Electronic Supplementary Material (ESI) for Dalton Transactions.

Extension of conjugation: probing anion binding strength and reporter mechanisms in (phenyl)cyclopentadienyl and indenyl receptors

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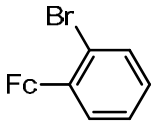
1. Syntheses of phenylferrocene precursors 1a-c

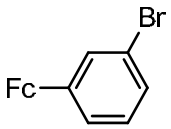
The three (known) (bromophenyl)ferrocene isomers (ortho, meta and para) were synthesised following a common procedure, differing somewhat from those reported in the literature: A mixture of bromoaniline (2.0 equiv.), concentrated H_2SO_4 and water was cooled to -10 °C and treated with an aqueous solution of $NaNO_2$ (2.02 equiv.) over 20 min. The cold reaction mixture was added slowly to a cold solution (0 °C) of ferrocene (1.0 equiv.), H_2SO_4 and hexadecyltrimethylammonium bromide in diethyl ether. The mixture was stirred for 5 h at -5 °C and warmed to room temperature overnight. After neutralization by the addition of NaOH (aq. 10%), the ether layer was separated and the aqueous fraction extracted with ether. The combined organic fractions were dried over $MgSO_4$, filtered and pumped down to dryness under reduced pressure. The crude products were purified using an alumina column eluted with hexane; crystalline materials were obtained in each case from hexane solutions cooled to -25°C. Purity was assessed by ^{1}H NMR and elemental analysis.

(2-bromophenyl)ferrocene (**1a**)



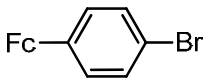
2-bromoaniline (10.67 g, 62.0 mmol), concentrated H_2SO_4 (10 mL) and water (20 mL) were treated with an aqueous solution (20 mL) of $NaNO_2$ (4.36 g, 63.2 mmol). The reaction mixture was then added to a mixture of ferrocene (5.82 g, 31.3 mmol) (250 mL), H_2SO_4 (1 mL) and hexadecyltrimethylammonium bromide (400 mg) in diethyl ether. Yield: 2.64 g, 25%. Characterizing data were in line with those reported in the literature.[s1]

(3-bromophenyl)ferrocene (**1b**)



3-bromoaniline (6.6 g, 38.4 mmol), concentrated H_2SO_4 (6 mL) and water (20 mL) were treated with an aqueous solution (20 mL) of $NaNO_2$ (2.70 g, 39.1 mmol). The reaction mixture was then added to a mixture ferrocene (3.6 g, 19.4 mmol), H_2SO_4 (1 mL) and hexadecyltrimethylammonium bromide (360 mg) in diethyl ether (250 mL). Yield: 2.85 g, 43%. Characterizing data were in line with those reported in the literature.[s2]

(4-bromophenyl)ferrocene (**1c**)



4-bromoaniline (13.2 g, 76.8 mmol), concentrated H_2SO_4 (13 mL) and water (20 mL) was treated with an aqueous solution (20 mL) of $NaNO_2$ (5.40 g, 78.2 mmol). The reaction mixture was then added to a mixture of ferrocene (7.2 g, 38.8 mmol), H_2SO_4 (1 mL) and hexadecyltrimethylammonium bromide (700 mg) in diethyl ether (250 mL). Yield: 6.45 g, 49%. The ^{1}H NMR spectrum of the product was in agreement with literature data.[s3]

2. VT-NMR studies of 5a

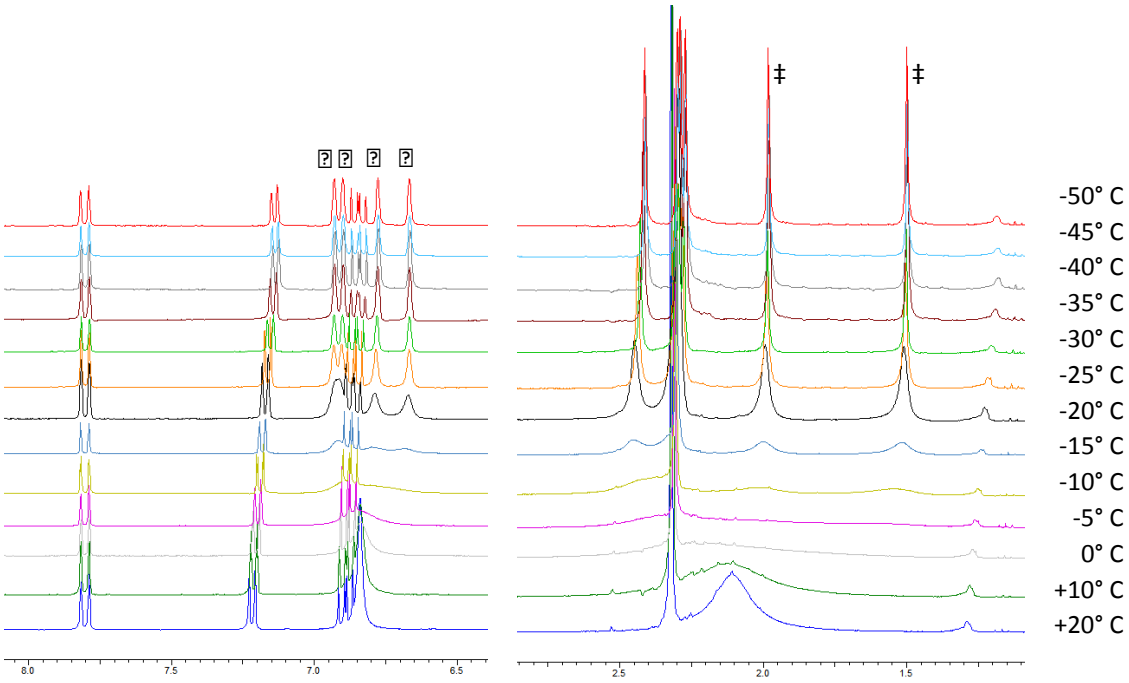


Figure s1: Alkyl and aromatic regions of the ^{1}H NMR spectrum of **5a** in chloroform as a function of temperature (^{1}H signals highlighted corresponding to the *meta*-CH (✧) and the *ortho*-methyl protons (‡) of the mesityl substituents).

3. Additional NMR studies of anion binding

Cyanide anion binding by **2a**: **2a** (20 mg, 0.06 mmol) and $[^nBu_4N][CN]\cdot 3H_2O$ (20 mg, 0.07 mmol) were dissolved in dry thf-d_8 and analysed in situ by multinuclear NMR spectroscopy. ^{1}H NMR (300 MHz, thf-d_8, 20 °C): δ_H 0.92 (t, $^3J_{HH}$= 9.0 Hz, Me of $[^nBu_4N]$), 1.29 (sextet, $^3J_{HH}$= 5.9 Hz, CH_2 of $[^nBu_4N]$), 1.56 (m, CH_2 of $[^nBu_4N]$), 1.92 (s, 12H, ortho-Me of Mes), 2.15 (s, 6H, para-Me of Mes), 3.15 (t, $^3J_{HH}$= 9.1 Hz, NCH_2 $[^nBu_4N]$), 3.84 (s, 2H, aromatic CH of C_5H_4), 3.90 (s, 5H, Cp), 4.56 (s, 2H, aromatic CH of C_5H_4), 6.49 (s, 4H, meta-CH of Mes), 6.61 (t, $^3J_{HH}$= 9.1 Hz, 1H, C4), 6.86 (t d, $^3J_{HH}$= 6.2 Hz and $^4J_{HH}$ = 1.5 Hz, 1H, C5), 7.01 (d, $^3J_{HH}$= 6 Hz, 1H, C3), 7.79 (d, $^3J_{HH}$= 9.0 Hz, 1H, C6). $^{13}C\{^1H\}$ NMR (76 MHz, thf-d_8, 20 °C): δ_C 14.1 (Me of $[^nBu_4N]$), 20.6 (CH_2 of $[^nBu_4N]$), 21.3 (para-Me of Mes), 24.9 (CH_2 of $[^nBu_4N]$), 26.5 (ortho-Me of Mes), 59.2 (CH_2 of $[^nBu_4N]$), 66.8 (aromatic CH of C_5H_4), 69.9 (Cp), 72.9 (aromatic CH of C_5H_4), 93.9 (quaternary C of C_5H_4), 123.2 (para-CH of Ph), 124.6 (para-CH of Ph), 129.5 (meta-CH of Mes), 131.4 (para-CH of Ph), 131.8 (para-quaternary C of Mes), 138.1 (ortho-CH of Ph), 143.6 (ortho-quaternary C of Mes), 143.8 (ipso-quaternary C of Ph bound to Fc), 154.0 (b s, ipso-quaternary C of Mes), 157.4 (b s,ortho-quaternary C of Ph bound to B). $^{11}B\{^1H\}$ NMR (96 MHz, thf-d_8, 20 °C): δ_B -13.

Fluoride anion binding by **2c**: **2c** (20 mg, 0.06 mmol) and $[^nBu_4N]F\cdot 4H_2O$ (19 mg, 0.07 mmol) were dissolved in dry thf-d_8 and analysed in situ by multinuclear NMR spectroscopy. ^{1}H NMR (300 MHz, thf-d_8, -20 °C): δ_H 0.97 (b m, Me of $[^nBu_4N]$), 1.39 (b m, CH_2 of $[^nBu_4N]$), 1.64 (b m, CH_2 of $[^nBu_4N]$), 1.93 (s, 12H, ortho-Me of Mes), 2.11 (s, 6H, para-Me of Mes), 3.32 (b m, CH_2 of $[^nBu_4N]$), 3.92 (s, 5H, Cp), 4.15, 4.58 (s, each 2H, aromatic CH of C_5H_4), 6.41 (s, 6H, aromatic CH of Mes), 6.93 (d, $^3J_{HH}$ = 6.0 Hz, 1H, aromatic CH of Ph), 7.02 (d, $^3J_{HH}$ = 9.1 Hz, 1H, aromatic CH of Ph), 7.22 (d, $^3J_{HH}$ = 8.9 Hz, 1H, aromatic CH of Ph), 7.69 (d, $^3J_{HH}$ = 6.1 Hz, 1H, aromatic CH of Ph). $^{13}C\{^1H\}$ NMR (76 MHz, thf-d_8, -20 °C): δ_C 14.4 (Me of $[^nBu_4N]$), 20.6 (CH_2 of $[^nBu_4N]$), 21.4 (para-Me of Mes), 24.81 (CH_2 of $[^nBu_4N]$), 25.7 and 25.8 (ortho-Me of Mes), 59.0 (NCH_2 of $[^nBu_4N]$), 66.3, 68.0 (aromatic CH of C_5H_4), 70.2 (Cp), 89.0 (quaternary C of C_5H_4), 124.1, 124.4 (aromatic CH of Ph), 128.8 (aromatic CH of Mes), 130.9 (para-quaternary C of Mes), 132.7 (quaternary C of Ph), 134.0 and 135.1 (aromatic CH of Ph), 142.1 (ortho-quaternary C of Mes), 156.6 (b s, ipso-quaternary C of Mes), 162.9 (b s,C of Ph bound to B). $^{11}B\{^1H\}$ NMR (96 MHz, thf-d_8, 20 °C): δ_B 7. ^{19}F NMR (282 MHz, thf-d_8, -20°C): δ_F -171.6.

Cyanide anion binding by **5b**: **5b** (25 mg, 0.05 mmol) and $[^nBu_4N][CN]\cdot 3H_2O$ (17 mg, 0.06 mmol) were dissolved in dry thf-d_8 and analysed in situ by multinuclear NMR spectroscopy. ^{1}H NMR (500 MHz, bromobenzene-d_5, 100 °C): δ_H 1.05 (t, $^3J_{HH}$ = 6.0 Hz, Me of $[^nBu_4N]$), 1.40 (sextet, $^3J_{HH}$ = 6.0 Hz, CH_2 of $[^nBu_4N]$), 1.57 (b s, CH_2 of $[^nBu_4N]$), 2.37, 2.40 (b s, each 3H, para-Me of Mes), 2.50, 2.55 (b s, each 6H, ortho-Me of Mes), 3.15 (b t, $^3J_{HH}$ = 6.1 Hz, NCH_2 of $[^nBu_4N]$), 3.96 (s, 1H, five membered ring of ind), 4.04 (s, 5H, Cp), 4.59, 4.95 (s, each 1H, five membered ring of ind), 6.84, 6.95 (s, each 2H, aromatic CH of Mes), 7.47 (s, 1H, C7), 7.50, 8.24 (d, $^3J_{HH}$ = 2.9 Hz, each 1H, C5H and C4H). ^{1}H NMR (500 MHz, thf-d_8, 25 °C): δ_H 0.98 (t, $^3J_{HH}$ = 7.1 Hz, Me of $[^nBu_4N]$), 1.38 (sextet, $^3J_{HH}$ = 7.2 Hz, CH_2 of $[^nBu_4N]$), 1.66 (quintet, $^3J_{HH}$ = 7.3 Hz, CH_2 of $[^nBu_4N]$), 1.94, 1.98, 2.03, 2.05 (b s, each 3H, ortho-Me of Mes), 2.14, 2.17 (b s, each 3H, para-Me of Mes), 3.29 (t, $^3J_{HH}$ = 8.9 Hz, NCH_2 of $[^nBu_4N]$), 3.71 (b s, 5H, Cp), 3.74, 4.48, 4.64 (b s, each 1H, CH of five membered ring of ind), 6.47 and 6.52 (b s, each 2H, aromatic CH of Mes), 6.88 (s, 1H, C7H), 7.16 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C4H), 7.72 (d, $^3J_{HH}$ = 9.1 Hz, 1H, C5H). $^{13}C\{^1H\}$ NMR (126 MHz, bromobenzene-d_5, 100 °C): δ_C 13.2 (Me of $[^nBu_4N]$), 19.7 (CH_2 of $[^nBu_4N]$), 20.3 (para-Me of Mes), 23.9 (CH_2 of $[^nBu_4N]$), 25.3, 25.3, 25.6 and 25.7 (ortho-Me of Mes), 58.1 (CH_2 of $[^nBu_4N]$), 59.8, 60.1, 67.0 (C1, C2 and C9), 67.2 (Cp), 87.0 (C8), 90.1 (C3), 122.8 (C4), 128.3, 128.4 (aromatic CH of Mes), 130.5 (C7), 130.6 (para-quaternary C of Mes), 136.1 (C5), 141.3, 141.8, 141.8 and 141.9 (ortho-quaternary C

of Mes) 144.9 (CN), 151.4 (ipso-quaternary C of Mes), 153.2 (C of Ind bound to B). $^{11}B\{^{1}H\}$ NMR (160 MHz, bromobenzene-d_5, 100 °C): δ_B -13.

4. Determination of anion binding constants by UV-vis titration

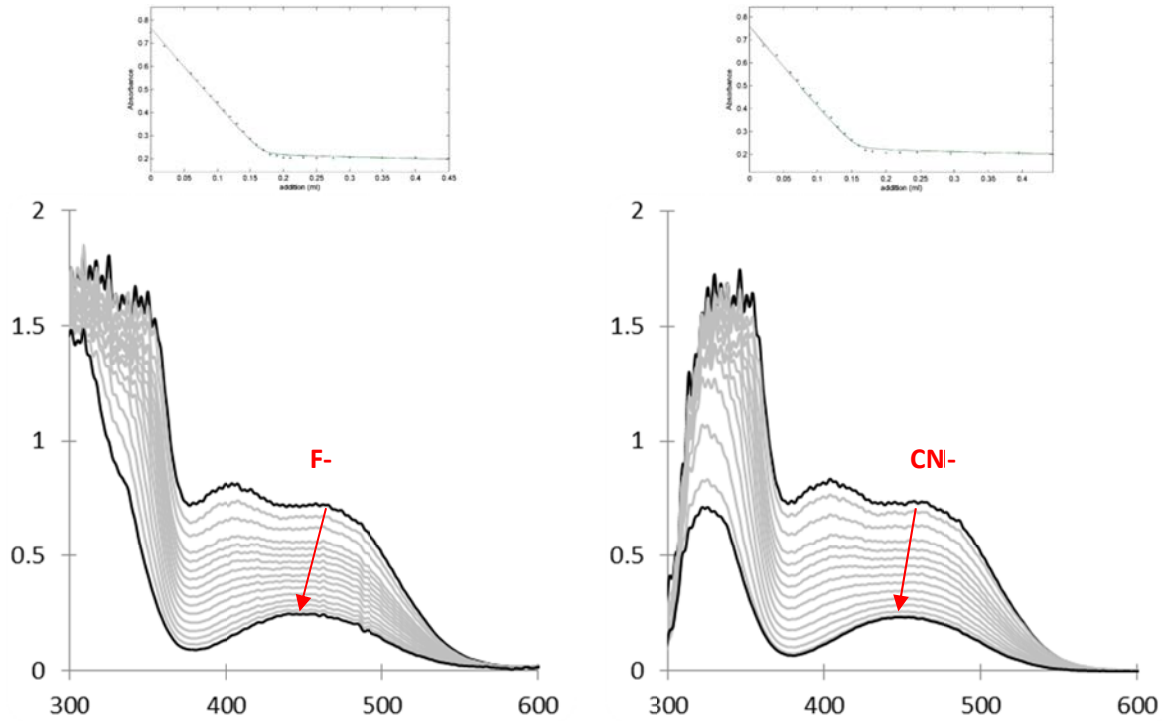


Figure s2: Left: Changes in the UV-vis absorption spectra of a solution of **2a** (3 m**L**, 9.72×10^{-4} M in thf) upon addition of $[^{n}Bu_4N]F{\cdot}4H_2O$ (1.90×10^{-2} M in thf). Right: Changes in the UV-vis absorption spectra of a solution of **2a** (3 mL, 9.76×10^{-4} M in thf) upon addition of $[^{n}Bu_4N][CN]{\cdot}3H_2O$ (2.12×10^{-2} M in thf). Inset: fitting curves log*K*(F)= 5.782 ± 0.033 (*σr*= 0.0074, *ssq*= 0.111); log*K*(CN)= 5.600 ± 0.052 (*σr*= 0.052, *ssq*= 0.361).

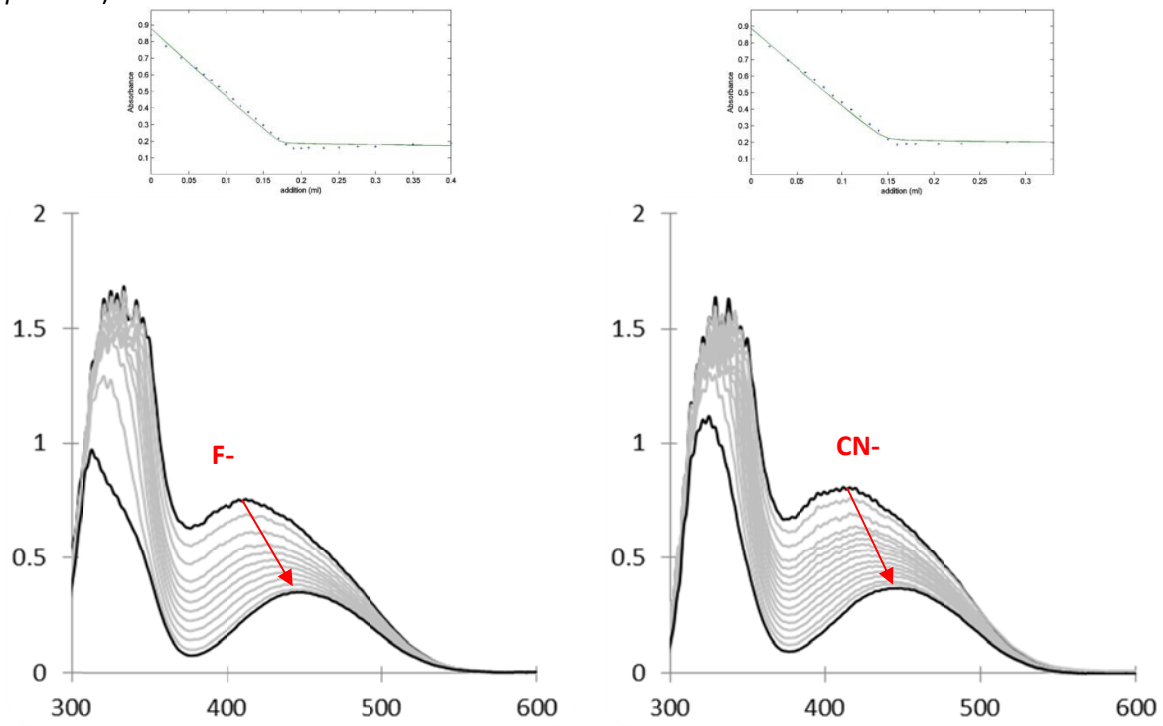


Figure s3: Left: Changes in the UV-vis absorption spectra of a solution of **2b** (3 mL, 1.39×10^{-4} M in thf) upon addition of $[^{n}Bu_4N]F{\cdot}4H_2O$ (2.39×10^{-2} M in thf). Right: Changes in the UV-vis absorption spectra of a solution of **2b** (3 mL, 1.34×10^{-4} M in thf) upon the addition of $[^{n}Bu_4N][CN]{\cdot}3H_2O$ (3.14×10^{-2} M in thf). Inset: fitting curves log*K*(F)= 6.429 ± 0.138 (*σr*= 0.0131, *ssq*= 0.327); log*K*(CN)= 5.846 ± 0.076 (*σr*= 0.0138, *ssq*= 0.288).

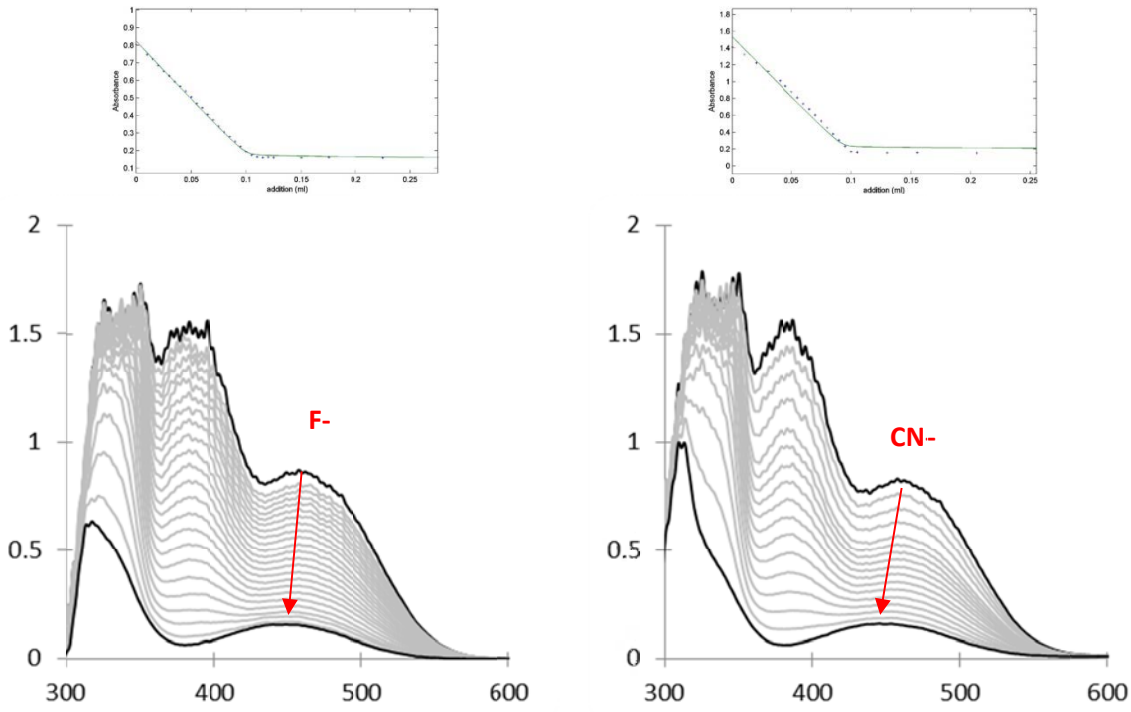


Figure s4: Left: Changes in the UV-vis absorption spectra of a solution of **2c** (3 mL, 3.61×10^{-4} M in thf) upon addition of $[^{n}Bu_4N]F{\cdot}4H_2O$ (1.23×10^{-2} M in thf). Right: Changes in the UV-vis absorption spectra of a solution of **2c** (3 mL, 3.61×10^{-4} M in thf**)** upon addition of $[^{n}Bu_4N][CN]{\cdot}3H_2O$ (1.20×10^{-2} M in thf). Inset: fitting curves log*K*(F)= 6.3138 ± 0.038 (*σr*= 0.0089, *ssq*= 0.134); log*K*(CN)= 6.447 ± 0.136 (*σr*= 0.0586, *ssq*= 5.05).

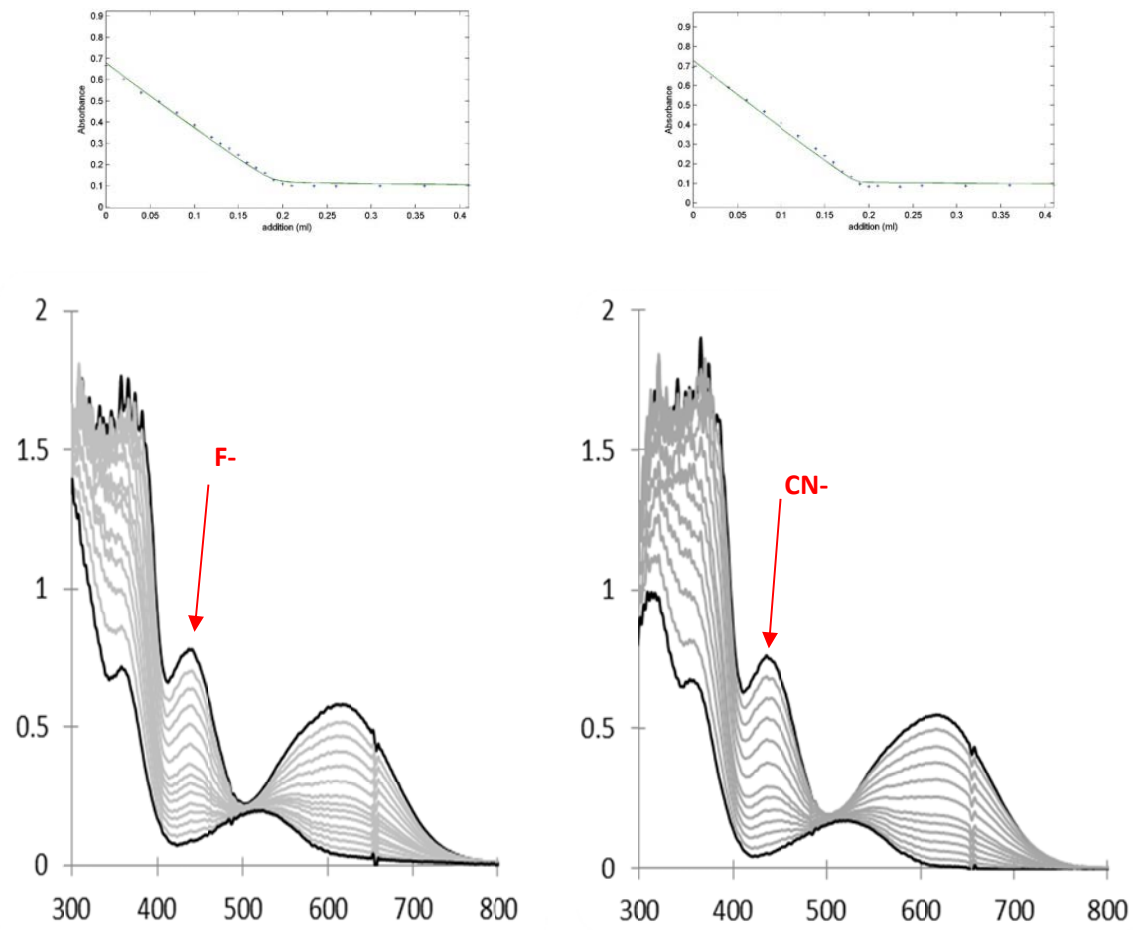


Figure s5: Left: Changes in the UV-vis absorption spectra of a solution of **5a** (3 mL, 6.37 × 10^{-4} M in thf) upon addition of [^{n}Bu$_4$N]F·4H$_2$O (1.0 × 10^{-2} M in thf). Right: Changes in the UV-vis absorption spectra of a solution of **5a** (3 mL, 6.29 × 10^{-4} M in thf) upon addition of [^{n}Bu$_4$N][CN]·3H$_2$O (1.07 × 10^{-2} M in thf). Inset: fitting curves. log*K*(F)= 6.358 ± 0.102 (*σr*= 0.0152, *ssq*= 0.291); log*K*(CN)= 7.008 ± 0.205 (*σr*= 0.0122, *ssq*= 0.196).

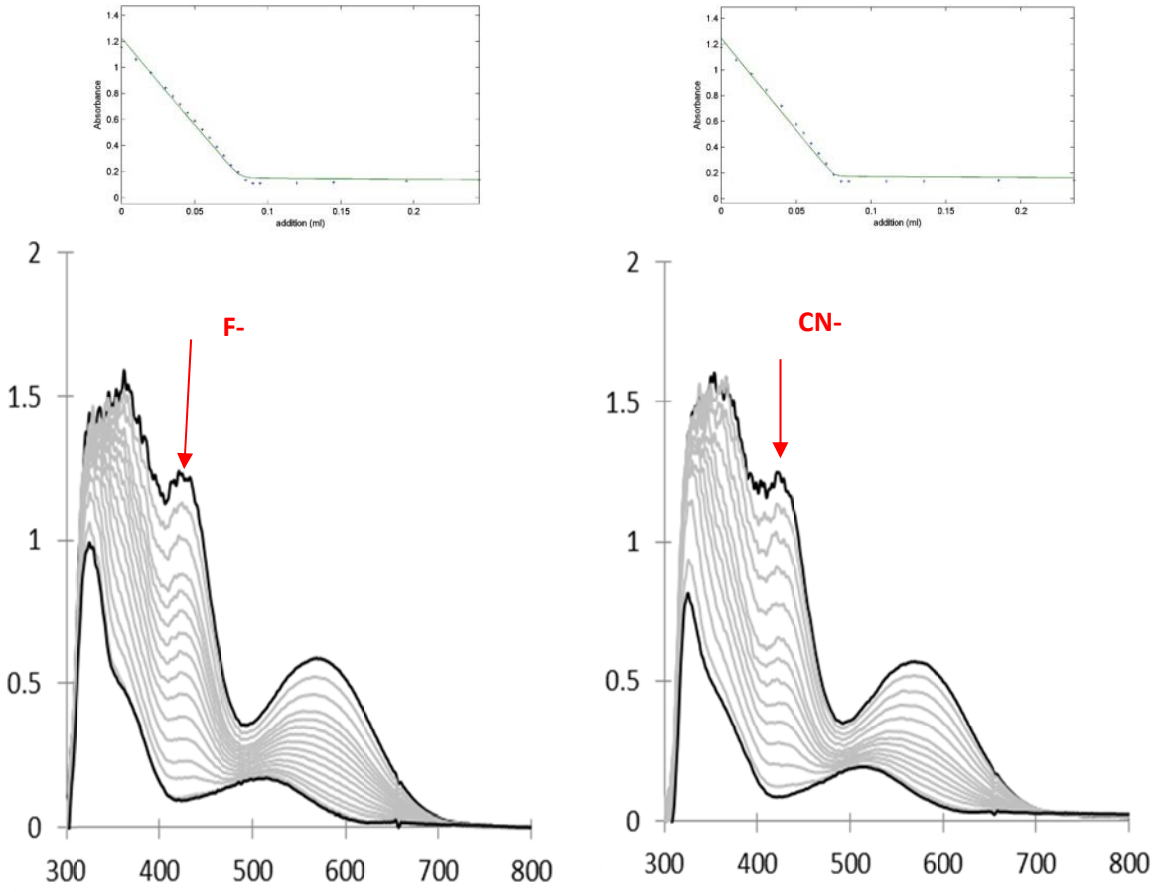


Figure s6: Left: Changes in the UV-vis absorption spectra of a solution of **5b** (3 mL, 6.27×10^{-4} M in thf) upon addition of $[^{n}Bu_4N]F{\cdot}4H_2O$ (2.30×10^{-2} M in thf). Right: Changes in the UV-vis absorption spectra of a solution of **5b** (3 mL, 6.10×10^{-4} M in thf) upon addition of $[^{n}Bu_4N][CN]{\cdot}3H_2O$ (2.04×10^{-2} M in thf). Inset: fitting curves log*K*(F)= 6.282 ± 0.0280 (*σr*= 0.00355, *ssq*= 0.0199); log*K*(CN)= 6.969 ± 0.392 (*σr*= 0.0427, *ssq*= 1.46).

5. Cyclic voltammograms

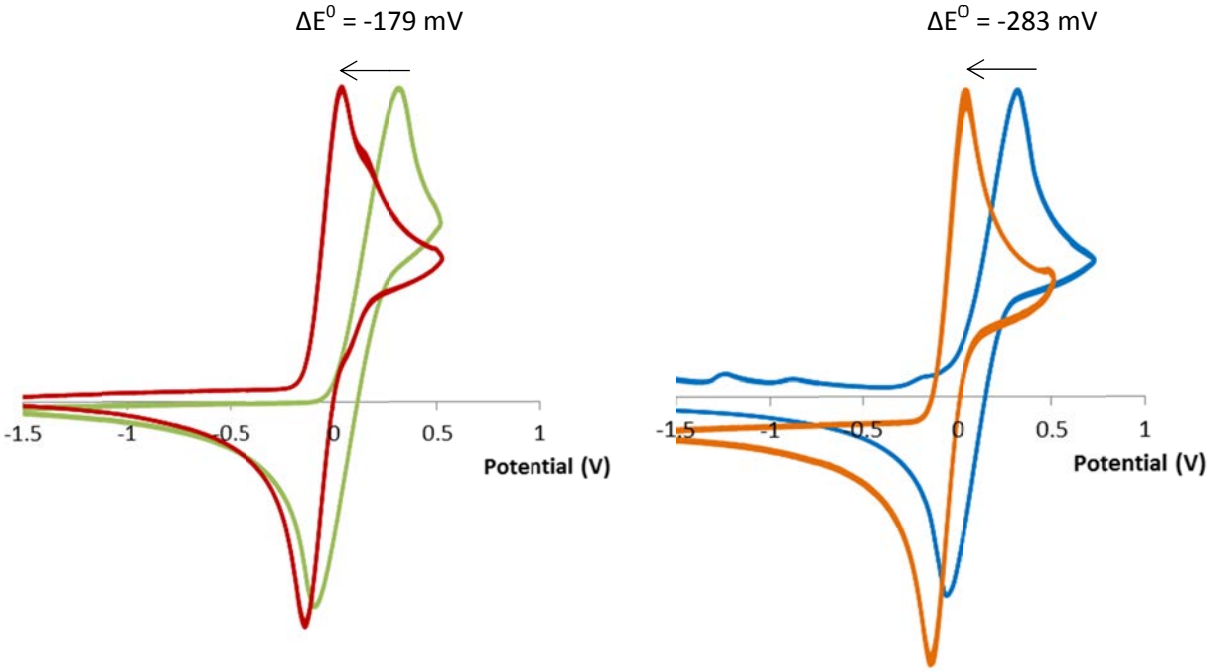


Figure s7: Cyclic voltammograms of (left) **2b** and [**2b**•CN]$^-$ and (right) **2c** and [**2c**•CN]$^-$ (0.1 M $[NH_4][PF_6]$ in thf, scan rate: 0.1 V s^{-1}) plotted with respect to the $FeCp_2$ / $FeCp_2^+$ couple.

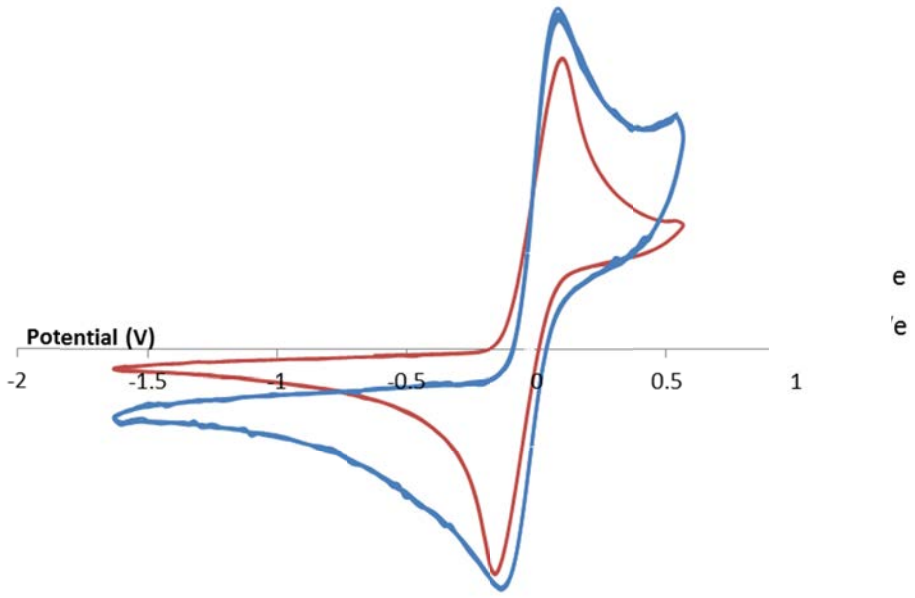


Figure s8: Cyclic voltammograms of receptors **5a** (red) and **5b** (blue); 0.1 M $[NH_4][PF_6]$ in thf, scan rate: 0.1 V s^{-1}, plotted with respect to the $FeCp_2$ / $FeCp_2^+$ couple.

6. Details of DFT calculations

Density Functional Theory (DFT) calculations were carried out using the Amsterdam Density Functional (ADF 2013) software package.[s4,s5] Calculations were performed using the Volko-Wilk-Nusair local density approximation with exchange from Becke[s6] and correlation functions from Perdew (BP).[s7] Slater-type orbitals[s8] were used for the triple zeta basis set with an additional set of polarization functions (TZP). The large frozen core basis set approximation was applied with no molecular symmetry. General numerical integration was 6. Frequency calculations were performed for optimized structures and no significant imaginary frequencies were found. Excellent agreement was achieved between the calculated and experimentally determined molecular structures.

DFT run files

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# ============================

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60 Fe       4.304883946000       2.948486202000       2.445616145000
61 B       1.668034820000       0.830467912000       2.787179992000
END

GUIBONDS
1 1 8 1.0
2 1 2 1.0
3 1 61 1.0
4 1 60 1.0
5 2 3 1.0
6 2 4 1.0
7 2 60 1.0
8 4 5 1.0
9 4 6 1.0
10 4 60 1.0
11 6 7 1.0
12 6 8 1.0
13 6 60 1.0
14 8 9 1.0
15 8 60 1.0
16 10 11 1.0
17 10 18 1.0
18 10 12 1.0
19 10 60 1.0
20 12 13 1.0
21 12 14 1.0
22 12 60 1.0
23 14 15 1.0
24 14 16 1.0
25 14 60 1.0
26 16 17 1.0
27 16 18 1.0
28 16 60 1.0
29 18 19 1.0
30 18 60 1.0
31 20 21 1.5
32 20 27 1.5
33 20 61 1.0
34 21 22 1.5
35 21 28 1.0
36 22 23 1.0
37 22 24 1.5
38 24 25 1.5
39 24 32 1.0
40 25 26 1.0
41 25 27 1.5
42 27 36 1.0
43 28 29 1.0
44 28 30 1.0
45 28 31 1.0
46 32 34 1.0
47 32 35 1.0
48 32 33 1.0
49 36 38 1.0
50 36 37 1.0
51 36 39 1.0
52 40 47 1.5
53 40 41 1.5
54 40 61 1.0
55 41 42 1.5
56 41 48 1.0
57 42 43 1.0
58 42 44 1.5
59 44 45 1.5
60 44 52 1.0
61 45 46 1.0
62 45 47 1.5
63 47 56 1.0
64 48 51 1.0
65 48 50 1.0
66 48 49 1.0
67 52 55 1.0
68 52 54 1.0
69 52 53 1.0
70 56 57 1.0
71 56 59 1.0
72 56 58 1.0
END
```

```
BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
    optim Delocalized
END

SAVE  TAPE21 TAPE13

SCF
iterations 200
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor


# ==============================
# Compound 2a
# ==============================

"$ADFBIN/adf" <<eor
ATOMS
1 C       8.793610000000       3.750470000000       6.948480000000
2 C       9.749110000000       4.490200000000       7.724320000000
3 C      10.671000000000       5.110680000000       6.816100000000
4 C      10.285000000000       4.755510000000       5.479920000000
5 C       9.126080000000       3.914600000000       5.562790000000
6 Fe       8.731920000000       5.772440000000       6.432820000000
7 C       8.329110000000       7.494730000000       5.335900000000
8 C       8.752390000000       7.837420000000       6.659100000000
9 C       7.829430000000       7.246850000000       7.583820000000
10 C       6.842580000000       6.535590000000       6.828510000000
11 C       7.128630000000       6.703750000000       5.420430000000
12 C       6.334440000000       6.142320000000       4.308010000000
13 C       6.207990000000       6.789340000000       3.040650000000
14 C       5.501270000000       6.093380000000       2.026900000000
15 C       4.860830000000       4.876200000000       2.251250000000
16 C       4.948130000000       4.284630000000       3.515520000000
17 C       5.692050000000       4.905120000000       4.515590000000
18 B       6.621590000000       8.265890000000       2.648740000000
19 C       6.417580000000       9.509740000000       3.609230000000
20 C       7.403450000000      10.536700000000       3.703510000000
21 C       8.721810000000      10.478100000000       2.959640000000
22 C       7.193350000000      11.648700000000       4.529100000000
23 C       6.013810000000      11.824300000000       5.256270000000
```

```
24 C       5.794120000000      13.040800000000       6.123880000000
25 C       5.035490000000      10.831300000000       5.144750000000
26 C       5.215380000000       9.685830000000       4.360560000000
27 C       4.066790000000       8.697670000000       4.332760000000
28 C       7.098390000000       8.483410000000       1.144880000000
29 C       6.357270000000       9.328760000000       0.267490000000
30 C       6.750870000000       9.474680000000      -1.067330000000
31 C       7.878000000000       8.827180000000      -1.589250000000
32 C       8.271110000000       9.000060000000      -3.037650000000
33 C       8.604630000000       8.003800000000      -0.727256000000
34 C       8.231660000000       7.813490000000       0.611929000000
35 C       9.122320000000       6.939570000000       1.468930000000
36 C       5.107930000000      10.057900000000       0.718078000000
37 H       7.964370000000       3.169240000000       7.343960000000
38 H       9.766900000000       4.573120000000       8.808220000000
39 H      11.506800000000       5.749120000000       7.092070000000
40 H      10.777000000000       5.076140000000       4.565250000000
41 H       8.578180000000       3.499860000000       4.720080000000
42 H       8.845240000000       7.762070000000       4.418420000000
43 H       9.627680000000       8.427650000000       6.916720000000
44 H       7.873730000000       7.318630000000       8.667440000000
45 H       5.994370000000       5.995080000000       7.240940000000
46 H       5.436460000000       6.549590000000       1.037490000000
47 H       4.307580000000       4.389310000000       1.446820000000
48 H       4.463020000000       3.326940000000       3.713430000000
49 H       5.813670000000       4.410010000000       5.480250000000
50 H       9.364500000000      11.318900000000       3.251750000000
51 H       9.276010000000       9.552250000000       3.171230000000
52 H       8.577270000000      10.520200000000       1.871500000000
53 H       7.978400000000      12.407400000000       4.598670000000
54 H       5.562320000000      12.753300000000       7.160310000000
55 H       6.681880000000      13.686100000000       6.141200000000
56 H       4.947220000000      13.642100000000       5.759300000000
57 H       4.093990000000      10.947900000000       5.690340000000
58 H       3.151710000000       9.168090000000       4.716880000000
59 H       3.855860000000       8.317900000000       3.324530000000
60 H       4.280110000000       7.820620000000       4.961100000000
61 H       6.152050000000      10.114300000000      -1.722900000000
62 H       9.253210000000       8.554860000000      -3.242660000000
63 H       8.313040000000      10.063100000000      -3.316280000000
64 H       7.539700000000       8.520240000000      -3.706480000000
65 H       9.490400000000       7.485040000000      -1.106160000000
66 H       9.684300000000       6.225690000000       0.851813000000
67 H       9.863550000000       7.548390000000       2.013070000000
68 H       8.549660000000       6.374840000000       2.214750000000
69 H       4.645750000000      10.590000000000      -0.123799000000
70 H       5.326870000000      10.787900000000       1.509580000000
71 H       4.356040000000       9.365150000000       1.125790000000
END
```

```
GUIBONDS
1 31 33 1.5
2 31 32 1.0
3 36 70 1.0
4 32 64 1.0
5 32 63 1.0
6 1 37 1.0
7 32 62 1.0
8 33 65 1.0
9 33 34 1.5
10 2 38 1.0
11 34 35 1.0
12 35 66 1.0
13 35 67 1.0
14 3 39 1.0
15 35 68 1.0
16 4 40 1.0
17 36 69 1.0
18 36 71 1.0
19 5 41 1.0
20 6 5 1.0
21 6 1 1.0
```

```
22 6 7 1.0
23 6 2 1.0
24 6 10 1.0
25 6 8 1.0
26 6 9 1.0
27 6 11 1.0
28 6 3 1.0
29 6 4 1.0
30 7 42 1.0
31 7 8 1.0
32 7 11 1.0
33 8 43 1.0
34 8 9 1.0
35 9 44 1.0
36 9 10 1.0
37 10 45 1.0
38 10 11 1.0
39 11 12 1.0
40 12 17 1.5
41 12 13 1.5
42 13 14 1.5
43 13 18 1.0
44 14 46 1.0
45 14 15 1.5
46 15 47 1.0
47 15 16 1.5
48 16 48 1.0
49 16 17 1.5
50 17 49 1.0
51 18 28 1.5
52 18 19 1.5
53 19 26 1.5
54 19 20 1.0
55 20 22 1.5
56 20 21 1.0
57 21 52 1.0
58 21 51 1.0
59 21 50 1.0
60 22 53 1.0
61 22 23 1.5
62 23 25 1.5
63 23 24 1.0
64 24 56 1.0
65 24 54 1.0
66 24 55 1.0
67 25 57 1.0
68 25 26 1.5
69 26 27 1.0
70 27 60 1.0
71 27 59 1.0
72 27 58 1.0
73 28 34 1.5
74 28 29 1.0
75 29 30 1.5
76 29 36 1.0
77 30 61 1.0
78 30 31 1.5
79 2 3 1.0
80 4 3 1.0
81 5 4 1.0
82 1 5 1.0
83 2 1 1.0
END


BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END

GEOMETRY
    optim Delocalized
    iterations 60
END

SAVE  TAPE21 TAPE13

SCF
iterations 600
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE
```

```
eor
# ============================
# Compound 2b
# ============================

"$ADFBIN/adf" <<eor
ATOMS
1 C      16.049817700000      12.417115790000      10.995112340000
2 C      16.888902890000       9.479759181000      13.197594520000
3 C      17.467653950000       9.401891573000      14.481335010000
4 C      17.684331120000       8.168558174000      15.096436010000
5 C      17.307153230000       6.987029614000      14.455124200000
6 C      16.330917530000      11.024347610000      11.171474210000
7 C      16.607367570000      10.782000790000      12.567182100000
8 C      16.739771270000       7.014023796000      13.161610950000
9 C      16.556556130000       8.274389211000      12.554536150000
10 B      16.291965080000       5.688307737000      12.446800730000
11 C      15.881872670000       4.461503762000      13.365613580000
12 C      14.860488850000       4.597957821000      14.349047000000
13 C      14.532178620000       3.518805132000      15.178170290000
14 C      15.197029470000       2.290104417000      15.099763080000
15 C      16.204818880000       2.160909436000      14.139627980000
16 C      16.545982860000       3.206942352000      13.270742120000
17 C      17.668499230000       2.967663473000      12.283046380000
18 H      15.810919200000      12.904258170000      10.053388890000
19 H      17.758796060000      10.319543040000      14.995166770000
20 H      18.137702680000       8.132391767000      16.088538320000
21 H      17.448540200000       6.027161236000      14.955863280000
22 H      16.108158090000       8.311079448000      11.559682040000
23 H      13.727390440000       3.643823876000      15.909130260000
24 H      16.743732460000       1.212466105000      14.055963520000
25 H      17.914442070000       1.899368023000      12.222942930000
26 H      18.586414550000       3.497227906000      12.584945370000
27 H      17.406385310000       3.320156164000      11.276934130000
28 H      15.660575650000       0.459930985700      16.165807970000
29 H      14.450435560000       1.488401298000      16.970257530000
30 H      14.003391310000       0.539134938300      15.542783500000
31 H      13.122535860000       5.681133534000      15.042364360000
32 H      14.627098120000       6.623241746000      15.104618470000
33 C      14.812001310000       1.135685590000      15.994729110000
34 C      14.067674130000       5.878940265000      14.518939210000
35 C      16.273037500000       5.629090045000      10.862561800000
36 H      13.828015710000       6.352347018000      13.557507680000
37 C      15.107349120000       5.243741125000      10.143034140000
38 C      15.121057140000       5.210141469000       8.740600396000
39 C      16.262927150000       5.520835582000       7.999478583000
40 C      17.413543780000       5.888003553000       8.708797966000
41 C      16.509618230000      12.057823790000      13.238646700000
42 C      16.157657170000      13.056558370000      12.274069800000
43 C      17.435936840000       5.961741106000      10.105747240000
44 C      18.744942600000       6.356190594000      10.761494480000
45 Fe      17.968375920000      12.168706020000      11.766098120000
46 C      16.267398960000       5.453059761000       6.490415263000
47 C      13.805278350000       4.908068747000      10.838000570000
48 C      19.607667590000      11.606612770000      10.601041560000
49 C      19.904889610000      11.414008760000      11.990659440000
50 H      14.207954730000       4.917773770000       8.213901359000
51 H      18.330822670000       6.115174972000       8.156546018000
52 H      19.578214070000       6.241724718000      10.055162410000
53 H      18.727076590000       7.403340177000      11.096471030000
54 H      18.967576150000       5.748256976000      11.648445380000
```

```
55 H      16.648621670000      12.229746830000      14.302522050000
56 H      16.005936430000      14.113433590000      12.476541620000
57 H      17.038460300000       4.758055029000       6.125441446000
58 H      16.485194830000       6.436824553000       6.047362526000
59 H      15.297677550000       5.116022021000       6.102417856000
60 H      13.103768300000       4.430559549000      10.141487340000
61 H      13.314644490000       5.816047391000      11.223444580000
62 H      13.960465570000       4.234903669000      11.690633920000
63 H      19.597167310000      10.833783890000       9.836551346000
64 H      20.146360810000      10.466741830000      12.466592970000
65 C      19.789796640000      12.683212660000      12.649232870000
66 C      19.423811090000      13.662460420000      11.665036220000
67 C      19.311346450000      12.996735910000      10.399017410000
68 H      16.343582240000      10.279357200000      10.380779630000
69 H      19.947342360000      12.870921870000      13.708455080000
70 H      19.252971130000      14.720547350000      11.847605770000
71 H      19.037436430000      13.460964760000       9.454797606000
END
```

```
GUIBONDS
1 45 7 1.0
2 6 68 1.0
3 6 1 1.0
4 6 7 1.0
5 7 41 1.0
6 45 6 1.0
7 7 2 1.0
8 41 55 1.0
9 45 65 1.0
10 41 42 1.0
11 42 56 1.0
12 42 1 1.0
13 45 41 1.0
14 1 18 1.0
15 2 9 1.5
16 2 3 1.5
17 3 19 1.0
18 3 4 1.5
19 45 48 1.0
20 45 67 1.0
21 45 66 1.0
22 45 1 1.0
23 45 42 1.0
24 4 20 1.0
25 4 5 1.5
26 5 21 1.0
27 5 8 1.5
28 8 9 1.5
29 8 10 1.0
30 45 49 1.0
31 9 22 1.0
32 10 35 1.5
33 10 11 1.5
34 11 12 1.5
35 11 16 1.0
36 12 13 1.5
37 12 34 1.0
38 13 23 1.0
39 13 14 1.5
40 17 27 1.0
41 14 15 1.5
42 34 36 1.0
43 34 32 1.0
44 35 37 1.5
45 35 43 1.0
46 37 38 1.5
47 37 47 1.0
48 38 50 1.0
49 38 39 1.5
50 39 40 1.5
51 39 46 1.0
52 40 51 1.0
53 40 43 1.5
54 43 44 1.0
55 44 54 1.0
56 44 53 1.0
57 44 52 1.0
58 33 29 1.0
59 33 30 1.0
60 46 57 1.0
61 46 59 1.0
62 46 58 1.0
63 47 62 1.0
64 47 60 1.0
65 33 28 1.0
66 47 61 1.0
67 48 63 1.0
68 48 49 1.0
69 48 67 1.0
70 49 64 1.0
71 49 65 1.0
72 65 69 1.0
73 34 31 1.0
74 65 66 1.0
75 14 33 1.0
76 15 24 1.0
77 15 16 1.5
78 16 17 1.0
79 17 25 1.0
80 17 26 1.0
81 66 70 1.0
82 66 67 1.0
83 67 71 1.0
```

```
END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END

GEOMETRY
    optim Delocalized
    iterations 50
END

SAVE  TAPE21 TAPE13

SCF
iterations 200
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor


# ==============================
# Compound 2c
# ==============================
"$ADFBIN/adf" <<eor
ATOMS
1 C      -2.659273486000       9.770915015000       6.375866110000
2 C      -2.999831060000       9.762975749000       4.985702535000
3 C      -2.134759900000       8.831194093000       4.323276748000
4 C      -1.263726324000       8.260498860000       5.304849966000
5 C      -1.566934372000       8.849277873000       6.590475058000
6 C      -0.880182242500       8.576116368000       7.861475396000
7 C      -0.000322484542       7.480927958000       8.007591626000
8 C       0.684845488300       7.265154432000       9.197607465000
9 C       0.520989067200       8.110613560000      10.322404990000
10 C      -0.377454612800       9.192015332000      10.167655190000
11 C      -1.048674499000       9.428273176000       8.972701038000
12 C       2.622325223000       6.990214749000      11.632245900000
13 C       2.719366604000       5.830198753000      12.458417830000
14 C       3.844679794000       5.004646526000      12.387521310000
15 C       4.921073650000       5.282631518000      11.534008710000
16 C       4.834426016000       6.426849595000      10.742078480000
17 C       3.715564961000       7.275340929000      10.771625610000
18 C       3.790613588000       8.528179338000       9.921429387000
19 C       6.122061269000       4.368136916000      11.474335000000
20 C       1.605705951000       5.430041134000      13.403139960000
21 C       0.777689920600       8.576230272000      12.982405270000
22 C       1.604613360000       9.487251064000      13.705009100000
23 C       1.111725917000      10.141023240000      14.838289760000
```

```
24 C      -0.185102489400       9.922830729000      15.320803730000
25 C      -0.986806266000       9.018289894000      14.624515210000
26 C      -0.536385602100       8.351965458000      13.474033080000
27 C      -1.476818195000       7.332100600000      12.863668600000
28 C      -0.697040857000      10.657667460000      16.537354580000
29 C       3.014706764000       9.811681734000      13.258739410000
30 C      -3.844586881000       6.372519319000       7.134776469000
31 C      -4.909268934000       7.308278958000       6.920541205000
32 C      -5.228993453000       7.303987812000       5.521191718000
33 C      -4.359085304000       6.366133776000       4.870956824000
34 C      -3.502271495000       5.791510196000       5.869525511000
35 Fe      -3.237469872000       7.860832058000       5.796173166000
36 B       1.311278779000       7.885709244000      11.656264830000
37 H      -3.151510822000      10.365149690000       7.140316996000
38 H      -3.786728784000      10.349421590000       4.519109473000
39 H      -2.144881794000       8.590429776000       3.263634708000
40 H      -0.485873698000       7.528444581000       5.107647382000
41 H       0.142882599300       6.792518929000       7.173710709000
42 H       1.369429568000       6.417855781000       9.273511421000
43 H      -0.532089841100       9.871445024000      11.008169250000
44 H      -1.702348638000      10.296997410000       8.887579385000
45 H       3.883224399000       4.114635020000      13.023007260000
46 H       5.667353034000       6.680103395000      10.078675990000
47 H       4.161779163000       8.297511417000       8.912521135000
48 H       4.496475318000       9.248106723000      10.366062530000
49 H       2.823306393000       9.030550542000       9.818141630000
50 H       6.931529212000       4.808770619000      10.878126280000
51 H       6.514544868000       4.157640769000      12.479941670000
52 H       5.861002437000       3.399308641000      11.020963000000
53 H       1.885870776000       4.539216718000      13.980459520000
54 H       1.366493935000       6.237979125000      14.108208260000
55 H       0.679314479800       5.193755622000      12.857456620000
56 H       1.764711233000      10.844868130000      15.363255130000
57 H      -1.999057890000       8.813845713000      14.987111880000
58 H      -1.471523385000       6.403937248000      13.458017410000
59 H      -1.204554894000       7.068994846000      11.836065160000
60 H      -2.511076114000       7.704233915000      12.859166930000
61 H      -1.575226963000      10.158579500000      16.967466620000
62 H       0.074342574750      10.727915700000      17.317007100000
63 H      -0.993200220600      11.687273240000      16.281025840000
64 H       3.494468390000      10.507112100000      13.959790860000
65 H       3.633857841000       8.906629633000      13.191155290000
66 H       3.024928662000      10.283401530000      12.264350410000
67 H      -3.359040456000       6.165059968000       8.085253527000
68 H      -5.383631782000       7.920790492000       7.683102306000
69 H      -5.988467560000       7.912063604000       5.036009504000
70 H      -4.344958445000       6.137851560000       3.808089216000
71 H      -2.726093766000       5.050397915000       5.695850796000
END
```

```
GUIBONDS
1 1 37 1.0
2 1 2 1.0
3 1 5 1.0
4 1 35 1.0
5 2 38 1.0
6 2 3 1.0
7 2 35 1.0
8 3 39 1.0
9 3 4 1.0
10 3 35 1.0
11 4 40 1.0
12 4 5 1.0
13 4 35 1.0
14 5 6 1.0
15 5 35 1.0
16 6 11 1.5
17 6 7 1.5
18 7 41 1.0
19 7 8 1.5
20 8 42 1.0
21 8 9 1.5
```

```
22 9 10 1.5
23 9 36 1.0
24 10 43 1.0
25 10 11 1.5
26 11 44 1.0
27 12 13 1.5
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83 30 34 1.0
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BASIS
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core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
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SAVE  TAPE21 TAPE13

SCF
iterations 500
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor


# ==============================
# Compound 5a
# ==============================

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4 C       6.135087586000       6.870127480000       2.435294326000
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6 C       4.798836701000       7.172008516000       2.133946569000
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12 C       8.552276831000       6.099209346000       5.355075098000
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14 C       9.991218456000       7.997268442000       6.338786126000
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17 C       9.602941902000       3.670307628000       8.846535549000
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19 C       8.008819324000       4.791879331000       5.544696664000
20 C       7.086958068000       4.145424909000       4.533232766000
21 C       9.670905048000      12.534580890000       2.582144833000
22 C       9.552988229000      11.769062240000       3.791340876000
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33 C       8.265972291000       9.403563390000       1.766403855000
34 C       9.302174385000       8.463110429000       2.122342864000
35 H       6.259227634000       5.507540261000       0.759939446000
36 H       7.484589203000       6.791494668000       0.744534528900
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38 H       4.383594254000       6.824194391000       1.183145931000
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END

BASIS
type TZP
core Large
createoutput None
END

XC
GGA Becke Perdew
END


GEOMETRY
    optim Delocalized
END

SAVE  TAPE21 TAPE13

SCF
diis
END

FULLSCF
INTEGRATION 6

NoBeckeGrid
NOPRINT LOGFILE

eor
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7. Crystallographic data

2a: $C_{34}H_{35}FeB$, M_r = 510.31, triclinic, P-1, a = 7.45110(10) Å, b = 11.4935(2) Å, c = 16.8162(3) Å, α = 71.4209(8)°, β = 83.5154(8)°, γ = 77.8551(8) °, V = 1332.88(4) Å^3, Z = 2, T = 150 K, λ = 0.71073 Å. 35607 reflections collected, 6037 independent [R(int) = 0.034] used in all calculations, with 371 refined parameters, GOF on F² = 0.9279. R_1 = 0.0454, wR_2 = 0.0934 for observed unique reflections [I>2σ(I)] and R_1 = 0.0659, wR_2 = 0.1126 for all unique reflections. Max. and min. residual electron densities 0.53 and -0.54 e Å^{-3}. CCDC reference: 1063454.

2b: $C_{34}H_{35}FeB$, M_r = 510.31, triclinic, P-1, a = 14.1028(3) Å, b = 14.4095(3) Å, c = 15.1800(3) Å, α = 67.3715(9)°, β = 70.3692(8)°, γ = 82.3985(11)°, V = 2681.81(10) Å^3, Z = 4, T = 150 K, λ = 0.71073 Å. 17351 reflections collected, 10379 independent [R(int) = 0.029] used in all calculations, with 649 refined parameters, GOF on F² = 0.9344. R_1 = 0.0424, wR_2 = 0.0862 for observed unique reflections [I>2σ(I)] and R_1 = 0.0615, wR_2 = 0.1000 for all unique reflections. Max. and min. residual electron densities 0.58 and -0.59 e Å^{-3}. CCDC reference: 1063455.

2c: $C_{34}H_{35}FeB$, M_r = 510.31, monoclinic, $P2_1/c$, a = 8.11722(6) Å, b = 11.63718(10) Å, c = 28.9944(2) Å, β = 94.5040(7)°, V = 2730.39(4) Å^3, Z = 4, T = 150 K, λ = 0.71073 Å. 24937 reflections collected, 5696 independent [R(int) = 0.025] used in all calculations, with 371 refined parameters, GOF on F² = 0.9140. R_1 = 0.0319, wR_2 = 0.0712 for observed unique reflections [I>2σ(I)] and R_1 = 0.0344, wR_2 = 0.0742 for all unique reflections. Max. and min. residual electron densities 0.29 and -0.33 e Å^{-3}. CCDC reference: 1063456.

[^{n}Bu$_4$N][**2a**$^-$F]: $C_{50}H_{69}BFFeN$, M_r = 769.76, trigonal, $P3_2$, a = 12.32960(10) Å, b = 12.32960(10) Å, c = 24.7600(3) Å, V = 3259.71(5) Å^3, Z = 3, T = 150 K, λ = 1.54180 Å. 6661 reflections collected, 6661 independent [R(int) = 0.028] used in all calculations, with 533 refined parameters, GOF on F² = 0.9938. R_1 = 0.0341, wR_2 = 0.0885 for observed unique reflections [I>2σ(I)] and R_1 = 0.0354, wR_2 = 0.0926 for all unique reflections. Max. and min. residual electron densities 0.33 and -0.33 e Å^{-3}. CCDC reference: 1063452.

[^{n}Bu$_4$N][**2b**$^-$F]: $C_{50}H_{71}BFFeN$, M_r = 771.78, triclinic, P1, *a* = 11.3315(4) Å, *b* = 11.9625(3) Å, *c* = 18.7698(5) Å, α = 77.888(2)°, β = 74.092(3)°, γ = 64.932(3)°, *V* = 2203.53(13) Å^3, *Z* = 2, *T* = 150 K, λ = 1.54180 Å. 28111 reflections collected, 9133 independent [R(int) = 0.056] used in all calculations, with 1001 refined parameters, GOF on F² = 0.9838. R_1 = 0.0552, wR_2 = 0.1493 for observed unique reflections [*I*>2σ(I)] and R_1 = 0.0589, wR_2 = 0.1538 for all unique reflections. Max. and min. residual electron densities 0.64 and -0.79 e Å^{-3}. CCDC reference: 1063453.

[K(18-crown-6)][**2b**$^-$CN]$^-$MeCN: $C_{49}H_{62}BFeKN_2O_6$, M_r = 880.80, triclinic, P-1, a = 13.0828(2) Å, b = 14.7366(2) Å, c = 14.9552(3) Å, α = 60.8147(7)°, β = 72.4211(7)°, γ = 69.3532(9)°, V = 2325.53(7) Å^3, Z = 2, T = 150 K, λ = 0.71073 Å. 111266 reflections collected, 10571 independent [R(int) = 0.029] used in all calculations, with 704 refined parameters, GOF on F² = 0.9555. R_1 = 0.0459, wR_2 = 0.0938 for observed unique reflections [I>2σ(I)] and R_1 = 0.0755, wR_2 = 0.1215 for all unique reflections. Max. and min. residual electron densities 0.67 and -0.60 e Å^{-3}. CCDC reference: 1063450.

[K(18-crown-6)][**2c**$^-$CN]$^-$3CHCl$_3$: $C_{50}H_{62}BCl_9FeKNO_6$, M_r = 2395.30, triclinic, P-1, a = 11.55760(10) Å, b = 12.45330(10) Å, c = 20.8917(3) Å, α = 103.3893(4)°, β = 90.8717(4)°, γ = 101.9001(4)°, V = 2856.08(5) Å^3, Z = 2, T = 150 K, λ = 0.71073 Å. 72790 reflections collected, 12945 independent [R(int) = 0.025] used in all calculations, with 784 refined parameters, GOF on F² = 0.9123. R_1 = 0.0683, wR_2 = 0.1473

for observed unique reflections [I>2σ(I)] and R_1 = 0.0918, wR_2 = 0.1720 for all unique reflections. Max. and min. residual electron densities 1.57 and -1.37 e $Å^{-3}$. CCDC reference: 1063451.

[Cs(18-crown-6][**5b**$^{\cdot}$F]$^{\cdot}$2CH_3CN: $C_{48}H_{63}BCsFFeN_2O_6$, M_r = 982.60, Triclinic, P-1, a = 10.70690(10) Å, b = 14.1228(2) Å, c = 17.6276(3) Å, α = 98.9703(6)°, β = 105.8289(7)°, γ = 105.9933(6)°, V = 2386.97(6) $Å^3$, Z = 2, T = 150 K, λ = 0.71073 Å. 105726 reflections collected, 10840 independent [R(int) = 0.039] used in all calculations, with 541 refined parameters, GOF on F^2 = 0.9522. R_1 = 0.0432, wR_2 = 0.0889 for observed unique reflections [I>2σ(I)] and R_1 = 0.0724, wR_2 = 0.1167 for all unique reflections. Max. and min. residual electron densities 1.71 and -1.69 e $Å^{-3}$. CCDC reference: 1063449.

8. References for supporting information

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s4 G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C.F. Guerra, S.J.A. Van Gisbergen, J.G. Snijders and T. Ziegler, *J. Comput. Chem.,* 2001, **22**, 931.

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