Electronic Supplementary Information for

Halogen bonding-enhanced electrochemical halide anion sensing by redox-active ferrocene receptors

Jason Y.C. Lim[a] , Matthew J. Cunningham[b], Jason J. Davis[b] and Paul D. Beer*[a]

[a] Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford, OX1 3TA, UK.
[b] Physical & Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3TA (UK).

E-mail: paul.beer@chem.ox.ac.uk

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S1. Experimental

S1.1 General Information

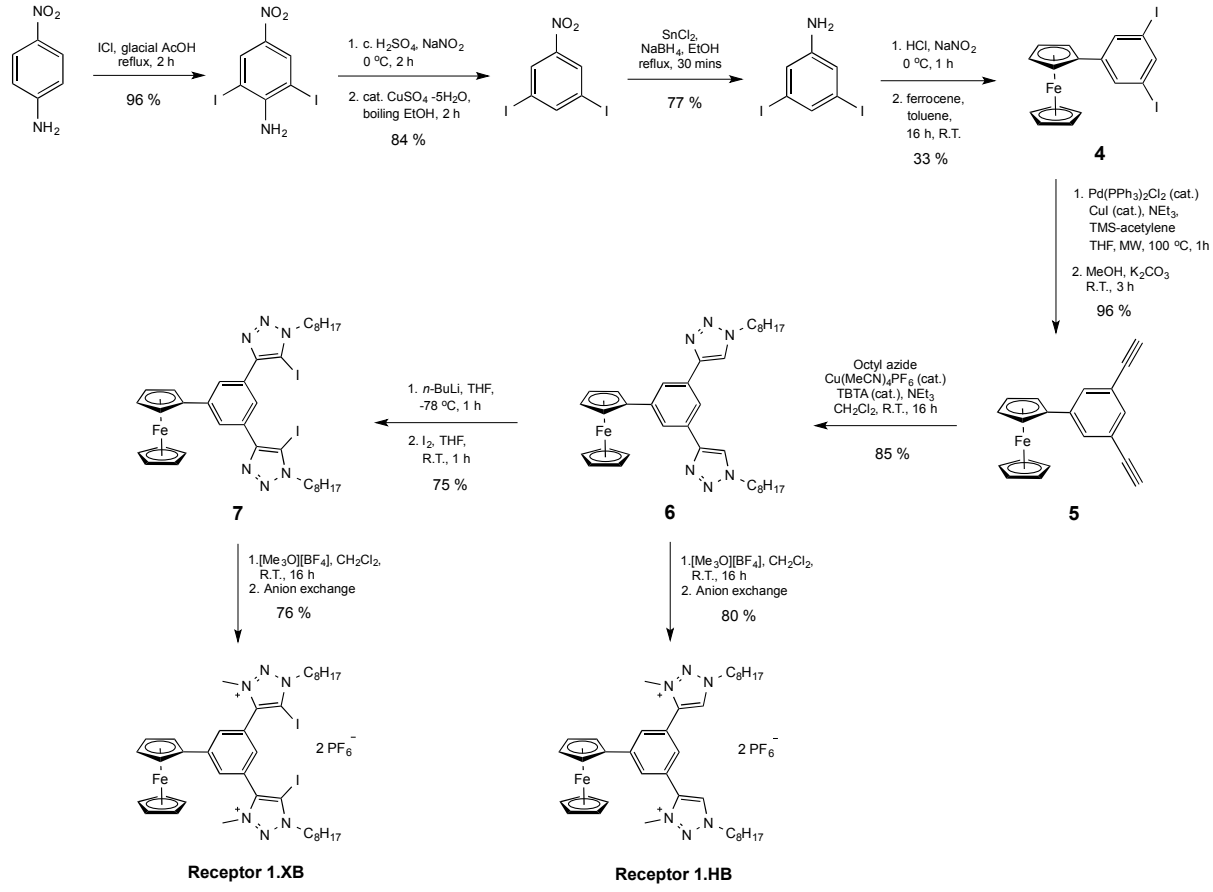
All commercially available chemicals and solvents were used as received without further purification. All dry solvents were thoroughly degassed with N_2, dried through a Mbraun MPSP-800 column and used immediately. Water used was deionized and passed through a Milli-Q® Millipore machine for microfiltration. TBTA (tris(benzyltriazolemethyl)amine) was prepared according to reported procedures.[1] Amberlite® was prepared by washing the commercial resin beads sequentially with 10 % NaOH (aq), water, 0.1 M NH_4PF_6 (aq), further water, and finally loaded with 0.1 M NH_4NO_3 (aq) before any anion exchange to the nitrate salt occurred.

NMR spectra were recorded on Bruker AVIII HD Nanobay 400 MHz, Bruker AVIII 500 MHz and Bruker AVIII 500 MHz (with ^{13}C cryoprobe) spectrometers. Low resolution electrospray ionisation mass spectrometry (ESI-MS) was performed using the Waters Micromass LCT for characterisation of compounds previously reported in the literature, and high resolution ESI-MS was recorded using Bruker microTOF spectrometer for novel compounds.

S1.2 Synthetic Procedures

S1.2.1 Synthesis of dicationic ferrocene-aryl receptors 1.HB and 1.XB

Overview of complete synthetic scheme:



3,5-diiodo-4-nitroaniline,[2] 3,5-diiodonitrobenzene[3] and 3,5-diiodoaniline[3] were synthesised following literature procedures. Starting from 5.0 g of para-nitroaniline, 7.8 g of 3,5-diiodoaniline (62 % overall yield over 3 steps) was obtained.

1-ferrocene-3,5-diiodobenzene **4**

To a slurry of 3,5-diiodoaniline (400 mg, 1.16 mmol) in 5 M HCl (3 mL) chilled to 0 °C was added a solution of sodium nitrite (176 mg, 2.55 mmol) in water (2 mL) dropwise over 5 minutes. The reaction was stirred for 1 hour at 0 °C till no further gas evolution occurred to form an orange-brown suspension of the diazonium salt. Separately, ferrocene (259 mg, 1.39 mmol) was dissolved in toluene (5 mL) and chilled to 0 °C, before the suspension of diazonium salt was added dropwise over 5 minutes. After stirring for 15 minutes at 0 °C, the reaction was warmed up to ambient temperature and stirred under N_2 for 16 hours. The reaction was then cooled to 0 °C again and aqueous saturated sodium bicarbonate was added dropwise to the reaction till a neutral pH was attained. Chloroform (10 mL) was then added and the organic and aqueous layers separated. The aqueous layer was extracted with chloroform (4 x 15 mL), and the combined organics were dried with brine, then $MgSO_4$. After removal of solvent, silica gel column chromatography (5 % EtOAc in hexane) yielded an orange solid, which was then further purified by recrystallisation (c.a. 10 mL of hexane with a minimal quantity of CH_2Cl_2) to give the product as orange crystals (194 mg, 33 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.85 (1H, s, Ar*H*), 7.74 (2H, s, Ar*H*), 4.59 (2H, m, Fc*H*), 4.36 (2H, m, Fc*H*), 4.08 (5H, s, Fc*H*); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 144.3, 142.1, 134.1, 94.9, 81.9, 69.8, 69.7, 66.6; **MS** (EI +ve) *m/z* 513.8372 ($[M]^+$, $C_{16}H_{12}FeI_2$, calc. 513.8372).

1-ferrocene-3,5-di(ethynyl)benzene **5**

Copper(I) iodide (14.8 mg, 0.078 mmol), bis(triphenylphosphine)palladium(II) chloride (27 mg, 0.038 mmol) and compound **4** (400 mg, 0.778 mmol) were mixed in a microwave vial and dissolved in dry degassed THF (2 mL). Dry triethylamine (1.09 mL, 7.78 mmol) and ethynyltrimethylsilane (0.33 mL, 2.3 mmol) were then added portionwise and the mixture briefly degassed with N_2 for 1 minute. The microwave vial was then sealed and the reaction reacted in the microwave for 1 hour at 100 °C. Upon cooling to ambient temperature, the crude reaction mixture was filtered through celite (washed with CH_2Cl_2), and solvent removed to give an orange solid. Silica gel chromatography (hexane) isolated the trimethylsilyl-protected bis-alkyne as orange crystals (342 mg). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.49 (2H, s, Ar*H*), 7.43 (1H, s, Ar*H*), 4.65 (2H, m, Fc*H*), 4.34 (2H, m, Fc*H*), 4.06 (5H, s, Fc*H*), 0.28 (18H, s, TMS); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 140.1, 133.0, 129.0, 123.4, 104.4, 94.6, 83.2, 69.7, 69.4, 66.5, 0.00; **MS** (EI +ve) *m/z* 454.1215 ($[M]^+$, $C_{26}H_{30}FeSi_2$, calc. 454.1230).

The orange crystals were then dissolved in a 1:1 mixture of CH_2Cl_2 and methanol (10 mL) and anhydrous potassium carbonate (540 mg, 3.91 mmol) was added portionwise. The reaction was stirred under N_2 for 5 hours. Following which, water (10 mL) was added and the aqueous layer was extracted with chloroform (2 x 10 mL). The combined organics were dried with $MgSO_4$ and solvent was removed *in vacuo* to afford the desired product **5** in good purity (231 mg, 96 % overall yield) without the need for further purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.57 (2H, s, Ar*H*), 7.45 (1H, s, Ar*H*),

4.65 (2H, m, Fc*H*), 4.36 (2H, m, Fc*H*), 4.07 (5H, s, Fc*H*), 3.11 (2H, s, ethyne-*H*); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 140.5, 132.9, 129.8, 122.5, 83.0, 82.8, 69.8, 69.5, 68.6, 66.5; **MS** (EI +ve) *m/z* 310.0436 ($[M]^+$, $C_{20}H_{14}Fe$, calc. 310.0440).

Bis(prototriazole) receptor precursor **6**

Octyl azide (40.1 mg, 0.258 mmol) and bis-alkyne **5** (40 mg, 0.13 mmol) were dissolved in degassed CH_2Cl_2 (1.5 mL), followed by TBTA (13.7 mg , 0.026 mmol), $Cu(MeCN)_4PF_6$ (24 mg, 0.065 mmol) and triethylamine (0.09 mL, 0.52 mmol). The reaction was stirred under N_2 for 16 h before 10 % aqueous ammonia (10 mL) was added, followed by chloroform (10 mL). The organic layer was separated from the aqueous layer, which was extracted with chloroform (2 x 10 mL). The combined organics was washed with 1 M HCl, and dried with brine and $MgSO_4$. Purification of the crude reaction mixture by silica gel chromatography (2 % MeOH in CH_2Cl_2) to afford an sticky orange solid (68 mg, 85 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.06 (1H, s, Ar*H*), 7.98 (2H, s, Ar*H*), 7.89 (2H, s, triazole*H*), 4.80 (2H, m, Fc*H*), 4.43 (4H, t, ^3J = 7.2 Hz, alkyl-*H*), 4.36 (2H, m, Fc*H*), 4.08 (5H, s, Fc*H*), 1.98 (4H, quintet, ^3J = 6.8 Hz, alkyl-*H*), 1.28-1.37 (20H, m, alkyl-*H*), 0.88 (6H, t, ^3J = 6.8 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 147.5, 140.9, 131.3, 122.8, 120.5, 119.8, 84.5, 69.7, 69.2, 66.7, 50.5, 31.7, 30.2, 29.1, 29.0, 26.5, 22.6, 14.1; **MS** (ESI +ve) *m/z* 621.3360 ($[M + H]^+$, $C_{36}H_{49}FeN_6$, calc. 621.3363).

Bis(iodotriazole) receptor precursor **7**

To a solution of compound **6** (33 mg, 0.053 mmol) in dry THF chilled to -78 ^{o}C was added a 2.5 M solution of *n*-butyllithium in hexane (0.08 mL, 0.212 mmol) under N_2 to afford an intense dark blue solution. After stirring the reaction at -78 ^{o}C for 1 hour, a solution of iodine (54 mg, 0.212 mmol) in dry THF (1 mL) was added dropwise and the reaction was allowed to gradually warm up to ambient temperature and stirred for a further 1 hour. The solvent was then removed *in vacuo* and chloroform (10 mL) was added to the resultant orange paste. The solution was washed successively with saturated sodium thiosulfate (10 mL) and water (10 mL), then dried with brine (10 mL) and $MgSO_4$. Purification of the crude product by silica gel chromatography (20 % EtOAc in hexanes) afforded compound **7** as an orange solid (35 mg, 75 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.38 (1H, s, Ar*H*), 8.12 (2H, s, Ar*H*), 4.80 (2H, m, Fc*H*), 4.48 (4H, t, ^3J = 7.2 Hz, alkyl-*H*), 4.37 (2H, m, Fc*H*), 4.12 (5H, s, Fc*H*), 1.99 (4H, quintet, ^3J = 6.8 Hz, alkyl-*H*), 1.26-1.41 (20H, m, alkyl-*H*), 0.87 (6H, t, ^3J = 6.8 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.4, 140.4, 130.7, 125.2, 123.8, 84.5, 76.5, 69.7, 69.2, 66.8, 51.1, 31.8, 30.0, 29.1, 29.0, 26.5, 22.6, 14.1; **MS** (ESI +ve) *m/z* 873.1267 ($[M + H]^+$, $C_{36}H_{47}FeN_6I_2$, calc. 873.1296).

Receptor **1.HB**

Precursor compound **6** (46 mg, 0.074 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and trimethyloxonium tetrafluoroborate (24 mg, 0.16 mmol) was added portionwise. The reaction was stirred under N_2 overnight before methanol (1 mL) was added. The solvent was removed *in vacuo* to yield an orange solid which was purified by preparatory thin layer chromatography (5 % MeOH in CH_2Cl_2). Anion exchange of the purified product to the $2PF_6^-$ salt was achieved by washing a chlorofom solution of the product with 0.1 M NH_4PF_6 (10 x 20 mL). Solvent removal then afforded the

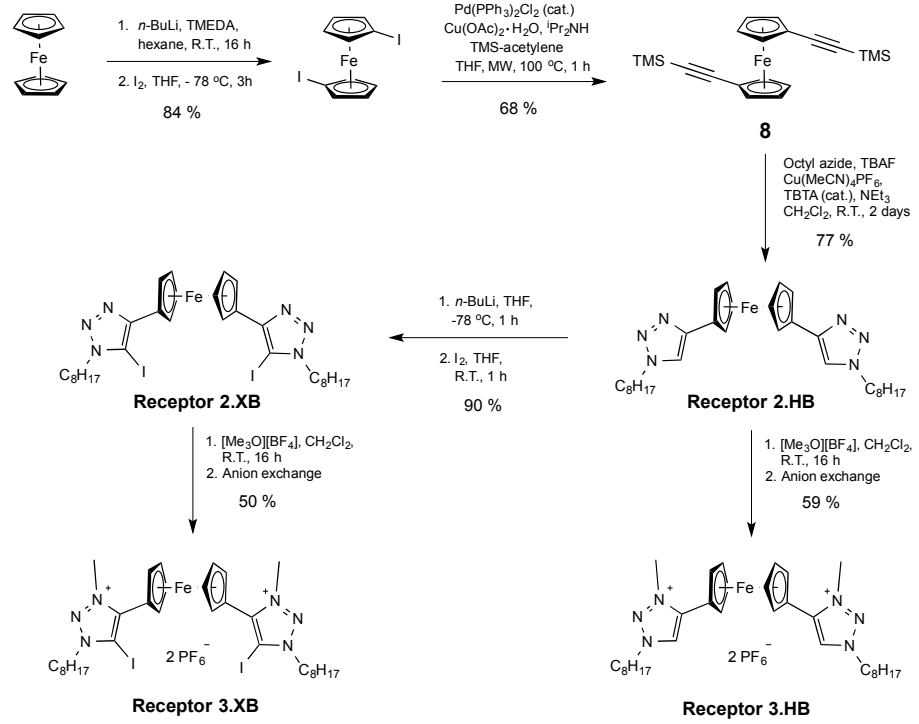
receptor **1.HB** as an orange solid (56 mg, 80 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.37 (2H, s, triazolium-*H*), 7.74 (2H, s, Ar*H*), 7.51 (1H, s, Ar*H*), 4.74 (2H, m, Fc*H*), 4.49 (4H, t, ^3J = 7.2 Hz, alkyl-*H*), 4.33 (2H, m, Fc*H*), 4.18 (6H, s, triazolium-CH_3), 3.99 (5H, s, Fc*H*), 2.05 (4H, quintet, ^3J = 6.8 Hz, alkyl-*H*), 1.26-1.35 (20H, m, alkyl-*H*), 0.90 (6H, t, ^3J = 6.8 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 144.3, 141.9, 128.8, 128.7, 126.5, 123.7, 80.8, 70.5, 70.1, 66.8, 54.4, 38.6, 31.7, 29.0, 28.9, 28.8, 26.2, 22.6, 14.1; **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -72.6 (d, J = 696 Hz); **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -144.7 (sept., J = 716 Hz); **MS** (ESI +ve) *m/z* 325.1870 ($[M]^{2+}$, $C_{38}H_{54}FeN_6$, calc. 325.1874).

Receptor **1.XB**

Precursor compound **7** (31 mg, 0.036 mmol) was dissolved in dry CH_2Cl_2 (1 mL) and trimethyloxonium tetrafluoroborate (12 mg, 0.079 mmol) was added portionwise. The reaction was stirred under N_2 overnight before methanol (1 mL) was added. After removal of solvent *in vacuo*, the crude product was purified by preparatory thin layer chromatography (2 % MeOH in CH_2Cl_2). Anion exchange of the purified product to the $2PF_6^-$ salt was achieved by washing a chlorofom solution of the product with 0.1 M NH_4PF_6 (10 x 20 mL). Solvent removal then afforded the receptor **1.XB** as an orange solid (32 mg, 76 %). **^{1}H-NMR** (400 MHz, d_4-MeOD) δ 8.08 (2H, s, Ar*H*), 7.64 (1H, s, Ar*H*), 4.96 (2H, m, Fc*H*), 4.71 (4H, t, ^3J = 7.2 Hz, alkyl-*H*), 4.51 (2H, m, Fc*H*), 4.31 (6H, s, triazolium-CH_3), 4.16 (5H, s, Fc*H*), 2.09 (4H, quintet, ^3J = 6.8 Hz, alkyl-*H*), 1.296-1.55 (20H, m, alkyl-*H*), 0.92 (6H, t, ^3J = 6.8 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, d_4-MeOD) δ 145.7, 144.4, 130.0, 127.8, 124.8, 90.7, 81.0, 70.3, 69.7, 66.7, 54.7, 38.4, 31.5, 28.8, 28.7, 28.6, 26.0, 22.3, 13.0; **^{19}F-NMR** (376 MHz, d_4-MeOD) δ -74.4 (d, J = 726 Hz); **^{31}P-NMR** (162 MHz, d_4-MeOD) δ -144.8 (sept., J = 709 Hz); **MS** (ESI +ve) *m/z* 451.0841 ($[M]^{2+}$, $C_{38}H_{52}FeN_6I_2$, calc. 451.0841).

S1.4.2 Synthesis of 1,1'-ferrocene receptors 2a, 2b, 3a and 3b.

Overview of complete synthetic route:



1,1'-diiodoferrocene was synthesised according to a literature procedure.[4]

1,1'-bis(trimethylsilylethynyl)ferrocene

Procedure was modified from an earlier reported method.[5]

1,1'-diiodoferrocene (1.50 g, 3.43 mmol) was dissolved in diisopropylamine (15 mL) in a microwave vial before bis(triphenylphosphine)palladium(II) chloride (241 mg, 0.343 mmol) and copper(II) acetate monohydrate (68.5 mg, 0.343 mmol) was added. The mixture was degassed with N_2 for 5 minutes, following which, ethynyltrimethylsilane (1.45 mL, 10.29 mmol) was added. The reaction was then reacted in the microwave at 105 ^oC for 1 h 15 minutes. After cooling to room temperature, hexane (10 mL) was added and the crude reaction mixture filtered through celite and washed with hexane. Following successive washes with 1 M HCl (2 x 20 mL) and water (20 mL), the organic layer was dried with brine and $MgSO_4$. Solvent removal *in vacuo* gave a red oil, which was purified by silica gel chromatography (hexane) to yield the produce as a red crystalline solid (884 mg, 68 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.41 (4H, m, Fc*H*), 4.22 (4H, m, Fc*H*), 0.24 (18H, s, -Si(CH_3)$_3$); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 103.1, 91.0, 73.5, 71.3, 65.7, 0.00; **MS** (ESI +ve) *m/z* 379.12 ([M + H]$^+$, $C_{20}H_{27}FeSi_2$, calc. 379.10).

Receptor **2.HB**

1,1'-bis(trimethylsilylethynyl)ferrocene (100 mg, 0.264 mmol), $Cu(MeCN)_4PF_6$ (197 mg, 0.528 mmol) and TBTA (28 mg, 0.053 mmol) and octyl azide (86 mg, 0.55 mmol) were dissolved in dry degassed THF. To this mixture was added tetrabutylammonium fluoride (207 mg, 0.792 mmol) and dry triethylamine (0.15 mL, 1.06 mmol) portionwise. The reaction was then left to stir in the dark under N_2 for 2 days. Following which, chloroform (10 mL) was added to the reaction, which was washed successively with 10 % aqueous ammonia (2 x 10 mL) and water (10 mL). After drying the organic phase with brine and $MgSO_4$, silica gel chromatography of the crude reaction mixture yielded receptor **2.HB** as an orange solid (111 mg, 77 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.28 (2H, s, triazole-*H*), 4.64 (4H, m, Fc*H*), 4.27 (4H, t, ^3J = 7.2 Hz, alkyl-*H*), 4.25 (4H, m, Fc*H*), 1.87 (4H, quintet, ^3J = 6.8 Hz, alkyl-*H*), 1.27-1.32 (20H, m, alkyl-*H*), 0.88 (6H, t, ^3J = 6.8 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 144.5, 119.4, 70.1, 69.4, 67.4, 50.2, 31.7, 30.2, 29.1, 24.0, 26.5, 22.6, 14.1; **MS** (ESI +ve) *m/z* 545.3039 ([M + H]$^+$, $C_{30}H_{45}FeN_6$, calc. 545.3050).

Receptor **2.XB**

To a solution of receptor compound **2.HB** (59 mg, 0.108 mmol) in dry THF (7 mL) chilled to -78 ^oC was added a 2.5 M solution of *n*-butyllithium in hexane (0.13 mL, 0.324 mmol) under N_2. After stirring the reaction at -78 ^oC for 30 minutes, a solution of iodine (82 mg, 0.324 mmol) in dry THF (1 mL) was added dropwise and the reaction was allowed to gradually warm up to ambient temperature and stirred for a further 30 minutes. After solvent removal *in vacuo*, chloroform (10 mL) was added and the organic phase was washed successively with saturated sodium thiosulfate (10 mL) and water (10 mL), then dried with brine (10 mL) and $MgSO_4$. Purification of the crude product by preparatory TLC (2 % MeOH in CH_2Cl_2) afforded receptor **2.XB** as an orange solid (77 mg, 90 %). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 5.08 (4H, m, Fc*H*), 4.35 (4H, t, ^3J = 7.6 Hz, alkyl-*H*), 4.30 (4H, m, Fc*H*), 1.92 (4H, quintet,

^3J = 7.2 Hz, alkyl-*H*), 1.27-1.36 (20H, m, alkyl-*H*), 0.89 (6H, t, ^3J = 7.0 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 148.0, 76.0, 74.5, 70.4, 68.0, 50.6, 31.7, 29.8, 29.1, 29.0, 26.5, 22.6, 14.1; **MS** (ESI +ve) *m/z* 797.0967 ($[M + H]^+$, $C_{30}H_{43}FeN_6I_2$, calc. 797.0982).

Receptor **3.HB**

Note: Due to slight product instability in the presence of light, the reaction, purification and anion exchange were performed under reduced lighting conditions. The product was stored under N_2 in the freezer in the dark after synthesis.

Receptor compound **2.HB** (40 mg, 0.073 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and trimethyloxonium tetrafluoroborate (24 mg, 0.16 mmol) was added portionwise. The reaction was stirred under N_2 overnight before methanol (1 mL) was added. The solvent was removed *in vacuo* to yield an orange solid which was purified by preparatory thin layer chromatography (8 % MeOH in CH_2Cl_2). Anion exchange of the purified product to the $2PF_6^-$ salt was achieved by washing a chlorofom solution of the product with 0.1 M NH_4PF_6 (10 x 20 mL). Solvent removal then afforded the receptor **3.HB** as an orange solid (37 mg, 59 %). **^{1}H-NMR** (400 MHz, d_3-MeCN) δ 8.39 (2H, s, triazolium-*H*), 4.92 (4H, m, Fc*H*), 4.66 (2H, m, Fc*H*), 4.53 (4H, t, ^3J = 7.6 Hz, alkyl-*H*), 4.19 (6H, s, triazolium-CH_3), 2.00 (4H, quintet, ^3J = 7.0 Hz, alkyl-*H*), 1.31-1.39 (20H, m, alkyl-*H*), 0.90 (6H, t, ^3J = 7 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, d_3-MeCN) δ 142.8, 128.2, 74.6, 71.2, 68.5, 54.4, 39.5, 32.0, 29.4, 29.3, 29.1, 26.2, 22.9, 14.0; **^{19}F-NMR** (376 MHz, d_3-MeCN) δ -72.8 (d, J = 718 Hz); **^{31}P-NMR** (162 MHz, d_3-MeCN) δ -144.6 (sept., J = 706 Hz); **MS** (ESI +ve) *m/z* 287.1713 ($[M]^{2+}$, $C_{32}H_{50}FeN_6$, calc. 287.1718).

Receptor **3.XB**

Note: Due to slight product instability in the presence of light, the reaction, purification and anion exchange were performed under reduced lighting conditions. The product was stored under N_2 in the freezer in the dark after synthesis.

Receptor compound **2.XB** (40 mg, 0.050 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and trimethyloxonium tetrafluoroborate (16 mg, 0.11 mmol) was added portionwise. The reaction was stirred under N_2 overnight before methanol (1 mL) was added. The solvent was removed *in vacuo* to yield an orange solid which was purified by preparatory thin layer chromatography (8 % MeOH in CH_2Cl_2). Anion exchange of the purified product to the $2PF_6^-$ salt was achieved by washing a chlorofom solution of the product with 0.1 M NH_4PF_6 (10 x 20 mL). Solvent removal then afforded the receptor **3.XB** as an orange solid (28 mg, 50 %). **^{1}H-NMR** (400 MHz, d_6-acetone) δ 5.40 (4H, m, Fc*H*), 4.97 (2H, m, Fc*H*), 4.77 (4H, t, ^3J = 7.4 Hz, alkyl-*H*), 4.19 (6H, s, triazolium-CH_3), 2.09 (4H, quintet, ^3J = 7.2 Hz, alkyl-*H*), 1.29-1.52 (20H, m, alkyl-*H*), 0.88 (6H, t, ^3J = 6.8 Hz, alkyl-CH_3); **^{13}C-NMR** (100 MHz, d_6-acetone) δ 144.9, 141.3, 113.3, 87.3, 73.9, 71.2, 69.0, 54.9, 40.0, 31.6, 25.8, 22.4, 13.4; **^{19}F-NMR** (376 MHz, d_6-acetone) δ -72.8 (d, J = 708 Hz); **^{31}P-NMR** (162 MHz, d_6-acetone) δ -144.4 (sept., J = 708 Hz); **MS** (ESI +ve) *m/z* 287.1713 ($[M]^{2+}$, $C_{32}H_{50}FeN_6$, calc. 287.1718).

S2. Spectral Characterisation of Novel Redox-active Receptors

Receptor **1.XB**

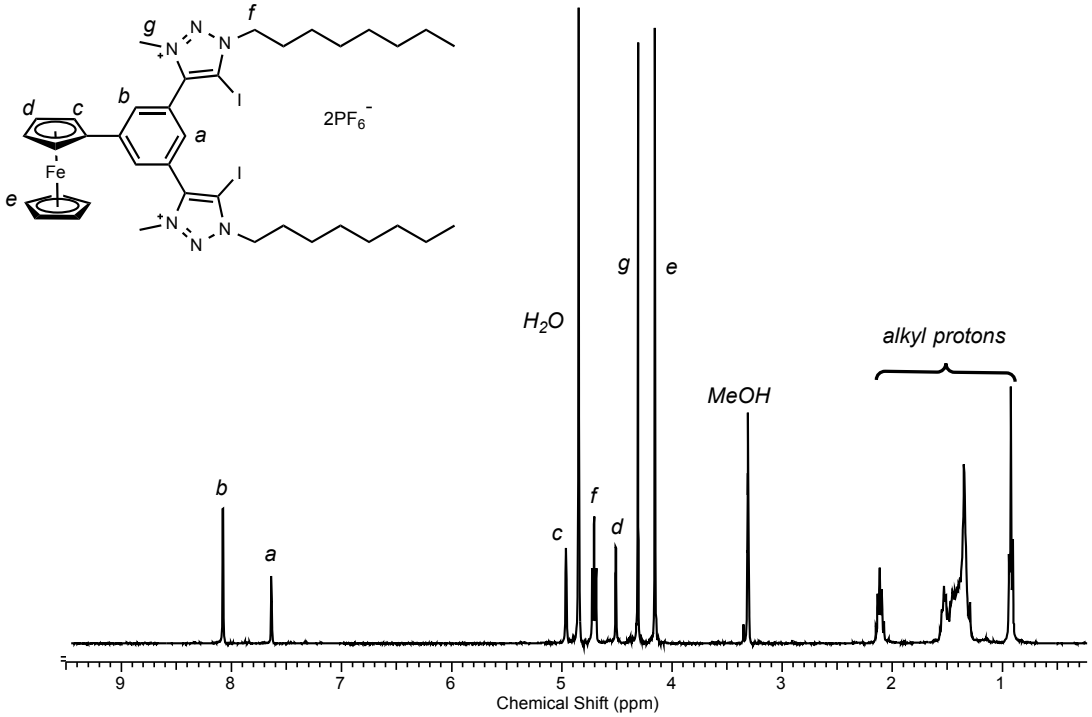


Fig S2-1. ^{1}H NMR of receptor **1.XB** in $CDCl_3$ at 298 K (400 MHz).

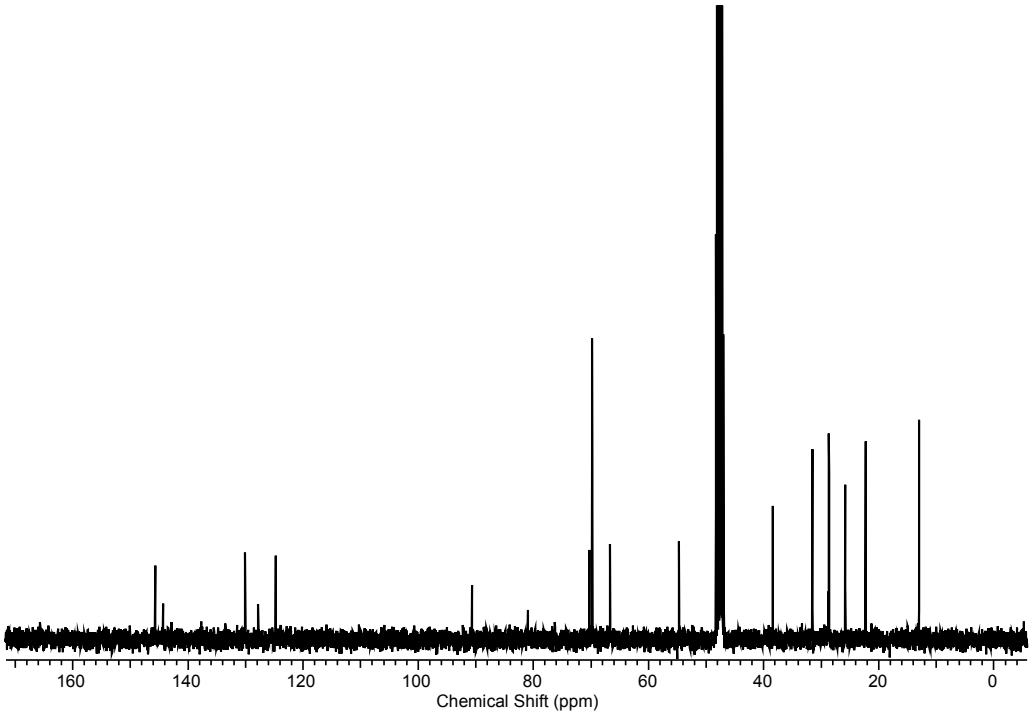


Fig S2-2. ^{13}C NMR of receptor **1.XB** in $CDCl_3$ at 298 K (100 MHz).

Receptor **1.HB**

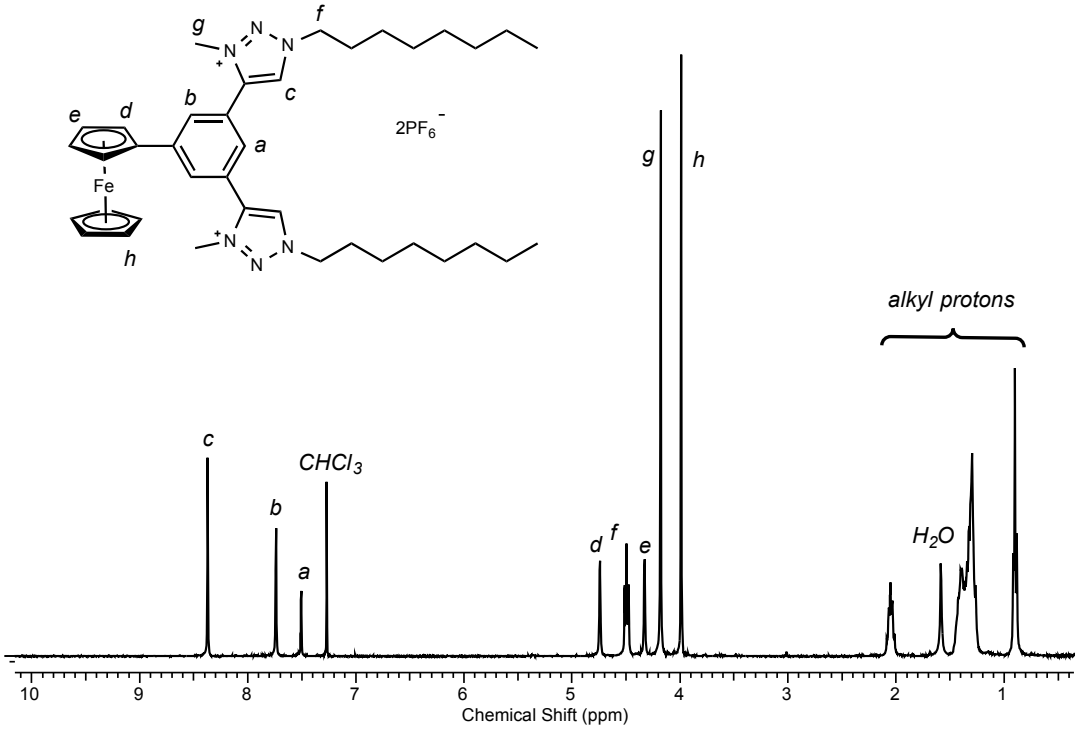


Fig S2-3. ^{1}H NMR of receptor **1.HB** in $CDCl_3$ at 298 K (400 MHz).

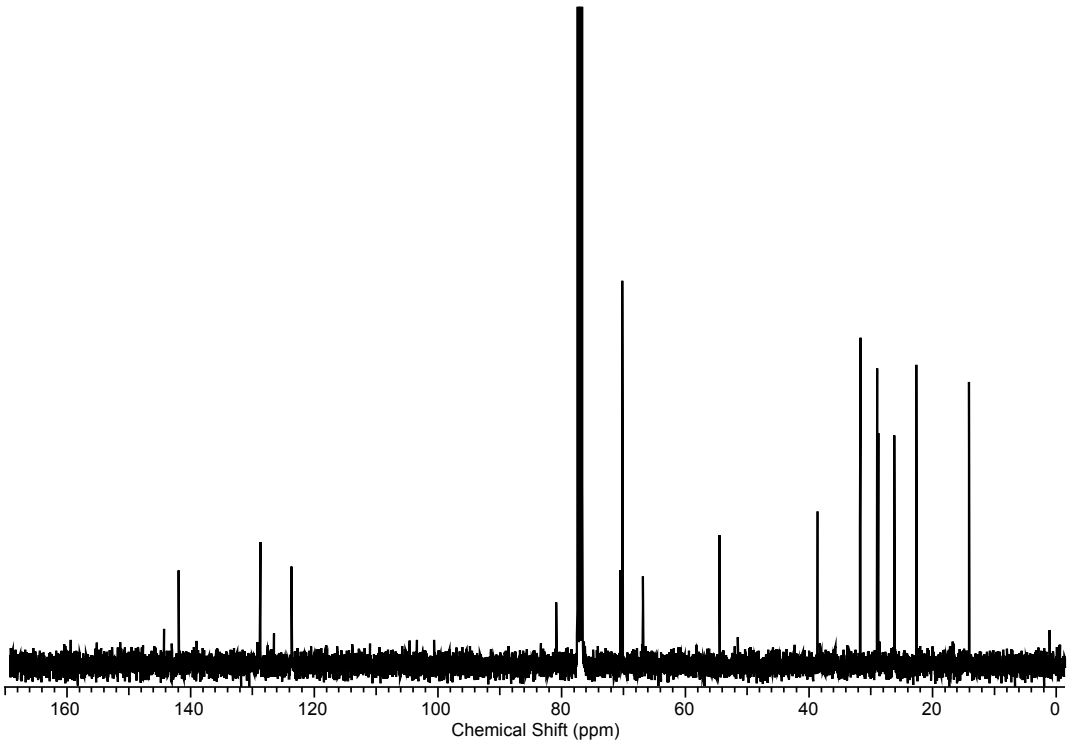


Fig S2-4. ^{13}C NMR of receptor **1.HB** in $CDCl_3$ at 298 K (100 MHz).

Receptor **2.XB**

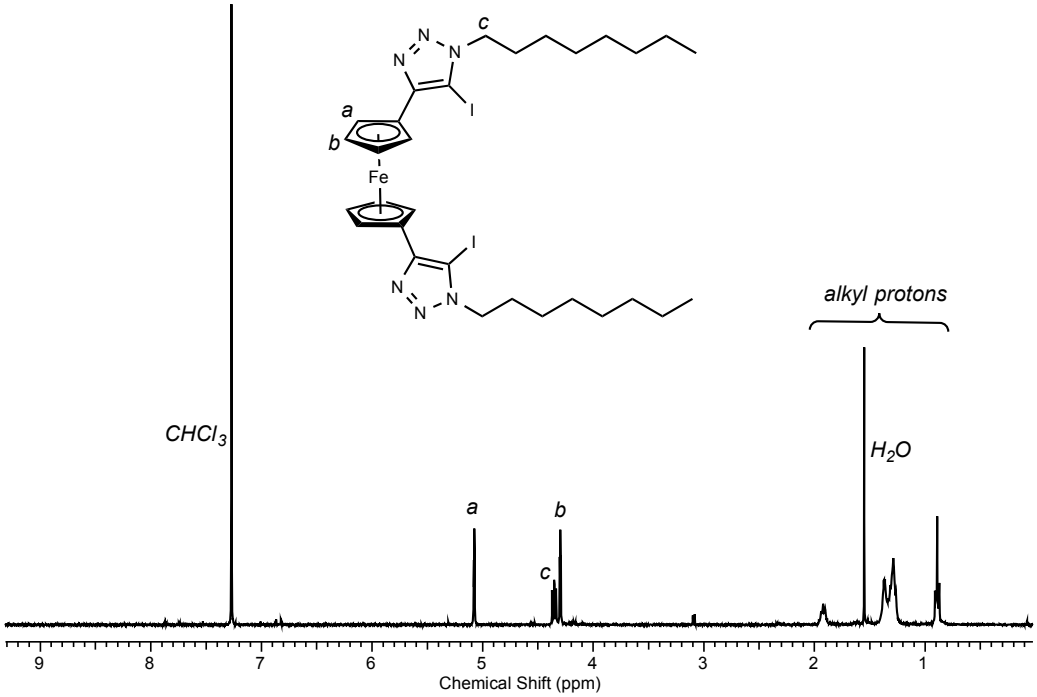


Fig S2-5. ^{1}H NMR of receptor **2.XB** in $CDCl_3$ at 298 K (400 MHz).

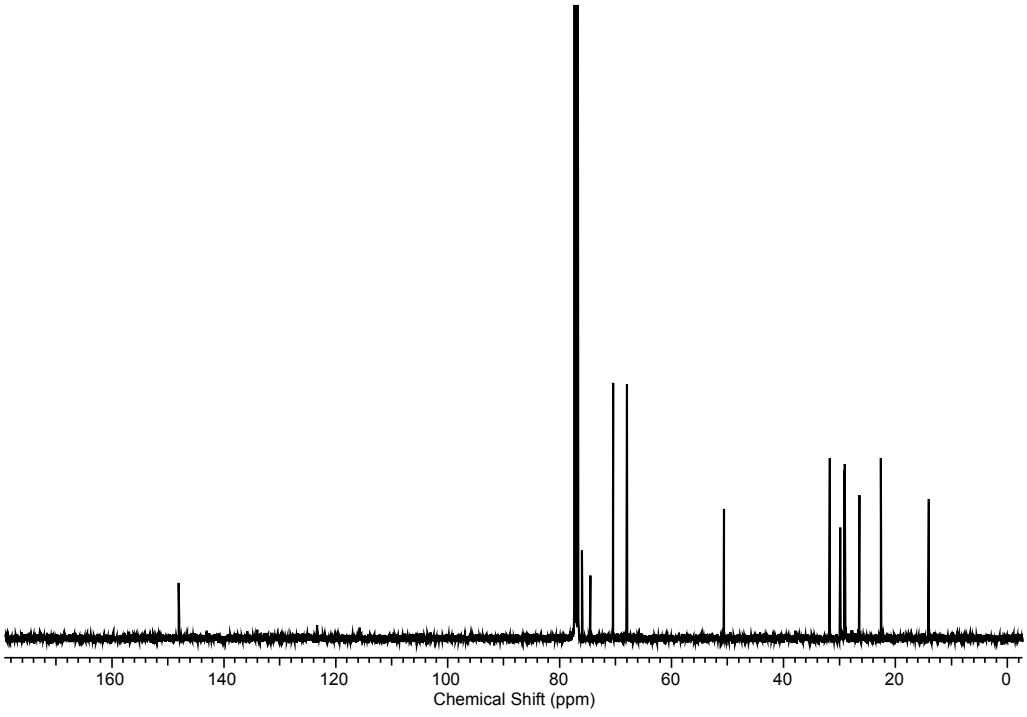


Fig S2-6 ^{13}C NMR of receptor **2.XB** in $CDCl_3$ at 298 K (100 MHz).

Receptor **2.HB**

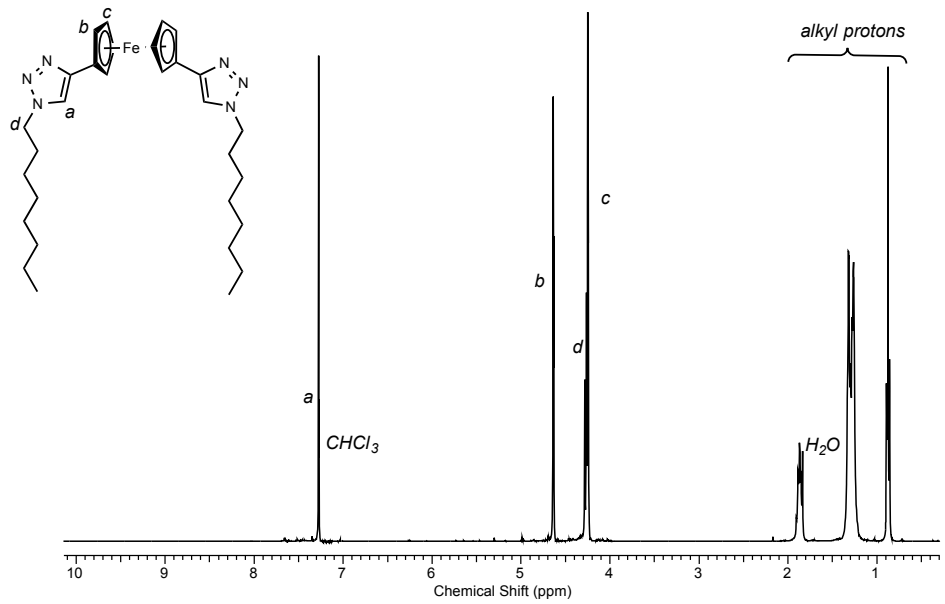


Fig S2-7 ^{1}H NMR of receptor **2.HB** in $CDCl_3$ at 298 K (400 MHz).

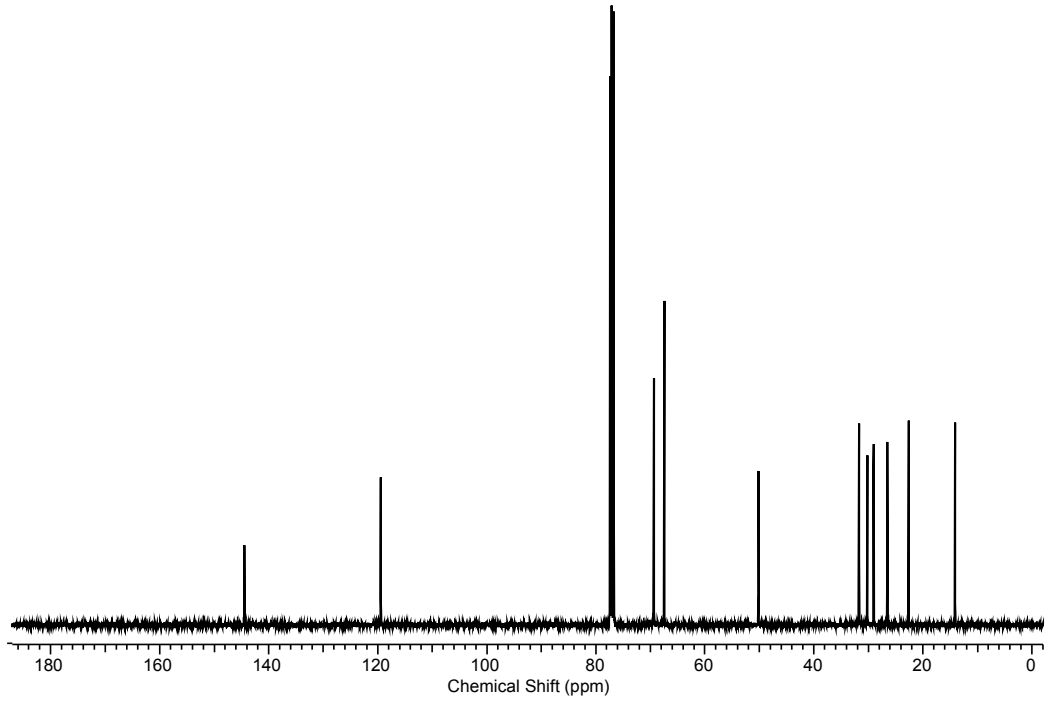


Fig S2-8 ^{13}C NMR of receptor **2.HB** in $CDCl_3$ at 298 K (100 MHz).

Receptor **3.XB**

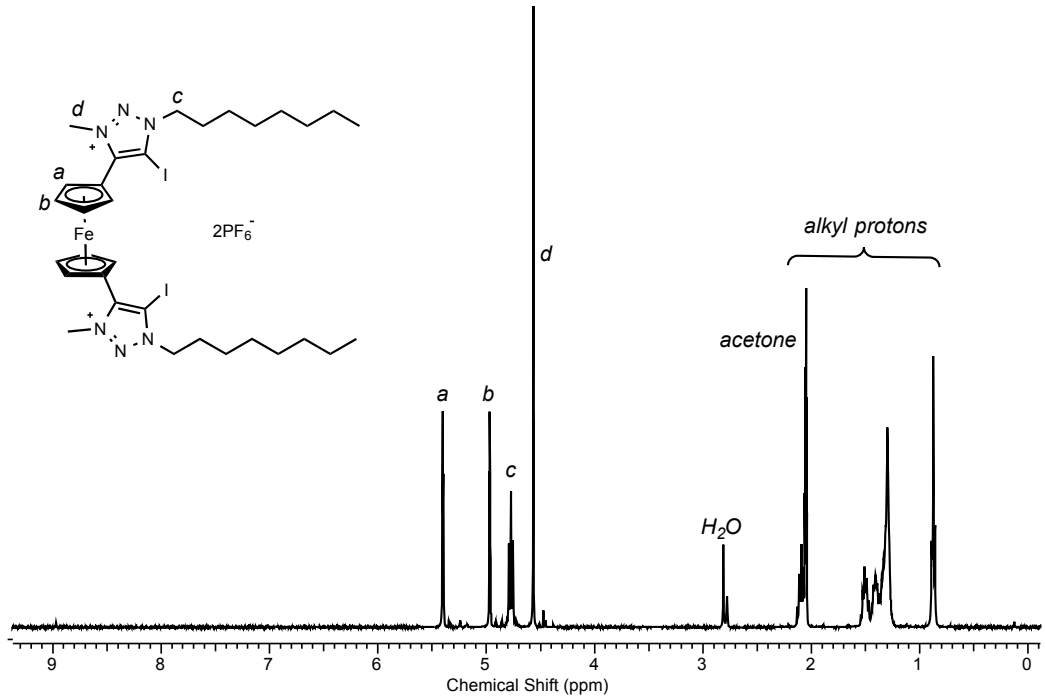


Fig S2-9. [1]H NMR of receptor **3.XB** in d_6-acetone at 298 K (400 MHz).

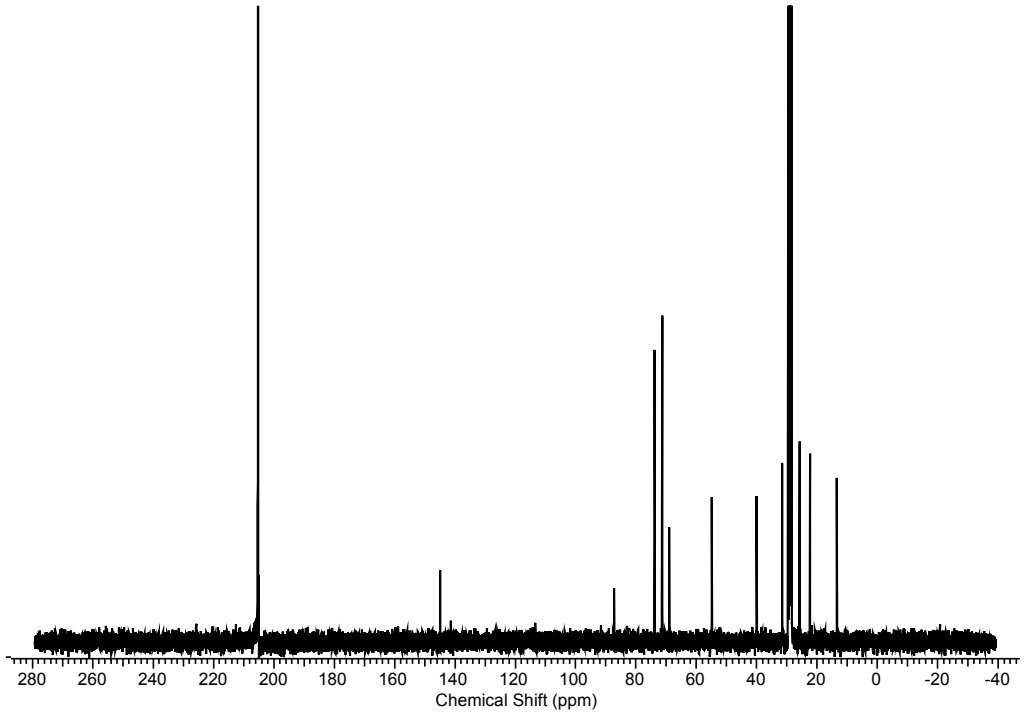


Fig S2-10 [13]C NMR of receptor **3.XB** in d_6-acetone at 298 K (100 MHz).

Receptor **3.HB**

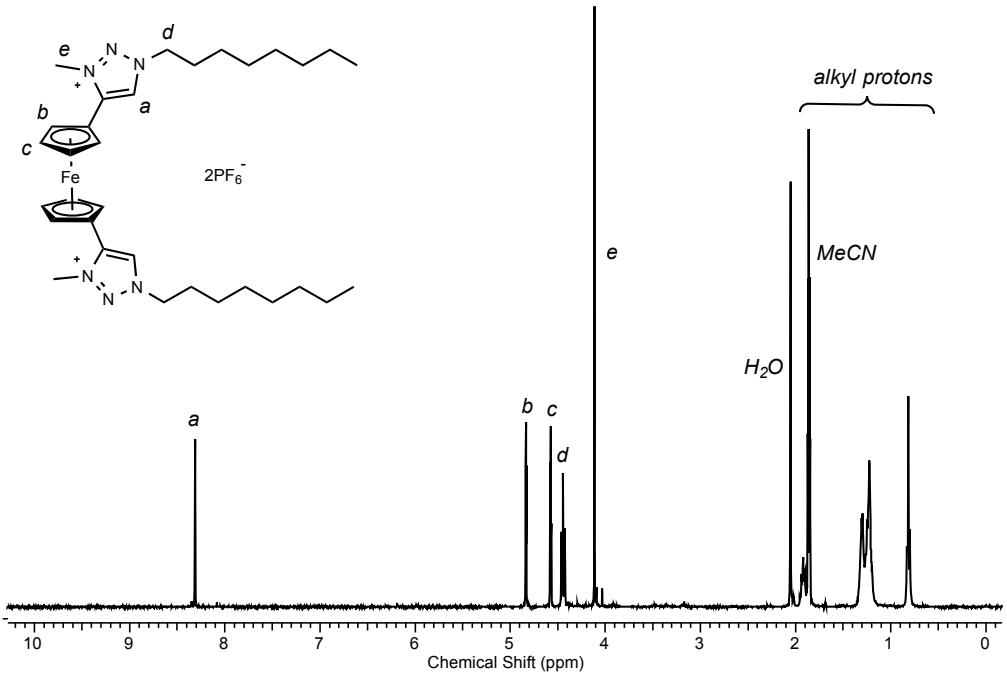


Fig S2-11. ^{1}H NMR of receptor **3.HB** in d_3-acetonitrile at 298 K (400 MHz).

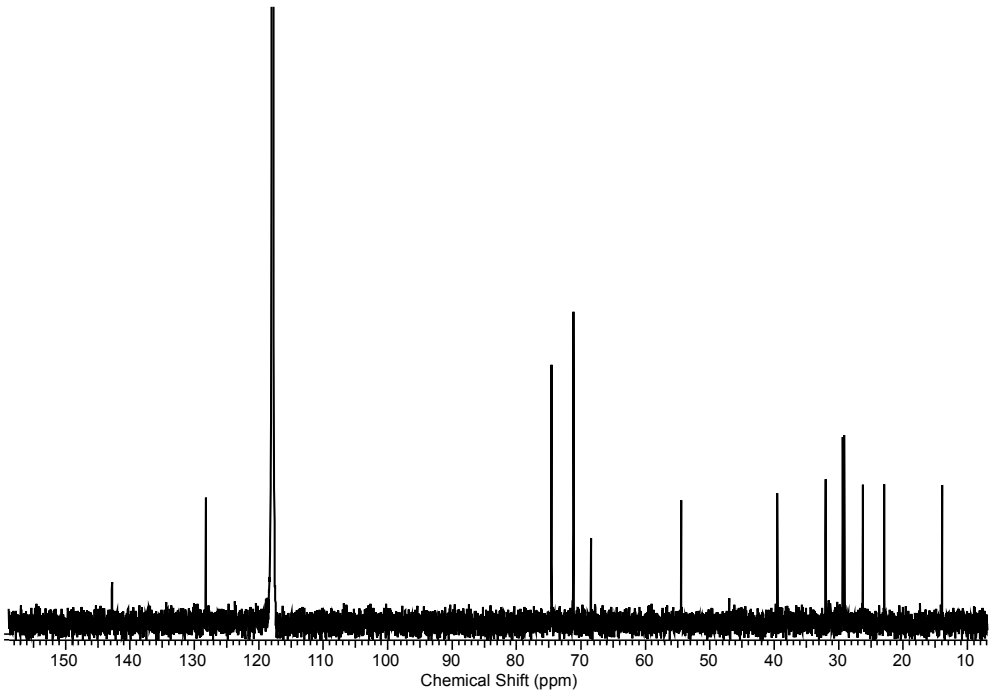


Fig S2-12. ^{13}C NMR of receptor **3.HB** in d_3-acetonitrile at 298 K (100 MHz).

S3. Anion Recognition Studies of Redox-active Receptors by ^{1}H NMR titrations

S3.1 General Titration Protocol

^{1}H NMR titration experiments were performed on a Bruker AVIII 500 MHz spectrometer. In a typical experiment, a solution of the appropriate tetrabutylammonium (TBA) salt was added to the receptor solution at 298 K. Both TBA salt and receptor were dissolved in the appropriate solvent mixture containing d_3-MeCN. TBA was chosen as the counter-cation due to its non-coordinating nature. For all receptors, the binding of anions was found to be fast on the NMR timescale. The values of the observed chemical shift and concentration of anion were entered into the WinEQNMR2[6] computer programme for every titration point. From initial estimates made of the binding constants and limiting chemical shifts, these parameters were refined using non-linear least-squares analyses to obtain the best fit between empirical and calculated chemical shifts based on a 1:1 binding stoichiometry. The input parameters were varied till convergence of the best fit values of the binding constants and their errors were obtained. For all subsequent binding isotherms presented in the following pages, empirical data points are represented by the filled dots, while continuous lines represent the calculated binding curves.

S3.2 ^{1}H NMR titration data

Receptor **1.XB**

A 0.075 M solution of the salt was added to 0.50 mL of a 1.5 mM solution of receptor, where 1.0 equivalent of salt added corresponds to 10 μL of the salt solution. The chemical shift of the internal aromatic proton flanked by the two iodotriazolium groups (H_a in Fig. 2A of the main paper) were monitored for 17 data points corresponding to 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents of added guest anion.

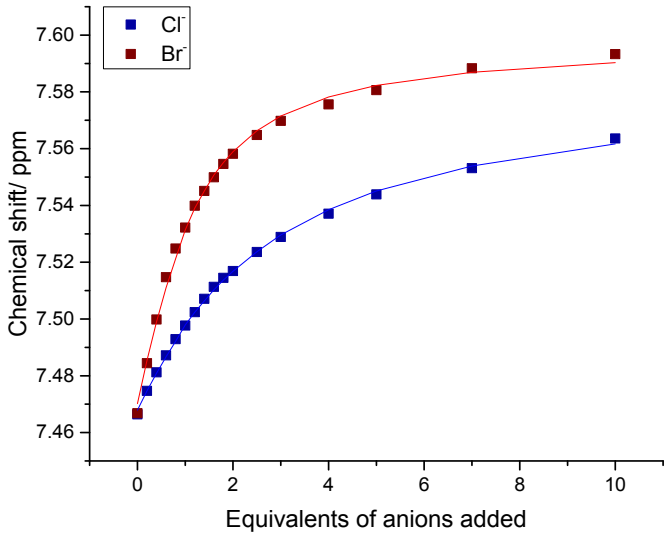


Figure S3-1. Plot of chemical shift of the internal aromatic proton of **1.XB** against equivalents of anions added in 9:1 CD_3CN/D_2O ([host] = 1.5 mM, 500 MHz, T = 298 K).

Receptor **1.HB**

An identical procedure as that for receptor **1.XB** was followed.

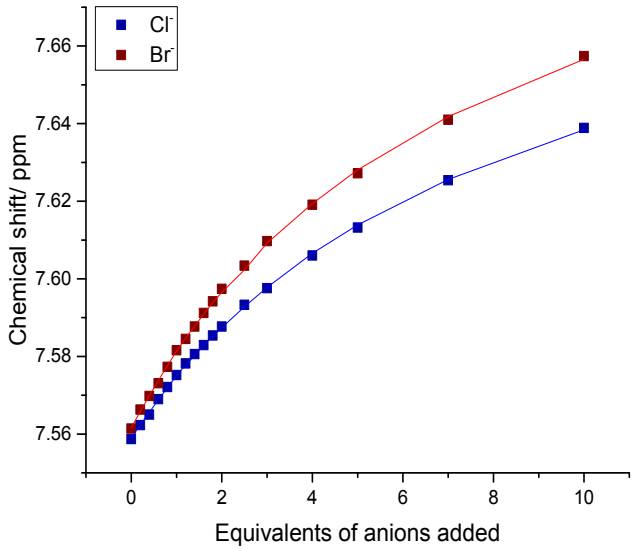


Figure S3-2. Plot of chemical shift of the internal aromatic proton of **1.HB** against equivalents of anions added in 9:1 CD_3CN/D_2O ([host] = 1.5 mM, 500 MHz, T = 298 K).

Receptor **2.XB**

Due to the weaker binding exhibited by neutral receptor **2.XB** towards the halides in solution, a modified titration protocol was used. A 0.150 M solution of the salt was added to 0.50 mL of a 1.5 mM solution of receptor, where 1.0 equivalent of salt added corresponds to 5 µL of the salt solution. The chemical shift of the ferrocene proton immediately adjacent to the iodotriazole units (H_g in Fig. 2B in the main paper) were monitored for 17 data points corresponding to 0.0, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0, 60.0 and 70.0 equivalents of added guest anion.

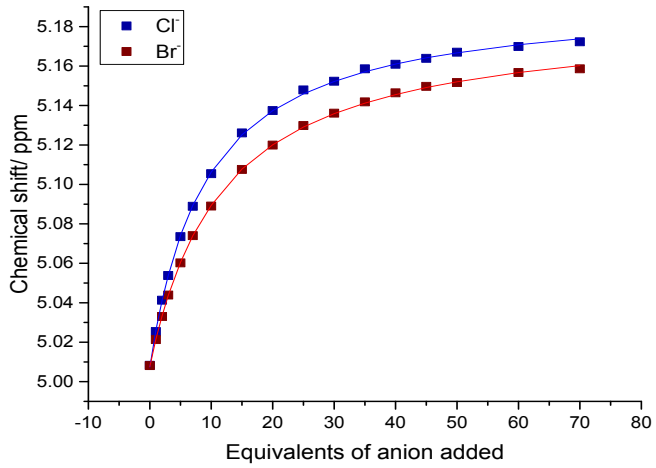


Figure S3-3. Plot of chemical shift of the ferrocene proton of **2.XB** against equivalents of anions added in CD_3CN ([host] = 1.5 mM, 500 MHz, T = 298 K).

Receptor **2.HB**

An identical procedure as that for receptor **2.XB** was followed, except that the prototriazole protons were monitored during the titration. The ferrocene proton signal was not monitored as its perturbations during titration were too small to give reliable association constants.

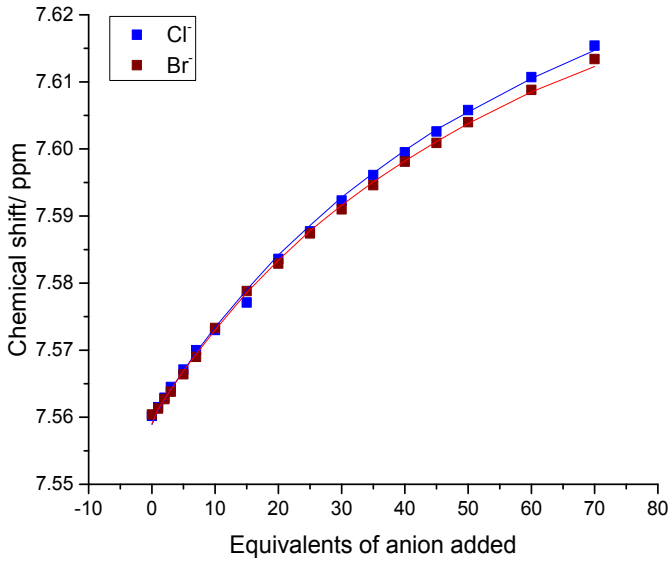


Figure S3-4. Plot of chemical shift of the prototriazole proton of **2.HB** against equivalents of anions added in CD_3CN ([host] = 1.5 mM, 500 MHz, T = 298 K).

Receptor **3.XB**

An identical procedure as that for receptor **1.XB** was followed, except that the ferrocene proton immediately adjacent to the iodotriazolium moieties were monitored.

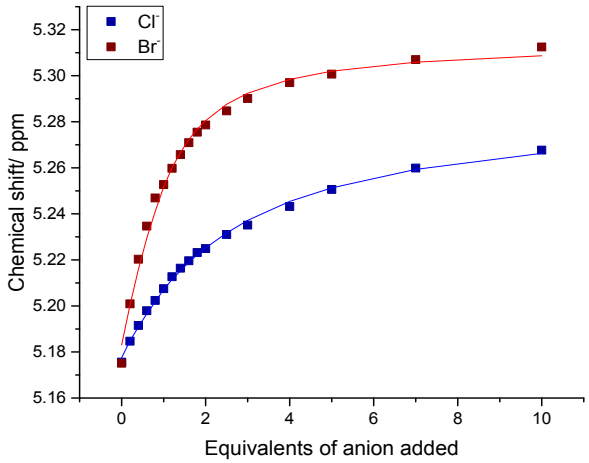


Figure S3-5. Plot of chemical shift of the ferrocene proton of **3.XB** against equivalents of anions added in 9:1 CD_3CN/D_2O ([host] = 1.5 mM, 500 MHz, T = 298 K).

Receptor **3.HB**

An identical procedure as that for receptor **1.XB** was followed, except that the prototriazolium protons were monitored during the titration.

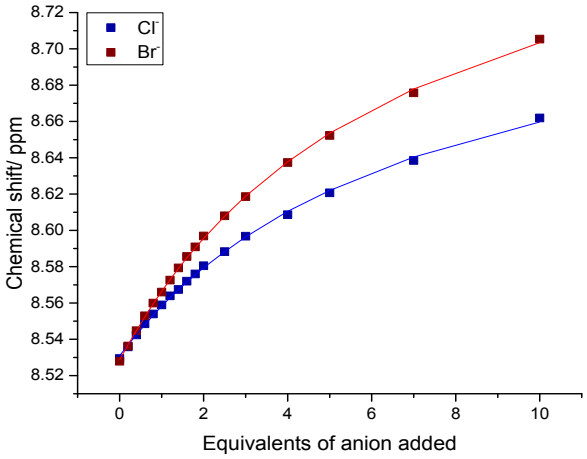


Figure S3-6. Plot of chemical shift of the prototrazolium proton of **3.HB** against equivalents of anions added in 9:1 CD_3CN/D_2O ([host] = 1.5 mM, 500 MHz, T = 298 K).

S4. Electrochemical Studies

S4.1 General Protocol

Cyclic voltammetry (CV) was performed on an Autolab PGSTAT-12 system and all data was analyzed using General Purpose Electrochemical Software (GPES) version 4.9. All electrochemistry was undertaken in anhydrous acetonitrile unless otherwise stated, with 0.1 M $TBAPF_6$ supporting electrolyte. All diffusive voltammetry was undertaken at a 3 mm diameter glassy carbon working electrode (BASi), cleaned prior to use using 0.3 micron alumina powder (Buehler), and all potentials were referenced to a $Ag/AgNO_3$ reference electrode[7]; the latter was prepared using an anhydrous acetonitrile-based solution of 10 mM $AgNO_3$ and 0.15 M $TBAPF_6$. A $Ag/AgNO_3$ reference electrode was used in preference to the more commonly used Ag/AgCl reference electrode in order to prevent any potential interference in the sensory response of the receptors arising from any chloride anion leakage. All solutions were degassed with dry nitrogen prior to the recording of each CV. CVs were recorded with a 1 s equilibration time, step potential of 1 mV and at a scan rate of 100 mV s^{-1}. For all the host systems investigated, the host was dissolved in the electrolyte solution to afford a concentration of 0.5 mM. The electrochemical reversibility of each system was probed by vitue of varying the scan rate (25, 50, 75, 100, 250, 500 mV s^{-1}). After which, electrochemical anion binding experiments were performed by adding known aliquots of anions, (as a 0.25 M solution in the same electrolyte mixture) corresponding to 0.0, 0.5, 1.0, 2.0, 3.0, 5.0, 7.0 and 10.0 equivalents, respectively. Reliability in the electrochemical data were ensured by recording every CV five times, and no potential drift for the values of E_{max} and E_{min} values were found.

S4.2 Electrochemical Reversibility Studies

The electrochemical reversibility of our host systems are probed by recording CV scans at different scan rates. An electrochemical system is described as reversible, and hence exhibits fast electron transfer kinetics, when the following criteria are met:

1. ΔE_p = (59 / n) mV, where n = number of electrons transferred in the redox process. For our ferrocene-appended host systems, n = 1 during ferrocene redox chemistry. Hence, ΔE_p should be 59 mV for our systems.
2. Potentials E_{pa} and E_{pc} corresponding to peak oxidation and reduction currents respectively are independent of the scan rate.
3. The peak cathodic (I_{pc}) and anodic (I_{pa}) currents are of equal magnitude, i.e. $I_{pc} / I_{pa} = 1$.
4. The peak currents are proportional to the square root of the CV scan rate.

Unless otherwise stated, all CVs are recorded in 0.1 M $TBAPF_6$ electrolyte solution in acetonitrile and potentials are compared to the Ag / $AgNO_3$ reference electrode.

Receptor **1.XB**

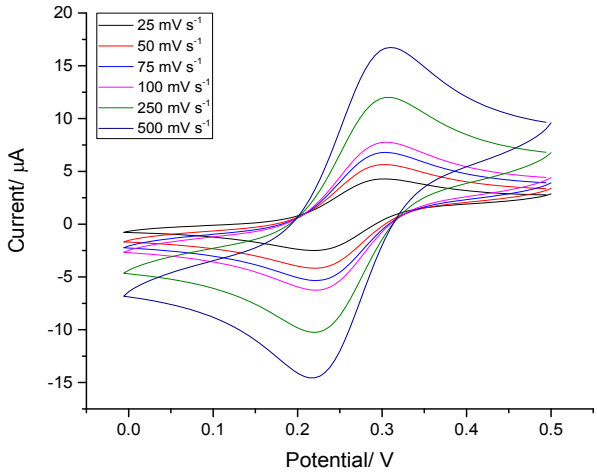


Fig. S4-1. CVs of receptor **1.XB** at different scan rates ([host] = 0.5 mM, T = 293 K).

Table S4-1. Values of E_{pc}, E_{pa}, I_{pa}, I_{pc} ΔE_p and I_{pa}/ I_{pc} for **1.XB** recorded at different scan rates.

Scan rate/ mV s^{-1}	E_{pa}/V	E_{pc}/V	I_{pa}/ µA	I_{pc}/ µA	ΔE_p/ V	I_{pa}/ I_{pc}
25	0.304	0.220	2.96	3.17	0.084	0.932
50	0.304	0.220	4.30	4.52	0.084	0.952
75	0.304	0.220	5.26	5.62	0.084	0.936
100	0.304	0.220	6.16	6.44	0.084	0.956
250	0.310	0.220	9.61	10.3	0.090	0.937
500	0.310	0.214	13.6	14.2	0.096	0.960

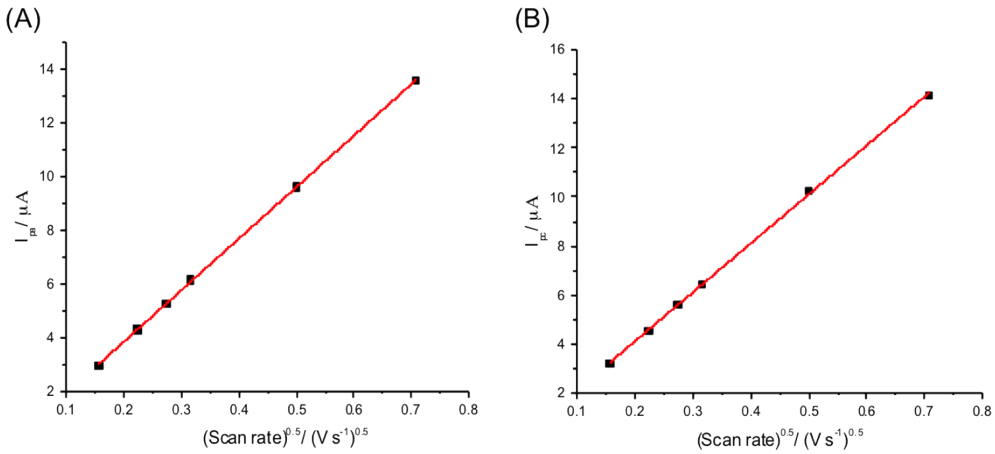


Fig. S4-2. Plots of (A) I_{pa} and (B) I_{pc} against (scan rate)$^{1/2}$ for **1.XB** ([host] = 0.5 mM, T = 293 K).

Receptor **1.XB** exhibits a quasi-reversible Fc/Fc^+ redox couple.

Receptor **1.HB**

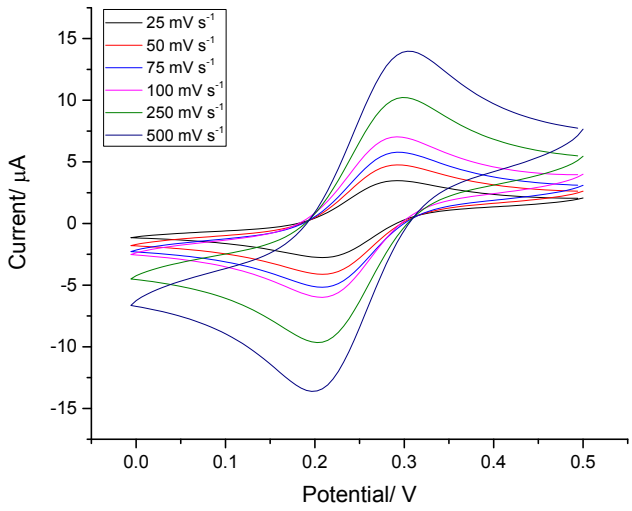


Fig. S4-3. CVs of receptor **1.HB** at different scan rates ([host] = 0.5 mM, T = 293 K).

Table S4-2. Values of E_{pc}, E_{pa}, I_{pa}, I_{pc} ΔE_p and I_{pa}/ I_{pc} for **1.HB** recorded at different scan rates.

Scan rate/ mV s^{-1}	E_{pa}/V	E_{pc}/V	I_{pa}/ µA	I_{pc}/ µA	ΔE_p / V	I_{pa} / I_{pc}
25	0.292	0.208	2.77	2.91	0.084	0.952
50	0.292	0.208	3.97	4.07	0.084	0.975
75	0.292	0.208	4.92	4.99	0.084	0.986
100	0.292	0.208	5.84	6.01	0.084	0.972
250	0.298	0.202	8.74	8.97	0.096	0.974
500	0.304	0.197	11.7	12.4	0.107	0.944

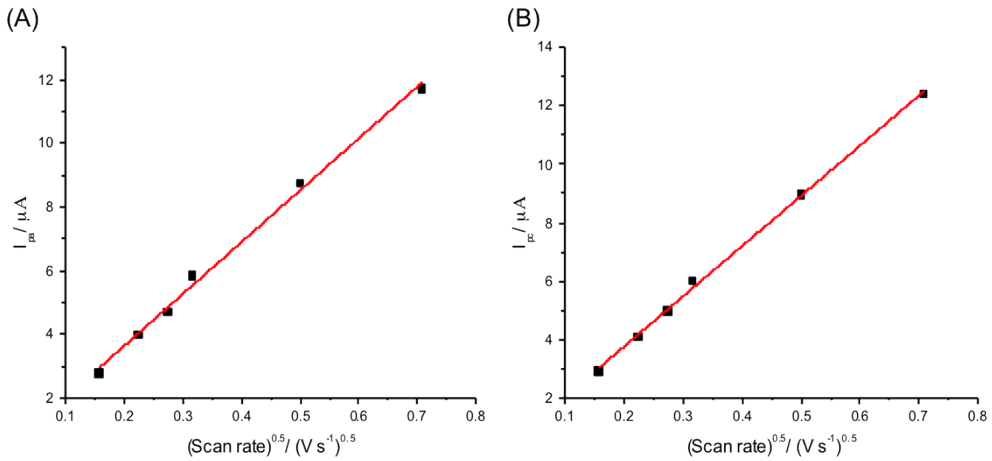


Fig. S4-4. Plots of (A) I_{pa} and (B) I_{pc} against (scan rate)$^{1/2}$ for receptor **1.HB** ([host] = 0.5 mM, T = 293 K).

Receptor **1.HB** exhibits a quasi-reversible Fc/Fc^+ redox couple.

Receptor **2.XB**

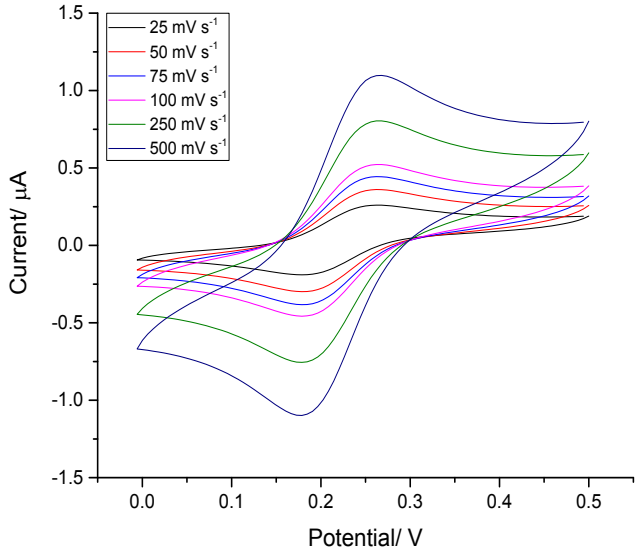


Fig. S4-5. CVs of receptor **2.XB** at different scan rates ([host] = 0.5 mM, T = 293 K).

Table S4-3. Values of E_{pc}, E_{pa}, I_{pa}, I_{pc} ΔE_p and I_{pa}/ I_{pc} for **2.XB** recorded at different scan rates.

Scan rate/ mV s^{-1}	E_{pa}/V	E_{pc}/V	I_{pa}/ µA	I_{pc}/ µA	ΔE_p / V	I_{pa} / I_{pc}
25	0.262	0.179	1.75	1.38	0.083	1.27
50	0.262	0.179	2.50	2.28	0.083	1.10
75	0.262	0.179	3.12	2.74	0.083	1.14
100	0.262	0.179	3.41	3.24	0.083	1.05
250	0.262	0.179	5.15	5.20	0.083	0.990
500	0.268	0.179	7.86	7.25	0.089	1.08

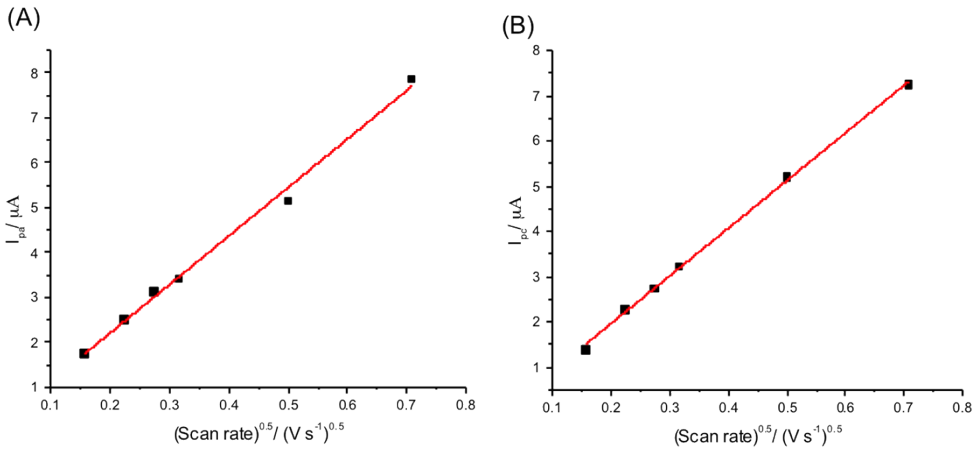


Fig. S4-6. Plots of (A) I_{pa} and (B) I_{pc} against (scan rate)$^{1/2}$ for receptor **2.XB** ([host] = 0.5 mM, T = 293 K).

Receptor **2.XB** exhibits a quasi-reversible Fc/Fc^+ redox couple.

Receptor **2.HB**

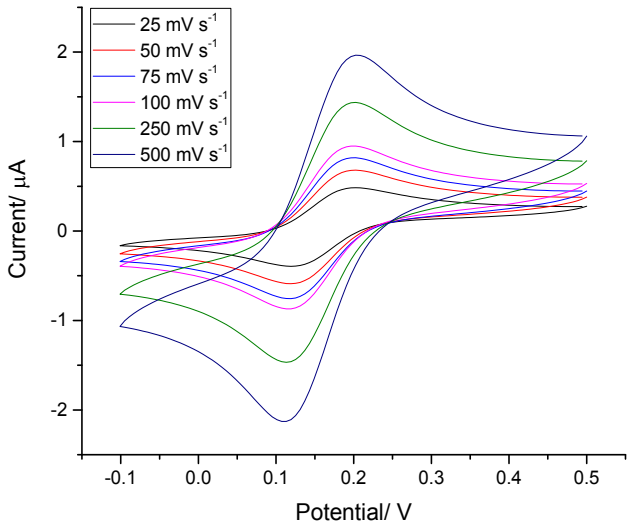


Fig. S4-7. CVs of receptor **2.HB** at different scan rates ([host] = 0.5 mM, T = 293 K).

Table S4-4. Values of E_{pc}, E_{pa}, I_{pa}, I_{pc} ΔE_p and I_{pa}/ I_{pc} for **2.HB** recorded at different scan rates.

Scan rate/ mV s^{-1}	E_{pa}/V	E_{pc}/V	I_{pa}/ µA	I_{pc}/ µA	ΔE_p / V	I_{pa} / I_{pc}
25	0.202	0.119	3.99	3.11	0.083	1.28
50	0.202	0.119	5.32	5.09	0.083	1.05
75	0.202	0.119	6.67	6.23	0.083	1.07
100	0.202	0.113	7.76	7.46	0.089	1.04
250	0.202	0.113	12.0	11.8	0.089	1.02
500	0.202	0.113	16.9	16.2	0.089	1.04

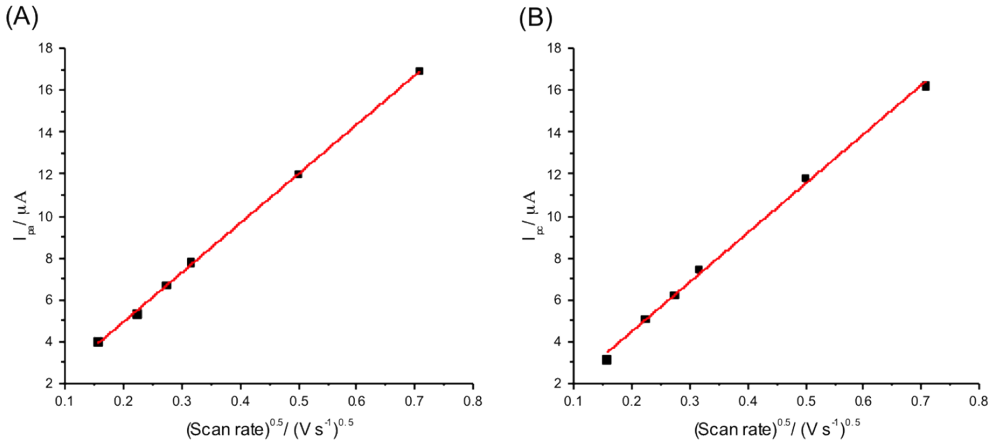


Fig. S4-8. Plots of (A) I_{pa} and (B) I_{pc} against (scan rate)$^{1/2}$ for receptor **2.HB** ([host] = 0.5 mM, T = 293 K).

Receptor **2.HB** exhibits a quasi-reversible Fc/Fc^+ redox couple.

Receptor **3.XB and 3.HB**

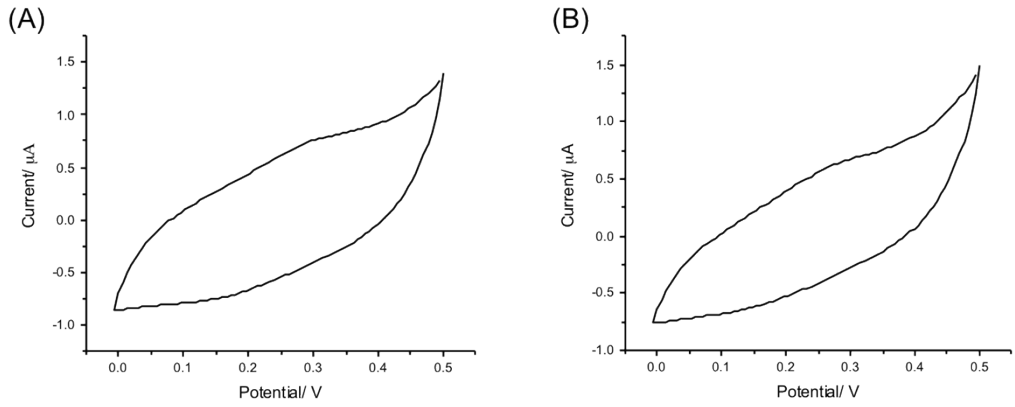


Fig. S4-9. CVs of dicationic receptors (A) **3.XB** and (B) **3.HB**, showing lack of electrochemical reversibility in the accessible solvent potential window. The onset of the anodic current at c.a. 0.5 V may possibly be due to oxidative decomposition of the receptors ([host] = 0.5 mM, T = 293 K).

S4.3 Data for Electrochemical Anion titrations in Dry Acetonitrile

Receptor **1.XB**

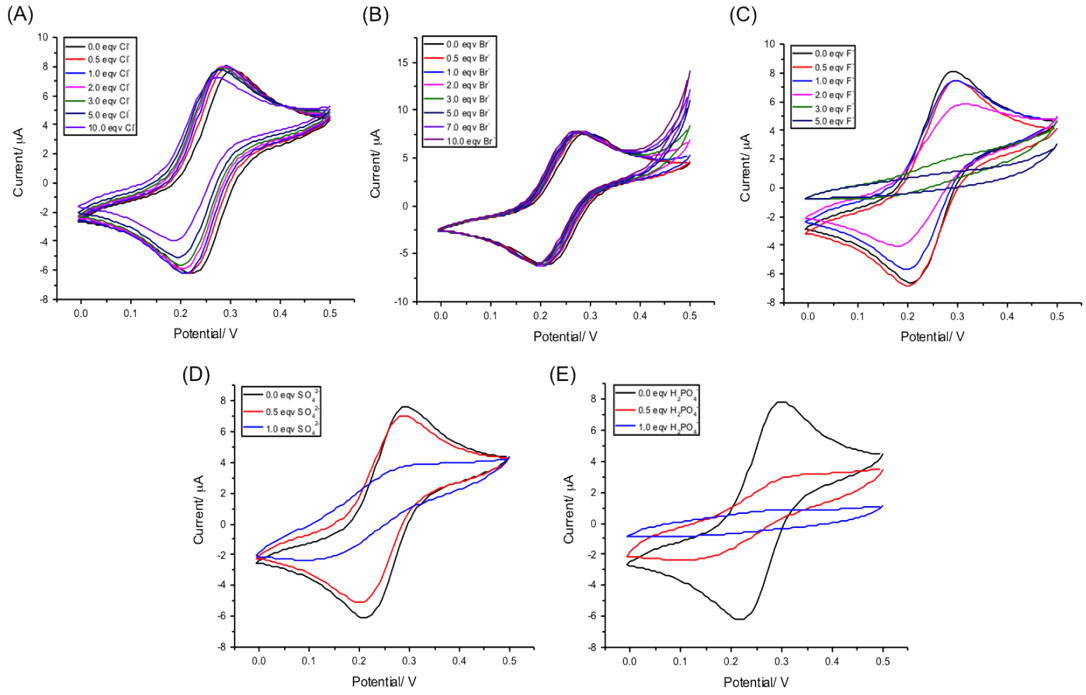


Fig. S4-10. CVs of receptor **1.XB** upon the addition of (A) TBACl; (B) TBABr; (C) TBAF; (D) $(TBA)_2SO_4$ and (E) $TBAH_2PO_4$. For $(TBA)_2SO_4$ and $TBAH_2PO_4$, loss of reversibility was observed at 1.0 equivalents of anion, hence no further titrations with excess anion were performed ([host] = 0.5 mM, T = 293 K).

Receptor **1.HB**

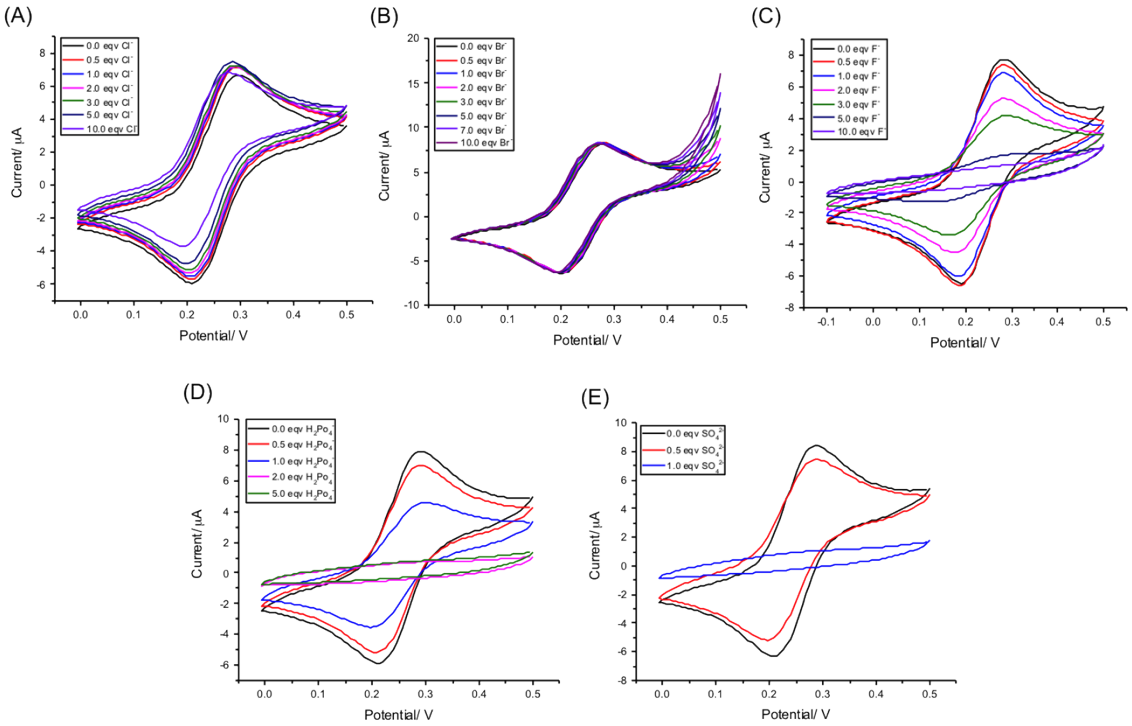


Fig. S4-11. CVs of receptor **1.HB** upon the addition of (A) TBACl; (B) TBABr; (C) TBAF; (D) $(TBA)_2SO_4$ and (E) $TBAH_2PO_4$. For $(TBA)_2SO_4$ and $TBAH_2PO_4$, loss of reversibility was observed at 1.0 equivalents of anion, hence no further titrations with excess anions were performed ([host] = 0.5 mM, T = 293 K).

Receptor **2.XB**

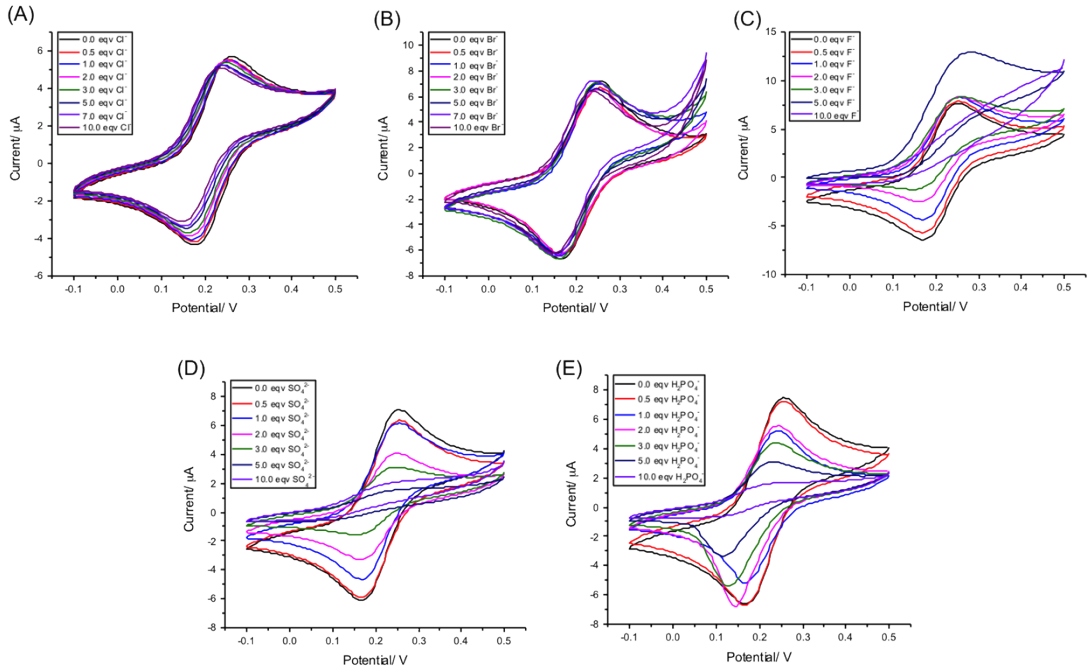


Fig. S4-12. CVs of receptor **2.XB** upon the addition of (A) TBACl; (B) TBABr; (C) TBAF; (D) $(TBA)_2SO_4$ and (E) $TBAH_2PO_4$ ([host] = 0.5 mM, T = 293 K).

Receptor **2.HB**

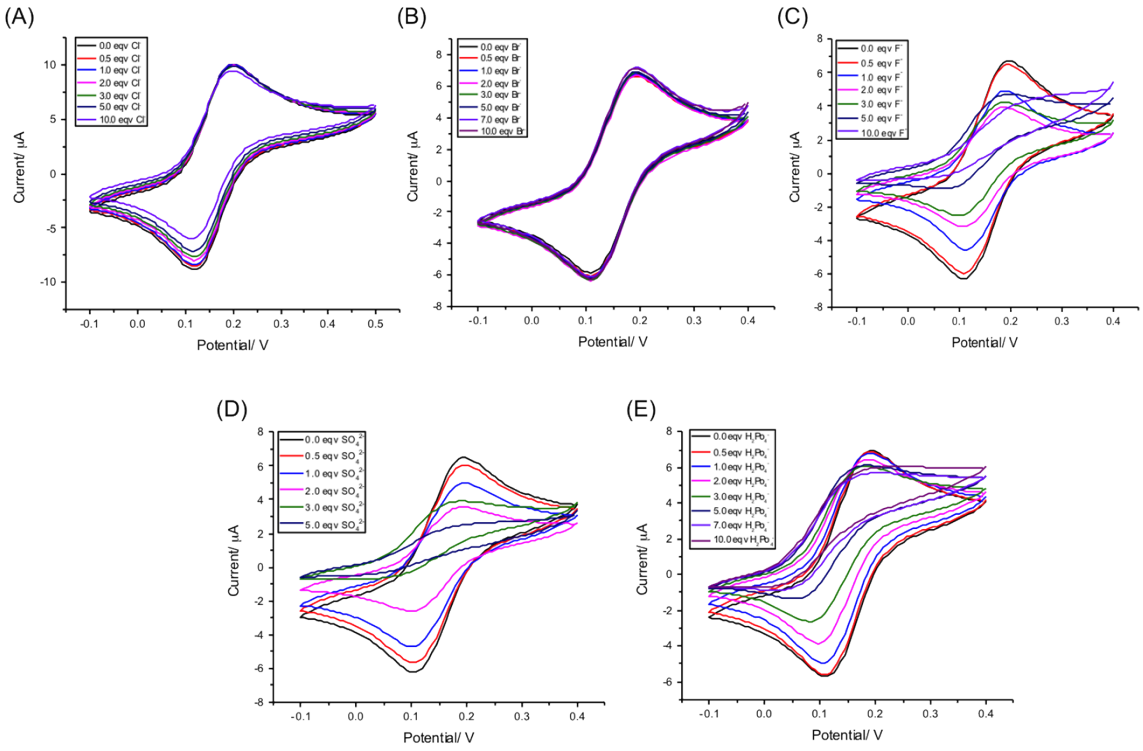


Fig. S4-13. CVs of receptor **2.HB** upon the addition of (A) TBACl; (B) TBABr; (C) TBAF; (D) $(TBA)_2SO_4$ and (E) $TBAH_2PO_4$ ([host] = 0.5 mM, T = 293 K).

S4.4 Data for Electrochemical Anion titrations in Acetonitrile/H_2O 9:1

Receptor **1.XB**

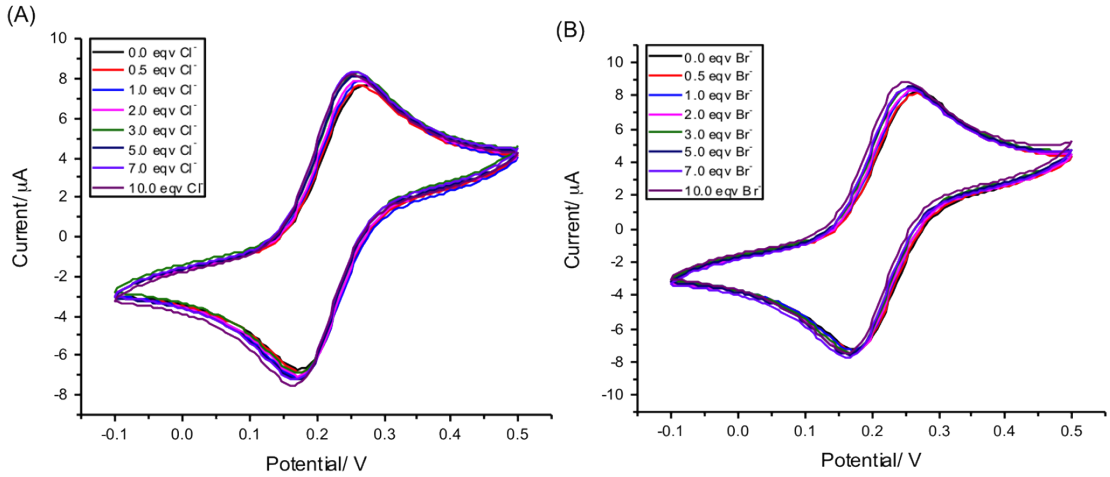


Fig. S4-14. CVs of receptor **1.XB** upon the addition of (A) TBACl and (B) TBABr ([host] = 0.5 mM, T = 293 K).

Receptor **1.HB**

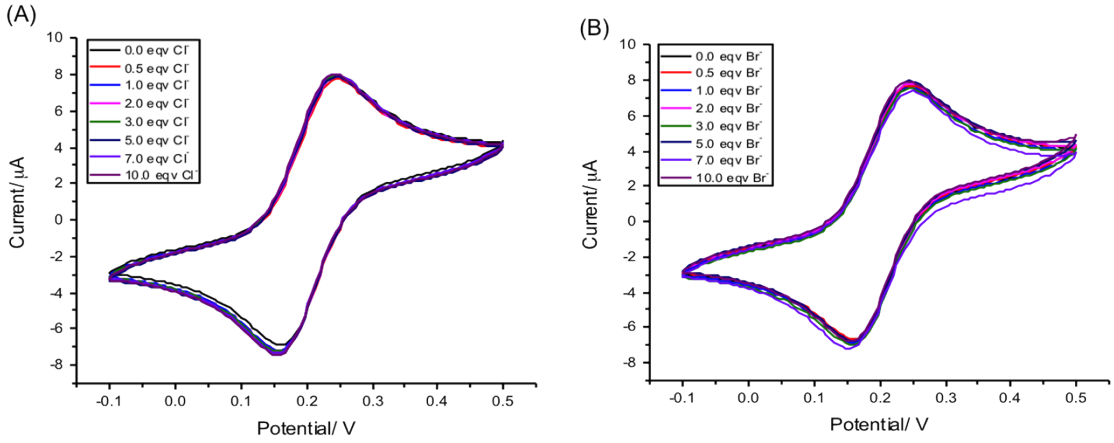


Fig. S4-14. CVs of receptor **1.HB** upon the addition of (A) TBACl and (B) TBABr ([host] = 0.5 mM, *T* = 293 K).

S5. References

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