# A molecular 'traffic light': highly selective cyanide sensing in aqueous media by a CpFe(indenyl)-functionalized borane

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Supporting Information (9 pages)

## 1. General methods

Manipulations of air-sensitive species were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS. NMR spectra were recorded in dichloromethane-$d_2$ or thf-$d_8$ which were dried over molecular sieves or potassium respectively, and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. $^1$H and $^{13}$C NMR spectra were recorded on Varian Mercury-VX-300 or Bruker AVII-500 spectrometers and referenced internally to residual protio-solvent ($^1$H) or solvent ($^{13}$C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). $^{11}$B and $^{19}$F NMR spectra were referenced to $Et_2O{\cdot}BF_3$ and $CFCl_3$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infrared spectra were measured on a Nicolet 500 FT-IR spectrometer. Electrochemical measurements were performed on a PAR AMETEK VersaSTAT 3 potentiostat under nitrogen within a Saffron Omega Scientific glove-box. Unless otherwise stated, the measurements were performed in a supporting electrolyte of a 0.1 M solution of tetrabutylammonium hexafluorophosphate in tetrahydrofuran. The cyclic-voltammetry measurements were performed with a silver quasi-reference electrode, a platinum working electrode and a platinum wire auxiliary electrode. UV-vis spectra were collected on a Scintio UV S-2100 UV/Vis spectrometer. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University. Starting materials 7-bromo-1*H*-indene [M. Adamczyk, D.S. Watt and D.A. Netzel, *J. Org. Chem.*, 1984, **49**, 4226], $[CpFe(\eta^6\text{-}C_{10}H_8)][PF_6]$ [E.P. Kündig, P. Jeger and G. Bernardinelli, *Inorg. Chim. Acta,* 2004, **357**, 1909], and $FBMes_2$ [J.J. Eisch, B. Shafii, J.D. Odom, A.L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 1847] were prepared by literature procedures.

## 2. Synthetic and characterizing data for new compounds

**1:** 7-bromo-1*H*-indene (2.75 g, 14.10 mmol) dissolved in dry thf (200 mL) was added to potassium hydride (594 mg, 14.80 mmol), and the reaction mixture stirred for 1h at room temperature. The resulting brown solution was transferred onto [CpFeCp($\eta^6$-$C_{10}H_8$)][$PF_6$] (5.83 g, 14.80 mmol) and the reaction mixture stirred for a further 12 h. Volatiles were then removed in vacuo yielding a purple oil, which was extracted with hexanes, and the crude product purified by air-free column chromatography yielding a purple solid. Purple crystals suitable for X-ray crystallography were obtained from a cooled solution in hexanes (2.99 g, 67%).

$^1$H NMR ($CD_2Cl_2$, 300 MHz, 20 °C): δ 3.87 (*s*, 5H, CH of Cp), 4.18 (*t*, $^3J_{HH}$ : 3 Hz, 1H, CH of C2), 5.05 (*s*, 1H, CH of C3), 5.09 (*s*, 1H, CH of C1), 6.79 (*dd*, $^3J_{HH}$ = 6 Hz, $^3J_{HH}$ = 9 Hz, 1H, CH of C6), 7.18 (*d*, $^3J_{HH}$ = 6 Hz, 1H, CH of C7), 7.59 (*d*, $^3J_{HH}$ = 9 Hz, 1H, CH of C5). $^{13}$C NMR ($CD_2Cl_2$, 76 MHz, 20 °C): δ 63.4 (C1), 64.0 (C3), 69.2 (Cp), 71.4 (C2), 89.0 (C8), 89.6 (C9), 124.1 (C6), 124.5 (C4), 125.6 (C7), 129.0 (C5). Elemental microanalysis: calc for $C_{14}H_{11}BrFe$, C 53.38, H 3.52; meas. C 52.98, H, 3.59. MS(EI): *m/z* = 313.9 [M+].

**[K(18-crown-6)][2-CN] and [$^n$Bu$_4$N][2-CN]**: **2** (0.300 g, 0.62 mmol) was treated with potassium cyanide (0.403 g, 6.20 mmol) and 18-crown-6 (0.163 g, 0.62 mmol) in acetone (30 mL). The red solution was filtered and concentrated. Crystals of [K(18-crown-6)][**2**-CN] suitable for X-ray crystallography were obtained from cold acetone. MS(ES): *m/z* = 510.2050 [M+]. For the tetra-*n*-butylammonium salt, **2** (0.050 g, 0.103 mmol) was treated with tetrabutylammonium cyanide monohydrate (0.031 g, 0.108 mmol) in deuterated dichloromethane (0.7 mL). $^1$H NMR ($CD_2Cl_2$, 300 MHz, 20°C): δ 1.01 (t, $^3J_{HH}$ = 6 Hz, 12H, $CH_3$ of [$^n$Bu$_4$N]$^+$), 1.49 (sextet, $^3J_{HH}$ = 6 Hz, 8H, $CH_2$ of [$^n$Bu$_4$N]$^+$), 1.57 (quintet, $^3J_{HH}$ = 6 Hz, 8H, $CH_2$ of [$^n$Bu$_4$N]$^+$), 1.65 (s, 6H, *o*-$CH_3$ of Mes), 2.14 (s, 9H, *o*- and *p*-$CH_3$ of Mes), 2.25 (s, 3H, *p*-$CH_3$ of Mes), 3.06 (t, $^3J_{HH}$ = 6 Hz, 8H, N$CH_2$ of [$^n$Bu$_4$N]$^+$), 3.88 (s, 5H, CH of Cp), 3.91 (t, $^3J_{HH}$ = 3 Hz, 1H, CH of C2), 4.78 (m, 1H, CH of C3), 5.22 (m, 1H, CH of C1), 6.36 (d, $^3J_{HH}$ = 6 Hz, 1H, CH of C5), 6.46 (s, 2H, *m*-CH of Mes), 6.66 (dd, $^3J_{HH}$ = 6 Hz, $^3J_{HH}$ = 9 Hz, 1H, CH of C6), 6.68 (s, 2H, *m*-CH of Mes), 7.23 (d, $^3J_{HH}$ = 9 Hz, 1H, CH of C7). $^{13}$C NMR ($CD_2Cl_2$, 75 MHz, 20°C): δ 14.0 ($CH_3$ of [$^n$Bu$_4$N]$^+$), 20.2 ($CH_2$ of [$^n$Bu$_4$N]$^+$), 21.0 (*p*-$CH_3$ of Mes), 21.1 (*p*-$CH_3$ of Mes), 24.4 ($CH_2$ of [$^n$Bu$_4$N]$^+$), 24.7 (*o*-$CH_3$ of Mes), 25.7 (*o*-$CH_3$ of Mes), 59.0 ($CH_2$ of [$^n$Bu$_4$N]$^+$), 59.9 (C3), 65.7 (C1), 68.5 (C2), 69.0 (Cp), 87.9 (C4), 97.6 (C8), 124.4 (C4), 124.8 (C6), 128.8 (*m*-CH of Mes), 128.9 (C5), 129.1 (*m*-CH of Mes), 132.0 (*p*-C of Mes), 132.4 (*p*-C of Mes), 142.9 (*o*-C of Mes), 143.2 (*o*-C of Mes), 145.2 (CN), 150.9 (*i*-C of Mes), 151.9 (*i*-C of Mes) 157.8 (C4). $^{11}$B NMR ($CD_2Cl_2$, 96 MHz, 20° C) : δ -15 (br s, $BMes_2CN$).

**[$^n$Bu$_4$N][2-F]**: **2** (0.050 g, 0.103 mmol) was treated with tetrabutylammonium fluoride trihydrate (0.034 g, 0.108 mmol) in thf-d$_8$ (0.7 mL). $^1$H NMR (thf-*d$_8$*, 300 MHz, 20°C): δ 0.99 (m, 12H, CH$_3$ of [$^n$Bu$_4$N]$^+$), 1.37 (br m, 8H, CH$_2$ of [$^n$Bu$_4$N]$^+$), 1.60 (br m, 8H, CH$_2$ of [$^n$Bu$_4$N]$^+$), 2.06 (br s, 6H, Me of Mes), 2.15, 2.17 (overlapping br s, 6H, Me of Mes), 2.55 (br s, 6H, Me of Mes), 3.12 (br m, 8H, NCH$_2$ of [$^n$Bu$_4$N]$^+$), 3.67 (overlapping s and m, 6H, CHs of Cp and C2), 4.54 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 3 Hz, 1H, CH of C3), 5.17 (br m, 1H, CH of C1), 6.29 (br s, 2H, *m*-CH of Mes), 6.44 (br m, 1H, CH of C5), 6.47(br s, 2H, *m*-CH of Mes), 6.55 (t, $^3J_{HH}$ = 6 Hz, 1H, CH of C6), 6.99 (d, $^3J_{HH}$ = 9 Hz, 1H, CH of C7). $^{13}$C NMR (thf-*d$_8$*, 75 MHz, 20°C): δ 14.2 (CH$_3$ of [$^n$Bu$_4$N]$^+$), 20.6 (CH$_2$ of [$^n$Bu$_4$N]$^+$), 21.4 (*p*-Me of Mes), 24.6 (CH$_2$ of [$^n$Bu$_4$N]$^+$), 25.0 (*o*-Me of Mes), 59.1 (CH$_2$ of [$^n$Bu$_4$N]$^+$), 59.6 (C3), 66.4 (C1), 68.5 (C2), 69.1 (Cp), 88.5 (C9), 98.1 (C8), 123.3 (C7), 125.4 (C6), 126.9 (C5),127.0 (*p*-C of Mes), 128.8 (2 overlapping signals *m*-CH of Mes), 130.7 (*p*-C of Mes), 142.5 (*o*-C of Mes), 143.1 (*o*-C of Mes), 156.3 (br, *i*-C of Mes), 165.3 (br, C4). $^{11}$B NMR (thf-*d$_8$*, 96 MHz, 20°C): δ 5.88 (BMes$_2$F). $^{19}$F NMR (thf-*d$_8$*, 282 MHz, 20°C): δ -179.51 (BF). MS(ES): *m/z* = 503 [M$^+$]; accurate mass: calc. 503.2020, meas. 503.2020.

## 3. Crystallographic data

| | **1** | **2** | **[K(18-crown-6)] [2-CN]** |
|---|---|---|---|
| **Crystal Data** | | | |
| CCDC reference | 980844 | 980845 | 980846 |
| Formula | $C_{14}H_{11}BrFe$ | $C_{32}H_{33}BFe$ | $C_{45}H_{57}BFeKNO_6$ |
| $M_r$ | 314.99 | 484.27 | 813.71 |
| Cryst size (mm) | 0.21 × 0.10 × 0.09 | 0.22 x 0.18 x 0.16 | 0.25 x 0.21 x 0.18 |
| Cryst syst | Monoclinic | Monoclinic | triclinic |
| Space group | $P2_1/c$ | P 21/c | P -1 |
| a (Å) | 9.4289 (1) | 12.18666(5) | 11.80090(10) |
| b (Å) | 10.1614 (1) | 14.62360(6) | 12.70250(10) |
| c (Å) | 12.1495 (2) | 14.43211(6) | 14.5226(2) |
| $\alpha$ (deg) | 90 | 90 | 76.3891(5) |
| $\beta$ (deg) | 105.3181 (6) | 91.0308(4) | 84.0128(5) |
| $\gamma$ (deg) | 90 | 90 | 82.2242(6) |
| V ($Å^3$) | 1122.70 (2) | 2571.570(18) | 2090.42(4) |
| $\mu$ ($mm^{-1}$) | 4.87 | 4.813 | 0.508 |
| $Z$ | 4 | 4 | 2 |
| F(000) | 624 | 1024 | 864 |
| **Data collection** | | | |
| T (K) | 150 | 150 | 150 |
| λ (Å) | 0.71013 | 0.71013 | 0.71013 |
| Scan mode | ω | ω | ω |
| *hkl* range | -12 to 12<br>-13 to 13<br>-15 to 15 | -15 to 15<br>-18 to 18<br>-17 to 18 | -15 to 14<br>-16 to 16<br>-18 to 18 |
| measd reflns | 33225 | 60968 | 65025 |
| Unique reflns [$R_{int}$] | 2553 [0.022] | 5397 [0.026] | 9499 [0.021] |
| **Refinement** | | | |
| refined param | 145 | 599 | 496 |
| GOF on $F^2$ | 0.9918 | 0.9278 | 0.9115 |
| R1, wR2[a], [I > 2σ(I)] | 0.0333, 0.0715 | 0.0475, 0.0897 | 0.0375, 0.0853 |
| R1, wR2[a], (all data) | 0.0425, 0.0756 | 0.0460, 0.0892 | 0.0465, 0.0923 |
| $\rho_{fin}$ (max/min) (e $Å^{-3}$) | 0.96, -0.97 | 0.82, -1.01 | 0.39, -041 |

[a] $w = 1/[\sigma^2(F^2) + ( 0.03P)^2 + 2.81P]$ , where $P = (\max(F_o^2,0) + 2F_c^2)/3$

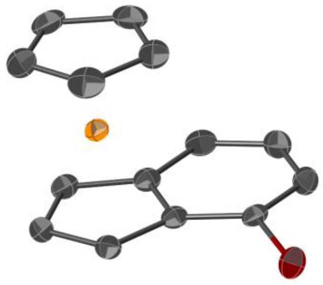

**Figure s1:** Molecular structure of **1** with displacement ellipsoids set at the 50 % probability level; hydrogen atoms are omitted for clarity. Key: burgundy, bromine; black, carbon; orange, iron).

## 4. Determination of the fluoride binding affinity of 2

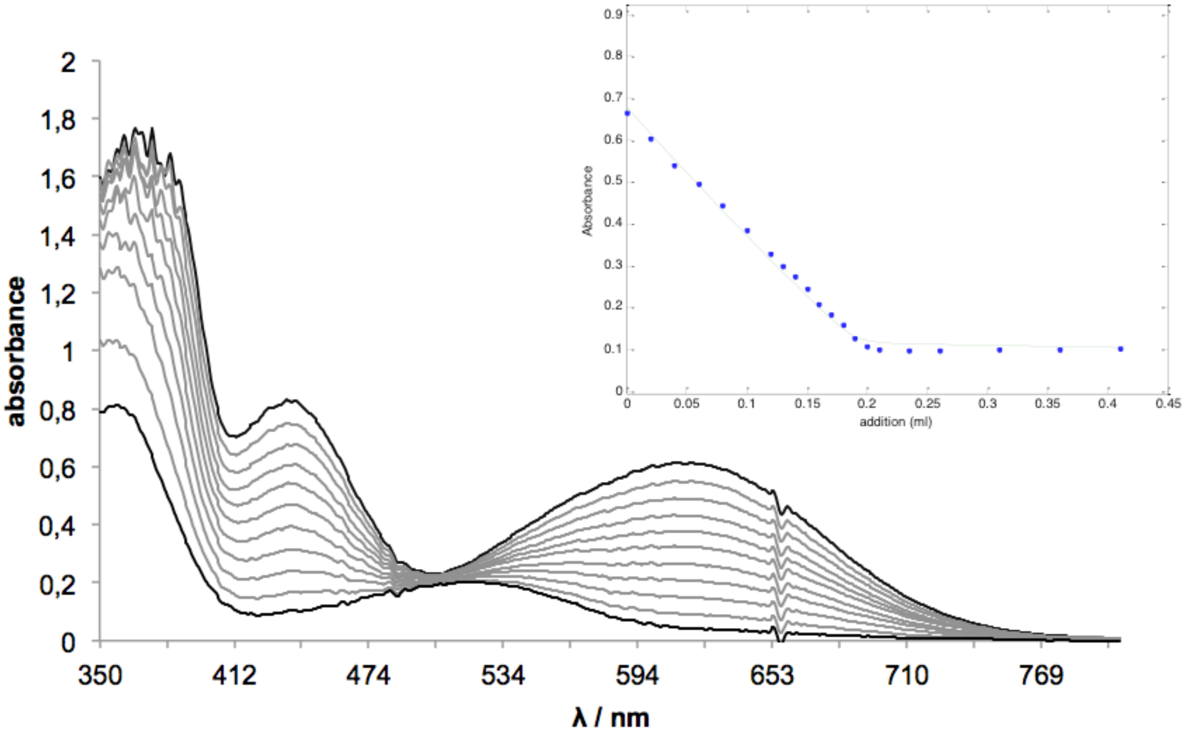

**Figure s2**: Changes in the UV-vis absorption spectrum of a solution of **2** (0.64 mM in thf) upon addition of $[^n\mathrm{Bu}_4\mathrm{N}]\mathrm{F}\cdot 3\mathrm{H}_2\mathrm{O}$. Inset: curve fitting using ReactLab yielding log$K_\mathrm{F}$= 6.36(0.10), *σr*= 0.0152, *ssq*= 0.291.

## 5. Determination of lower cyanide detection limit by UV-vis spectroscopy

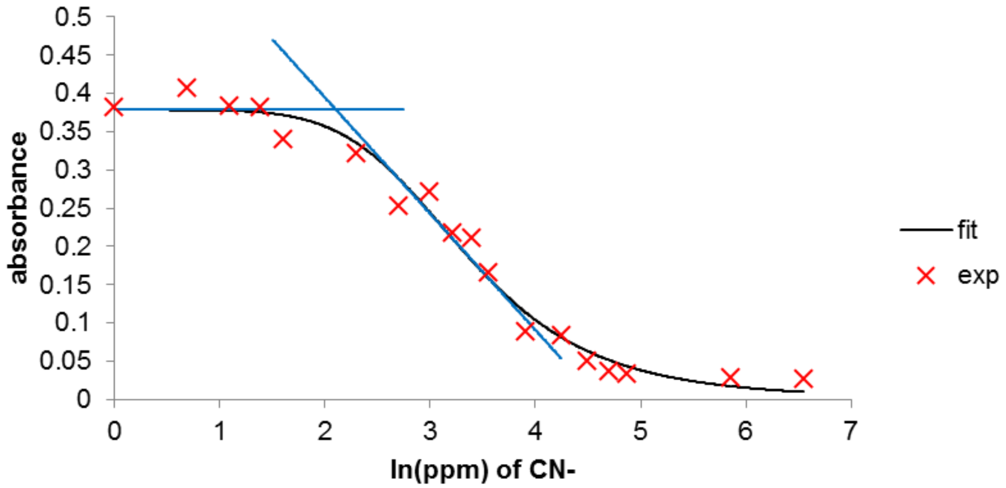

**Figure s3**: Response of the absorbance at 340 nm of a solution of **2** (1.2 mM in thf) upon addition of $CN^-$ in water (thf/$H_2O$ 1:1). Black trace: curve fitting using Origin: ($\chi^2 = 4.63 \times 10^{-4}$, rss = $6.48 \times 10^{-3}$); blue traces: straight line extrapolations (i) y = 0.378 and (ii) y = - 0.152 x + 0.699. Lower detection limit given by the intercept of straight line extrapolations: solution for x at the intercept gives x = $\ln(C_{min}/ppm)$ = 2.108, hence $C_{min}$/ppm = 8.2.

## 6. Electrochemical measurements

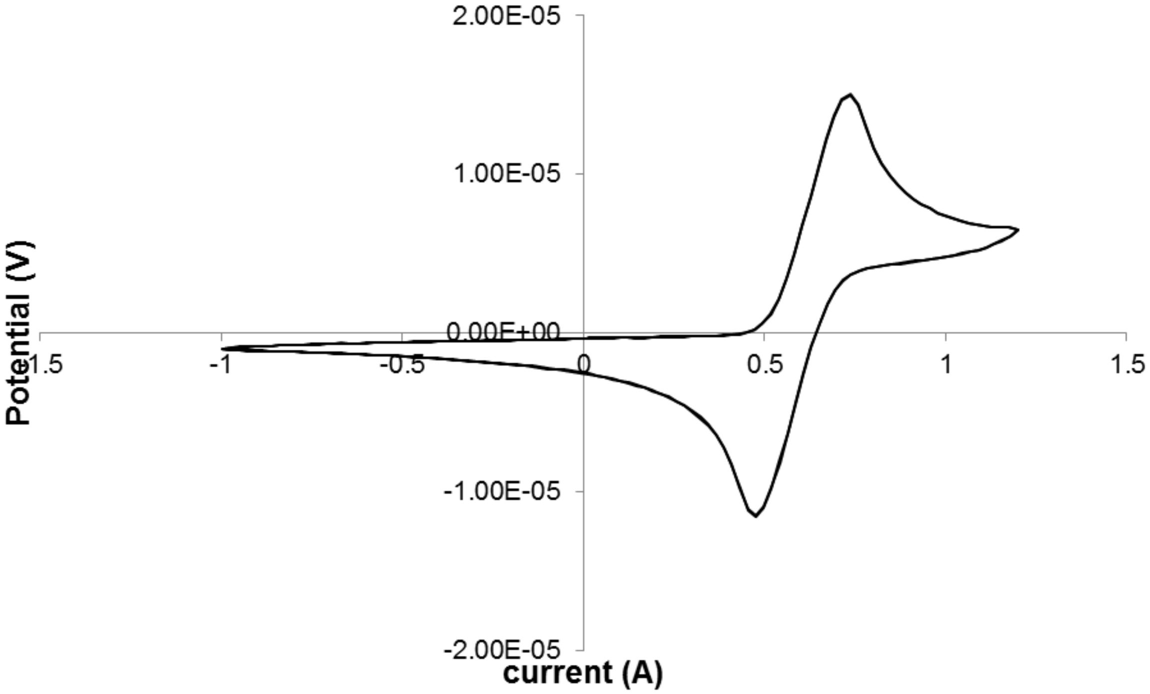

**Figure s4**: Cyclic voltammogram of **2** in thf (0.1 M $[NH_4][PF_6]$, scan rate: 0.1 V $s^{-1}$).