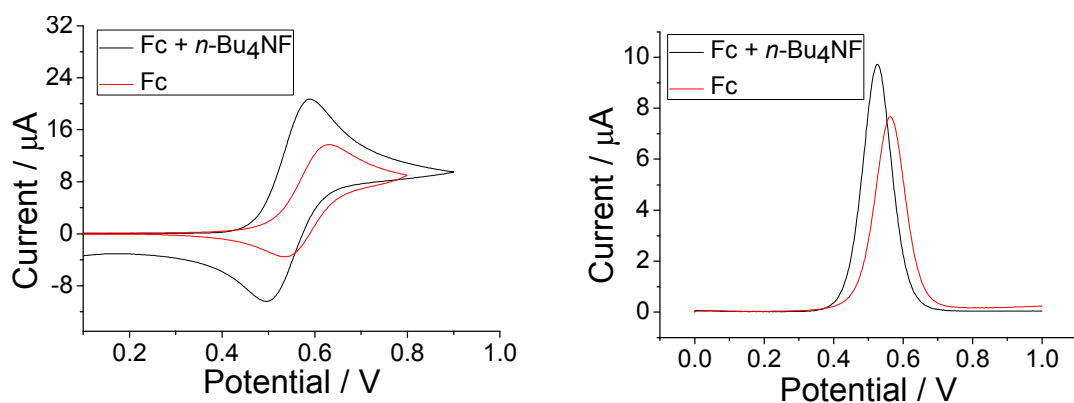
**Figure S6.** PL spectra of **1** and of **1**<sup>+</sup> in MeCN ( $\lambda_{\text{exc}}$  = 430 nm). **1**<sup>+</sup> was obtained from electrolysis of **1** (working electrode: Pt wire; reference electrode: silver wire; working potential = 0.8 V vs. silver wire), keep stirring during electrolysis for 2 h.



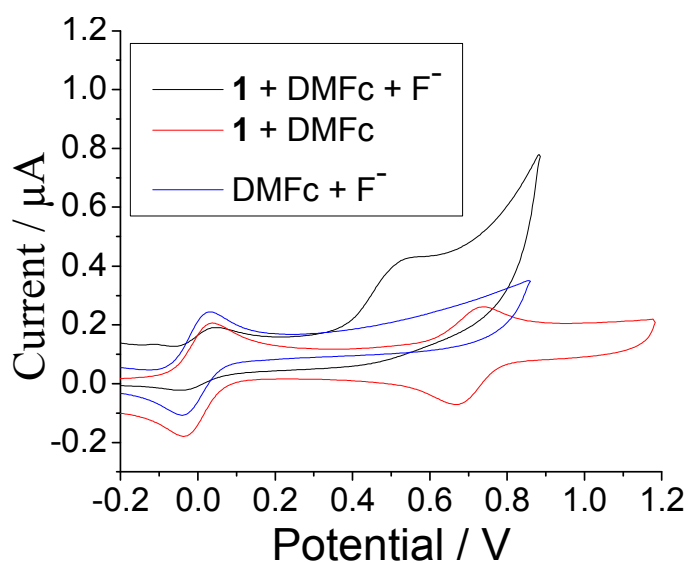
**Figure S7.** PL response of  $1^+$  in the absence and presence of  $n\text{-Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$  (5 min after mixing) in MeCN after ( $\lambda_{\text{exc}} = 330 \text{ nm}$ ).



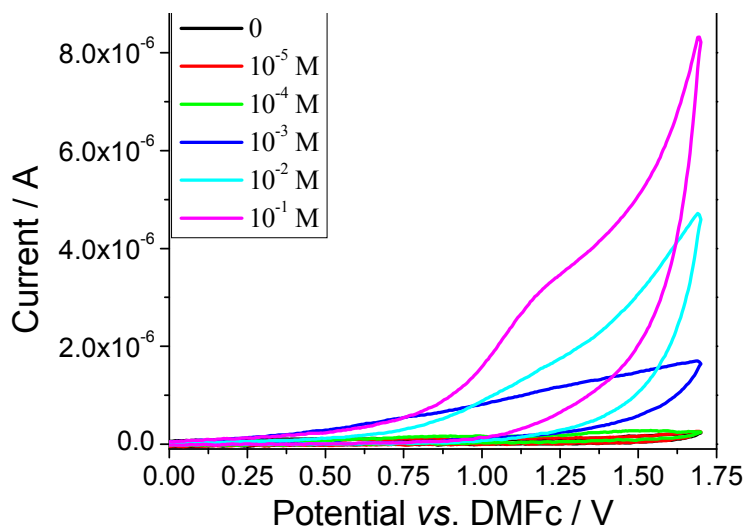
**Figure S8.** (a) CV and (b) DPV responses of DMFc (decamethylferrocene) upon addition of  $n\text{-Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$  in MeCN, Pt working electrode (2 mm in diameter) and Ag wire as reference electrode, scan rate:  $100 \text{ mV s}^{-1}$ . This measurement establishes that DMFc may be used as internal reference probe even in presence of fluoride.



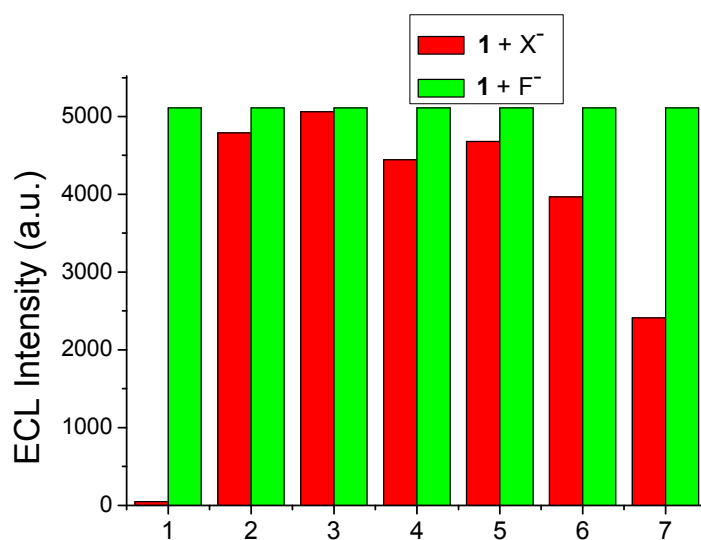
**Figure S9.** CV (left) and DPV (right) responses of ferrocene upon addition of  $n\text{-Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$  in MeCN, Pt as working electrode (2 mm in diameter) and Ag wire as reference electrode, scan rate:  $100\text{ mV s}^{-1}$ . The Ag wire is a reliable reference electrode even in presence of fluoride, see Figure S8.



**Figure S10.** CV of **1** in the presence of 200 equiv. of  $n\text{-Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$  in MeCN vs. DMFc at a scan rate  $100\text{ mV s}^{-1}$ .

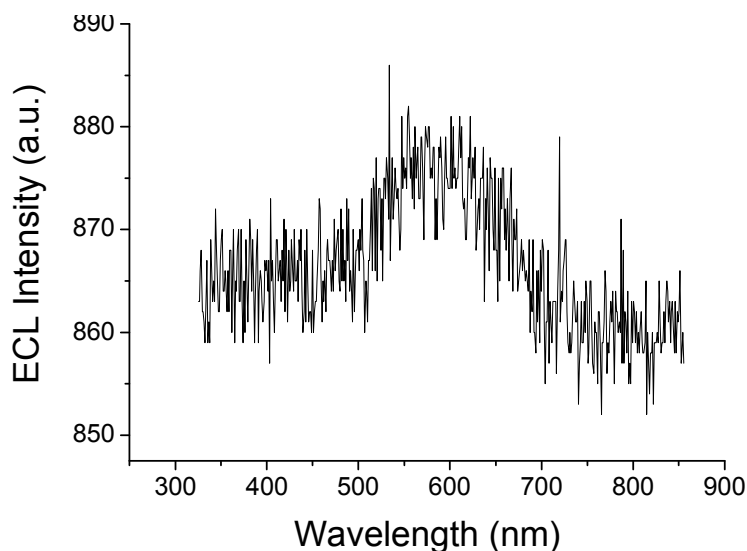


**Figure S11.** CV of various concentrations of  $n\text{-Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$  in MeCN containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) as electrolyte at a scan rate  $100 \text{ mV s}^{-1}$  (silver wire is used as the only internal reference, while after all measurements a calibration against DMFc was done).



**Figure S12.** ECL intensity of **1** ( $10 \mu\text{M}$ ) at  $\lambda_{\text{em}} = 605 \text{ nm}$  in the presence of 200 equiv of  $\text{F}^-$  (green bars) and 200 equiv of  $\text{X}^-$  each (red bars) [ $\text{X}^- = \text{None}$  (1),  $\text{Cl}^- + \text{F}^-$  (2),  $\text{AcO}^- + \text{F}^-$  (3),  $\text{Br}^- + \text{F}^-$  (4),  $\text{ClO}_4^- + \text{F}^-$  (5),  $\text{CN}^- + \text{F}^-$  (6),  $\text{I}^- + \text{F}^-$  (7)] in MeCN / aq. buffer (0.1 M Tris- $\text{ClO}_4$ , pH 7.24) = 90 : 10 (v/v), using 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  as electro-

lyte and 50 mM TPrA as co-reactant. The sweep range was 0.5 - 1.8 V, scan rate  $\nu = 100 \text{ mV s}^{-1}$ , all samples were measured within 2 minutes after mixing.



**Figure S13.** ECL intensity of **3** (10  $\mu\text{M}$ ) in MeCN / aq. buffer (0.1 M Tris-ClO<sub>4</sub>, pH 7.24) = 90 : 10 (v/v), using 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte and 30 mM TPrA as co-reactant. The sweep range was 0.5 - 1.8 V, scan rate  $\nu = 100 \text{ mV s}^{-1}$ .

## References

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  - (4) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647.
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