A selective fluoride sensor and a digital processor with "Write-Read-Erase-Read" behaviour

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Supplementary information

1. General Information

All solvents and reagents were purchased from commercial sources and used without further purification except for dry THF. Anions in the form of Tetra butyl ammonium (TBA) salts were stored prior to the use in a desiccator under vacuum containing silica. Copper nitrate was used as a source of Cu^{+2}. Mass spectra were recorded on a Bruker HR-MS spectrometer using CH_3CN as solvent. ^{13}C and ^1H nmr spectra were recorded using a Bruker instrument operating at 400 MHz. UV/Vis spectra were recorded on Agilent Spectrophotometer (Product no: G9821A, Serial no: MY1321007, Cary Win Uv software. Titrations were performed on 3 mL volume of samples of **1** in dry THF, by addition of THF (dry) stock solutions of the appropriate anions and Copper. The synthesis of receptor (**1**) was carried out openly in the ambient conditions.

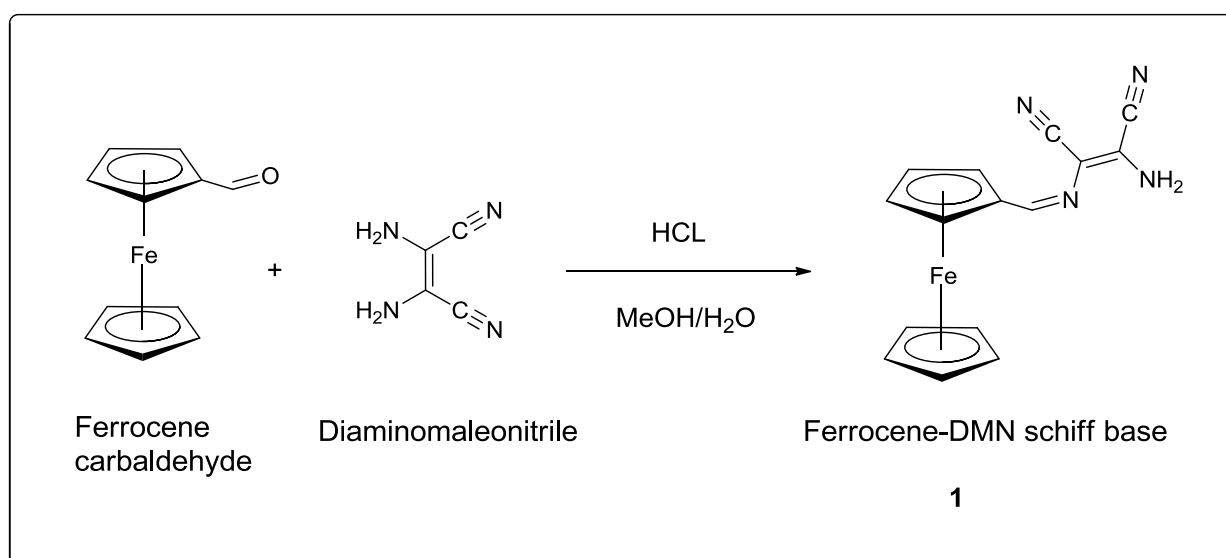# 2. Synthesis and characterisation of Schiff base (1)..S1

Figure 1. Synthetic scheme for formation of receptor **1**.

The synthetic procedure involved drop-wise addition of methanolic solution of diaminomeleonitrile (DMN) to the stirring solution of aldehyde (ferrocenecarboxaldehyde) in distilled water, containing 1–2 drops of conc. HCl. The resulting Schiff base precipitated immediately was filtered, washed and recrystallized with methanol–water, and finally characterized with standard spectroscopic techniques.

Receptor 1.

(Red colour, 95% yield); ^{1}H NMR (400 MHz, CDCl$_3$, TMS), δ (ppm) = 4.212 (s, 5H, Cp-H), 4.577 (s, 2H, β-Cp), 4.720 (s, 2H, α-Cp), 4.941 (s, 2H, -NH$_2$), 8.351 (s, 1H, -CH=N). ^{13}C NMR (400 MHz, CDCl$_3$, TMS), δ (ppm) = 69.384 ppm (β-Cp), 69.813 ppm (Cp-H), 72.586 ppm (α-Cp), 79.063 ppm (i-Cp), 121.909, 114.162, 112.596, 109.674 ppm (CN, C=C), 161.556 ppm (C=N). MS (HR-MS, positive mode) found 304.039. C$_{15}$H$_{11}$FeN$_4$ requires 304.04.

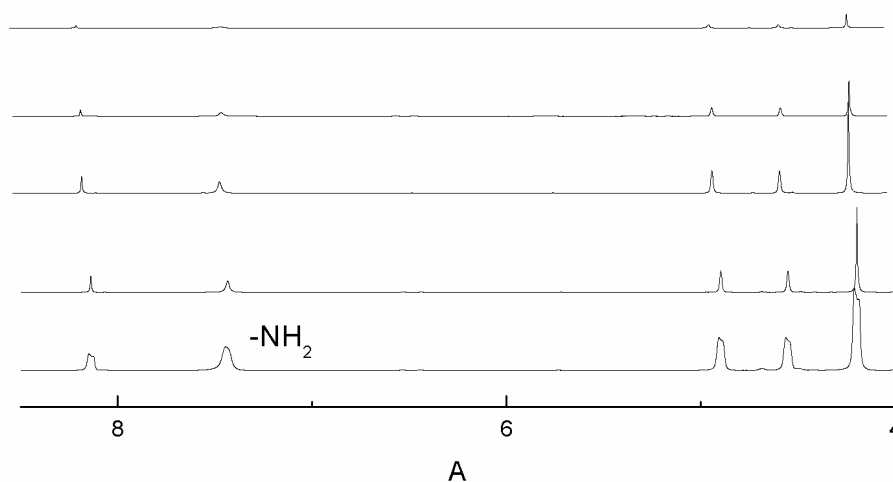## 3. ^{1}H NMR titration of F$^-$ with 1..S2

Figure 2. Partial ^{1}H NMR of **1** (31.75mM) in d$_6$-DMSO upon addition of 0-5 equivalents of fluoride (5mM) in dry THF. Here **A = ppm**

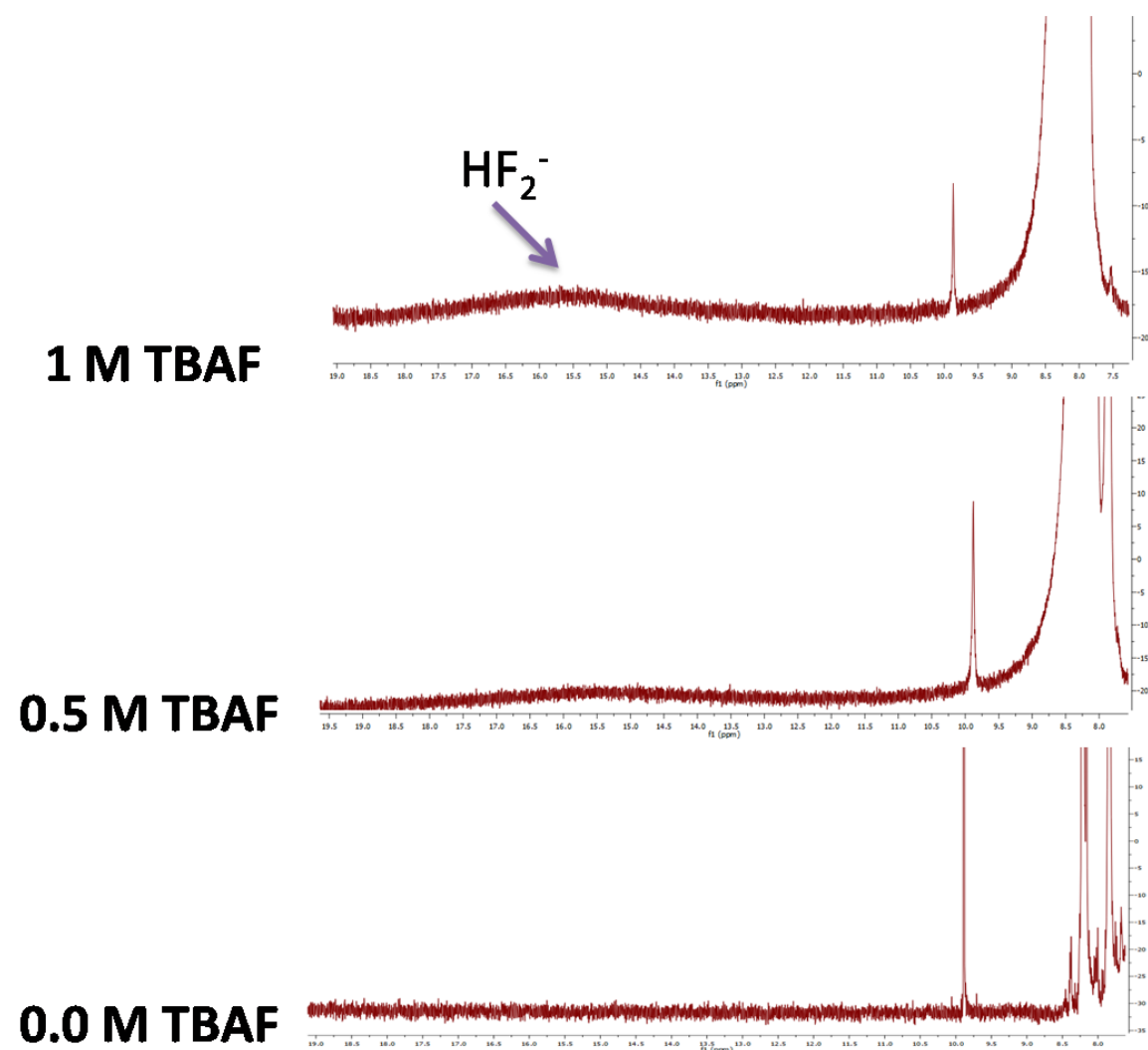## 4. Existence of HF$_2^-$ signal….S3

Figure 3. Partial ^{1}H nmr experiment demonstrating existence of HF2- signal around 16ppm at higher concentrations (0.5-1M) and further supporting the deprotonation phenomenon at higher concentrations.
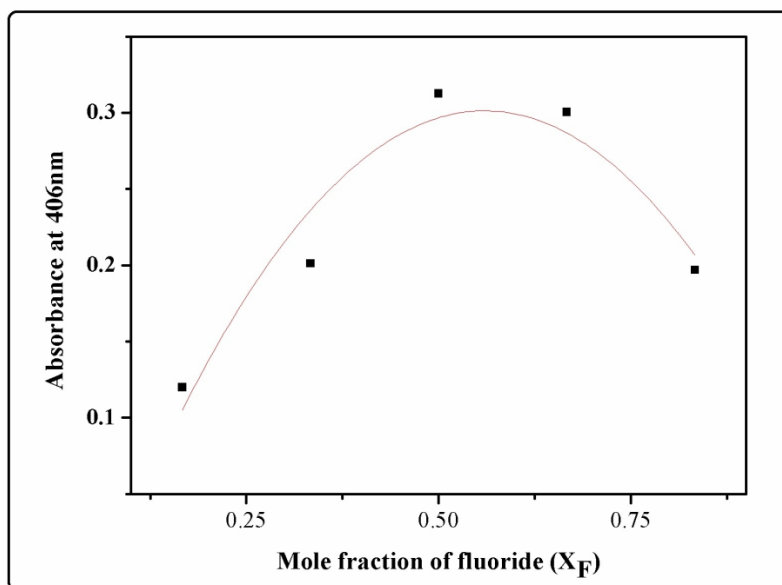
5. Jobs plot of 1 with F⁻..S4

Figure 4. Jobs plot for receptor **1** and F⁻ confirming 1:1stoichiometry. Here X_F refers to the mole fraction of fluoride in the mixture.

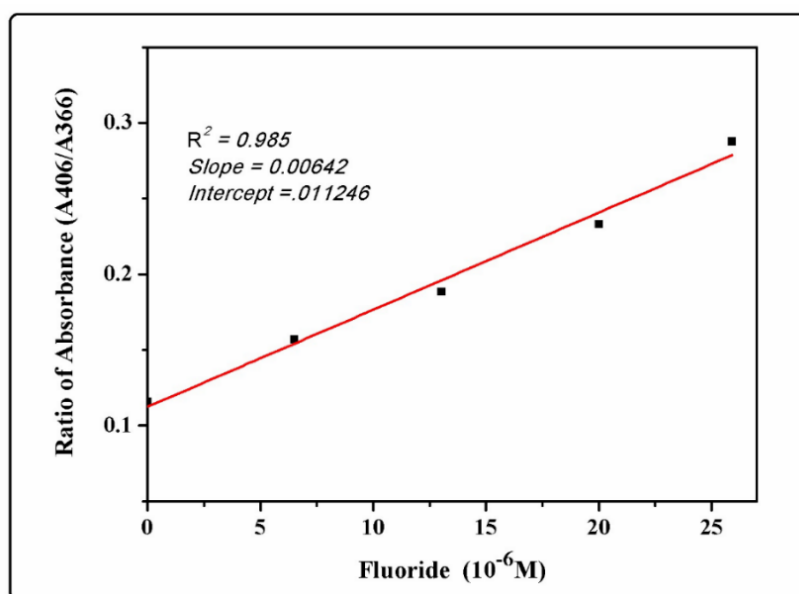## 6. Calibration Curve for F⁻ Determination..S5

Figure 5. Absorption ratiometric response of **1** with different concentrations of TBAF in dry THF. Ambient temperature conditions include an average of 298 K.
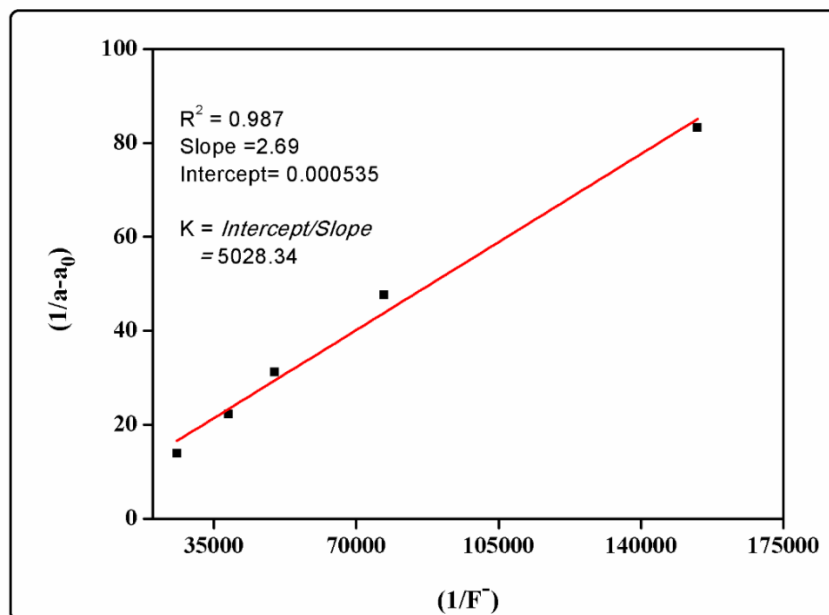
7. Binding Constant..S6

Figure 6. Binesi-Hildebrand plot for calculation of binding constant (K) of receptor **1** with fluoride. In this case, it is 5028.34 M^{-1}.
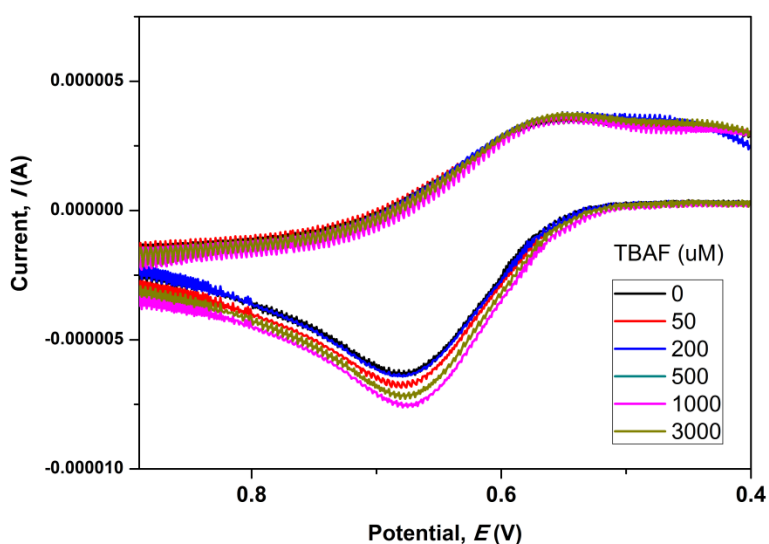
8. Cyclic Voltammetry..S7

Figure 7. CV profile of **1** (Oxidation Wave) upon addition of various concentrations of TBAF (10 mM). Experiment was carried out in dry THF under Argon atmosphere using [n-Bu$_4$] PF$_6$ (129.05 mM) as supporting electrolyte.