*Electronic Supplementary Information (ESI)*

# A redox-activated fluorescence switch based on a Ferrocene – fluorophore – boronic ester conjugate

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## 1. General Methods

All chemical reagents and solvents were analytical grade and purchased from commercial suppliers. Compound **FNB** were prepared by the established literature procedure.[1] $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on the Bruker AV-300 spectrometer with chemical shifts reported in ppm (in $CDCl_3$, TMS as internal standard) at room temperature. Electrospray mass spectra were recorded using a Bruker micro TOF spectrometer using reserpine as calibrant.

Fluorescence measurements were performed on a Perkin Elmer Luminescence spectrophotometer LS 50B, utilising sterna silica (quartz) cuvettes with 10 mm path length and four sides polished. Spectral-grade solvents were used for measurements of fluorescence.

For voltammetry studies a microAutolab III potentiostat system (EcoChemie, Netherlands) was employed with a glassy carbon counter electrode and a KCl-saturated Calomel (SCE) reference electrode (Radiometer). The working electrode was a 4.9 mm diameter basal plane pyrolytic graphite (Le Carbone UK Ltd., Pyrocarbon) disc electrode mounted in Teflon. The temperature during experiments was 15 ± 2 $^{0}C$.

**2-ferrocenylmethyl-6-(piperazin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione**

6-(piperazin-1-yl)benzo[de]isochromene-1,3-dione (0.37 g, 1.30 mmol) and Ferrocenylmethylamine (0.37 g, 1.72 mmol) were added into 30 mL ethanol. The mixture was refluxed for 5 h under a nitrogen atmosphere. After completion of the reaction, the solvent was removed in vacuo and the residue was purified with column chromatography (silica gel, DCM–MeOH, 1:1, v/v), and an orange solid was obtained (100 mg, 16%).1H NMR (300 MHz, CDCl3, ppm): δH 1HNMR (300 MHz, DMSO, ppm) δH 8.45 (d, J = 9.0 Hz, 1H), 8.39 (d, J = 8.5 Hz, 2H), 7.76 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 4.95 (s, 2H), 4.32 (t, J = 1.8 Hz, 2H), 4.20 (s, 5H), 4.05 (t, J = 1.8 Hz, 2H), 3.13 (d, J = 2.8 Hz, 4H), 2.99 (d, J = 4.5 Hz, 4H). 13C NMR (75 MHz, CDCl3, ppm): δC 163.6, 163.0, 156.6, 132.8, 131.1, 129.4, 126.3, 125.6, 122.7,

115.4, 115.3, 83.8, 70.0, 68.8, 67.9, 54.1, 45.8. HRMS (ESI μTOF) m/z calcd for $C_{27}H_{25}N_3O_2Fe$ $[M + Na]^+$ 502.1194, found 502.1203.

**2-ferrocenylmethyl-6-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)piperazin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione(FNB)**

2-ferrocenylmethyl-6-(piperazin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (70mg, 0.15 mmol) and 2-(2-(bromomethyl)phenyl)-4,4,5,5- tetramethyl-1,3,2-dioxaborolane ( 43.4 mg, 0.16 mmol) were dissolved in anhydrous acetonitrile. And $K_2CO_3$ (62.2 mg, 0.45 mmol) was added and the mixture was refluxed overnight. After completion of the reaction, most of the acetonitrile was evaporated and the residue was poured into water to give the precipitate (70 mg, 67%). 1H NMR (300 MHz, $CDCl_3$, ppm): δH 8.45 (dd, J1 = 7.3 Hz, J2 = 1.1 Hz, 1H), 8.37 (t, J = 8.2 Hz, 2H), 7.69 – 7.66 (m, 1H), 7.65 – 7.63(m, 1H), 7.38 (dd, J1 = 7.3 Hz, J2 = 1.5 Hz, 1H), 7.33 – 7.25(m, 2H), 7.16 (d, J = 8.2 Hz, 1H), 5.00 (s, 2H), 4.38 (t, J = 1.8 Hz, 2H), 4.20 (s, 5H), 4.06 (t, J = 1.8 Hz, 2H), 3.77(s, 2H), 3.18 (s, 4H), 2.69 (t, J = 4.6 Hz, 4H), 1.36 (s, 12H). 13C NMR (75 MHz, $CDCl_3$, ppm): δC 163.6, 163.0, 156.0, 143.9, 135.0, 132.7, 131.1, 131.0, 130.3, 129.5, 129.4, 126.8, 126.4, 125.5, 122.8, 115.6, 115.3, 83.8, 83.4, 70.0, 69.0, 67.9, 61.6, 52.9, 52.7, 25.2. HRMS (ESI μTOF) m/z calcd for $C_{40}H_{42}N_3O_4BFe$ $[M + Na]^+$ 718.2515, found 718.2559.

## Reference

1. W. Zhu, L. Song, Y. Yang and H. Tian, *Chemistry-A European Journal*, 2012, 18, 13388-13394.

## 2. fluorescent Test of FNB for L-Ascorbic acid Sodium salt (LAS)

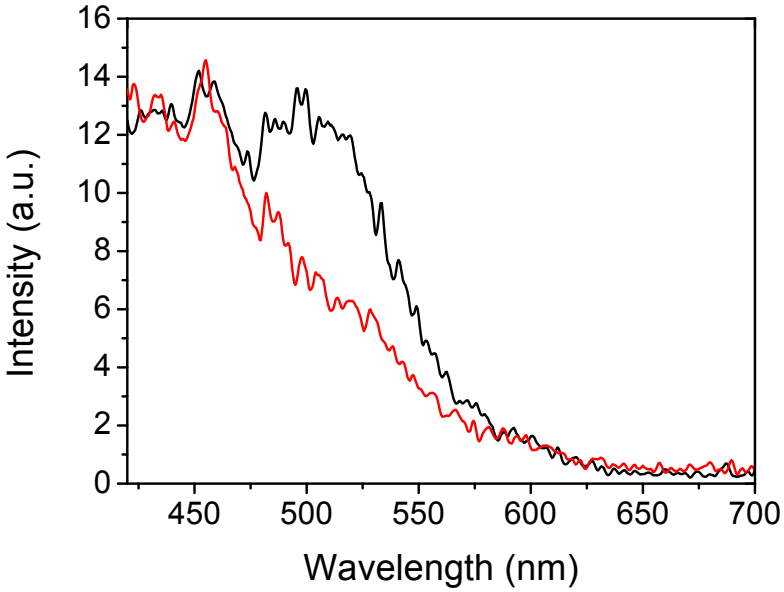


**Figure S1.** Emission spectra of FNB (10 μM) in THF upon titration of L-Ascorbic acid Sodium salt (LAS) by $\lambda_{ex}$ = 403 nm (0, 10.0 equiv.)

## 3. Fluorescent test of FNB for fluoride

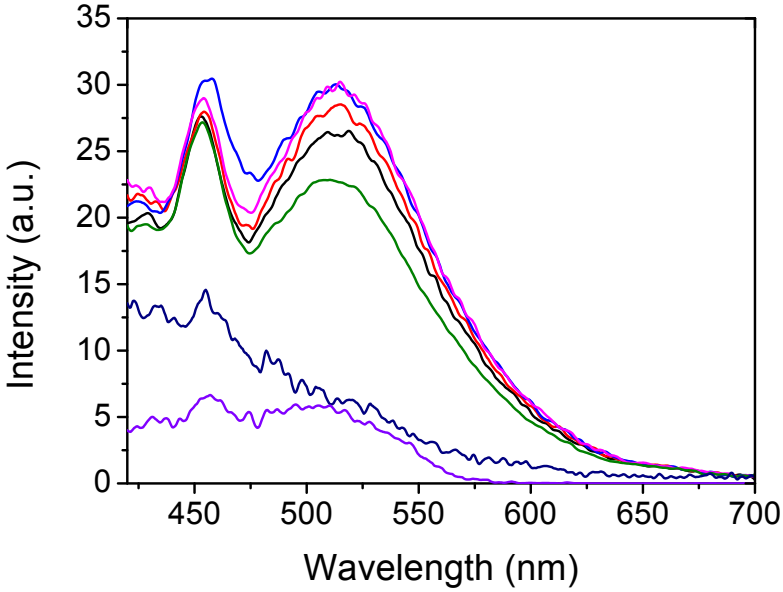


**Figure S2.** Emission spectra of FNB (10 μM) in THF upon titration of $F^-$ by $\lambda_{ex}$ = 403 nm (0, 1, 3, 5, 7, 8, 10.0 equiv.)

## 4. Fluorescent test of 20 μM FNB for $Fe^{3+}$ titration in presence of 20 μM $F^-$

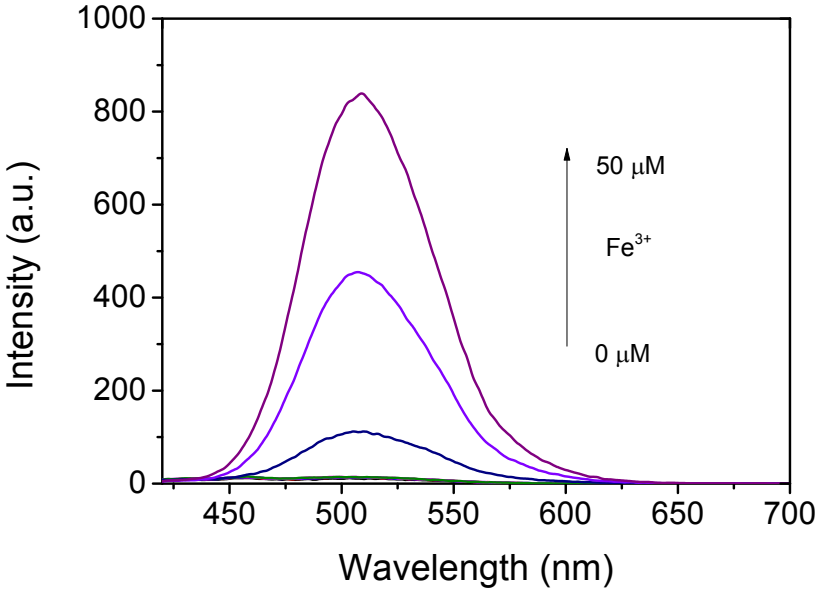


**Figure S3.** Fluorescent spectra of **FNB** (THF, 20 μM, λex = 403 nm) in the presence of 20μM $F^-$ upon the addition of various $Fe^{3+}$ (0, 2, 5, 10, 20, 30, 50 μM)

## 5. Fluorescent test of 2 for $Fe^{3+}$ with and without $F^-$

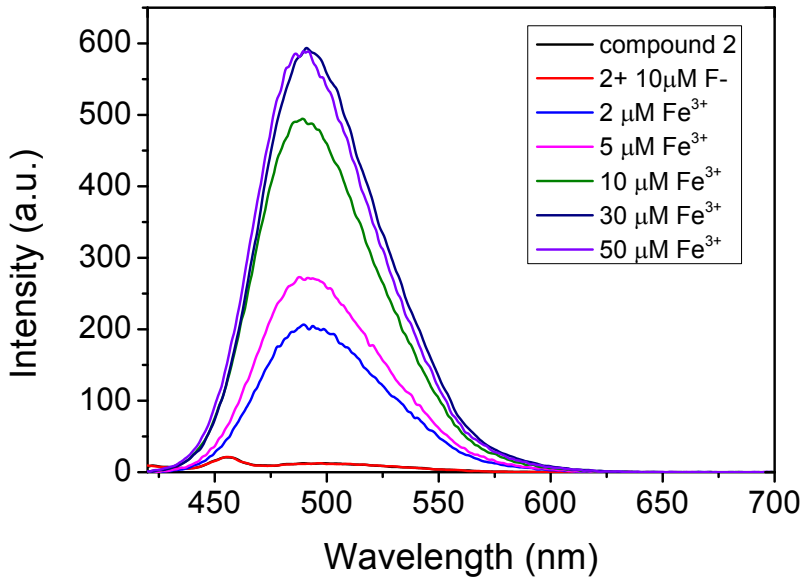


**Figure S4.** Fluorescent spectra of **2** (THF, 10 μM, λex = 403 nm) and **2** with 10 μM $F^-$ upon the addition of various $Fe^{3+}$ (0,2, 5, 10, 30, 50 μM)

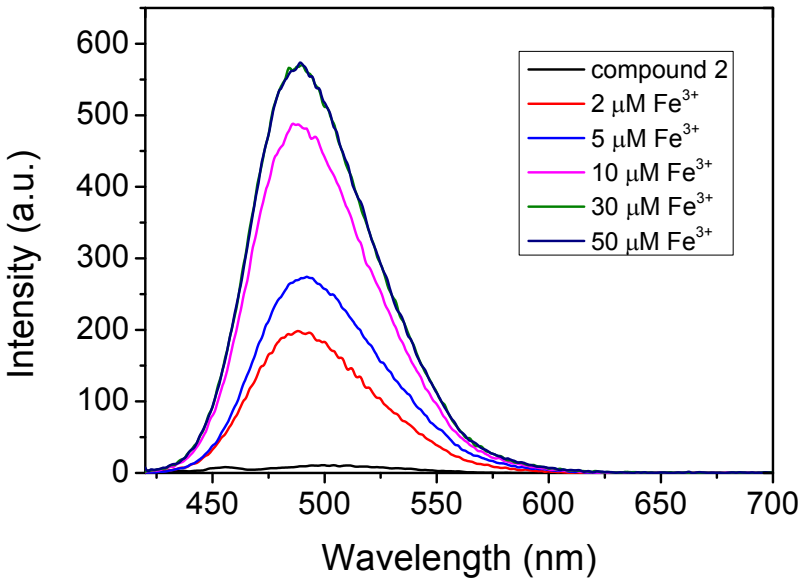


**Figure S5.** Fluorescent spectra of **2** (THF, 10 μM, λex = 403 nm) upon the addition of various $Fe^{3+}$ (0,2, 5, 10, 30, 50 μM)

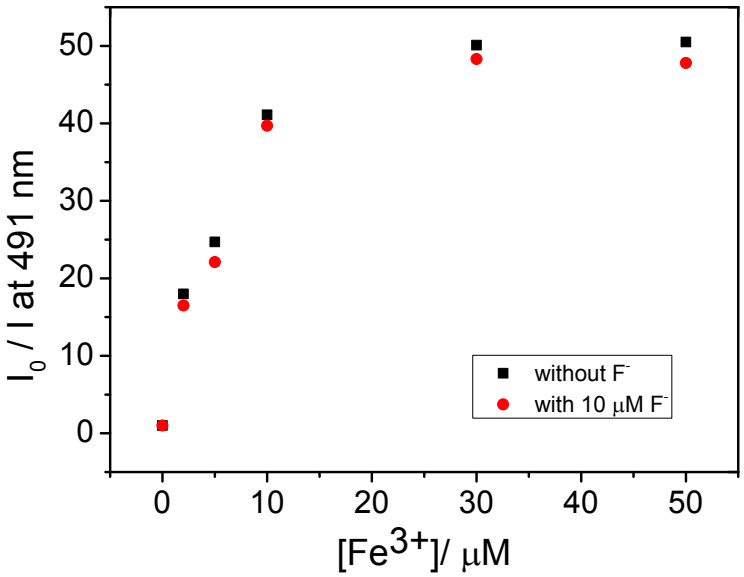


**Figure S6.** The values of $I/I_0$ at 491 nm upon the addition of various $Fe^{3+}$ (0, 2, 5, 10, 30, 50 μM) with and without 10μM $F^-$

## 6. Proposed schematic mechanism on PET and fluoride binding process and logic symbol schemes.

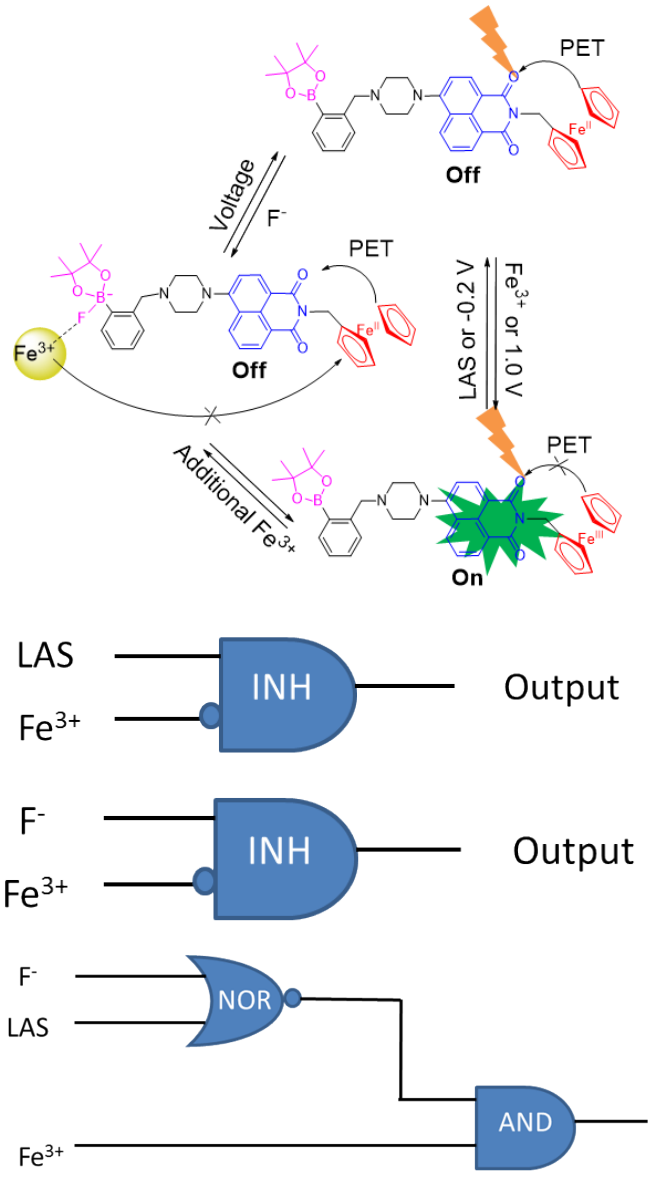


**Figure S7.** Proposed schematic mechanism on PET and fluoride binding process and the schemes with logic symbols and the assignment of the chemicals to each of these inputs corresponding to Figure 3a, b, c in the text.

## 7. Conjugating the FNB with polymeric carbohydrates

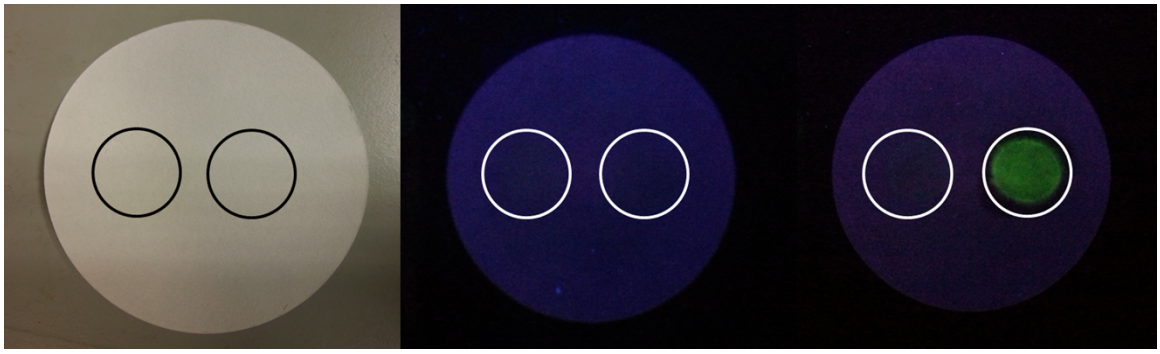

**Figure S8.** The photos were taken under day light and $UV_{365}$.a) Two drops of 10 μL FNB solution were dropped on filter paper in the black circle; b) No fluorescence can be seen under UV in the white circles; c) After dropping 10 μL $Fe^{3+}$ solution on the right spot, green fluorescence can be seen under UV in the right circle.

## 8. Fluorescent test of FNB for $Fe^{3+}$, $F^-$ and L-Ascorbic acid Sodium salt (LAS)

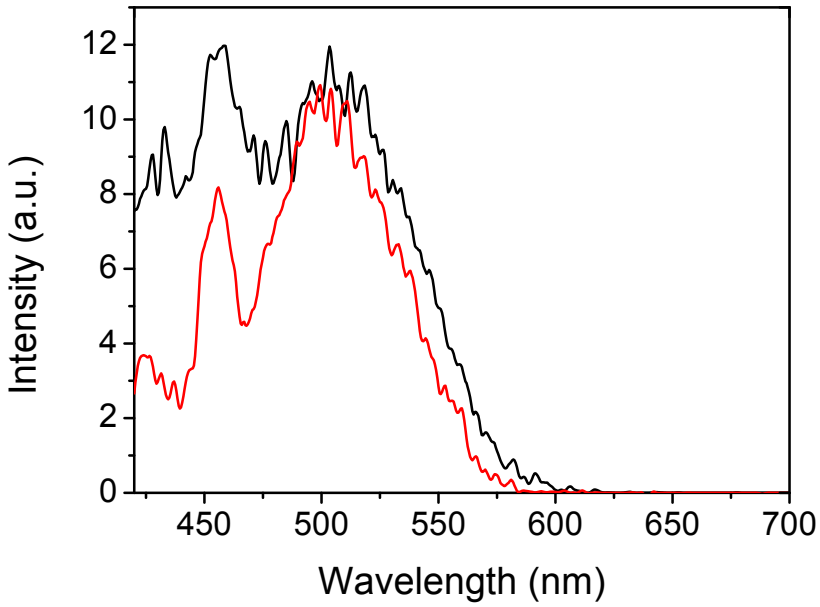


**Figure S9.** Fluorescent spectra of **FNB** (THF, 10 μM, λex = 403 nm) and FNB in the presence of 10 μM $F^-$, 10 $Fe^{3+}$ μM and 20μM LAS.

## 9. pH titration of FNB

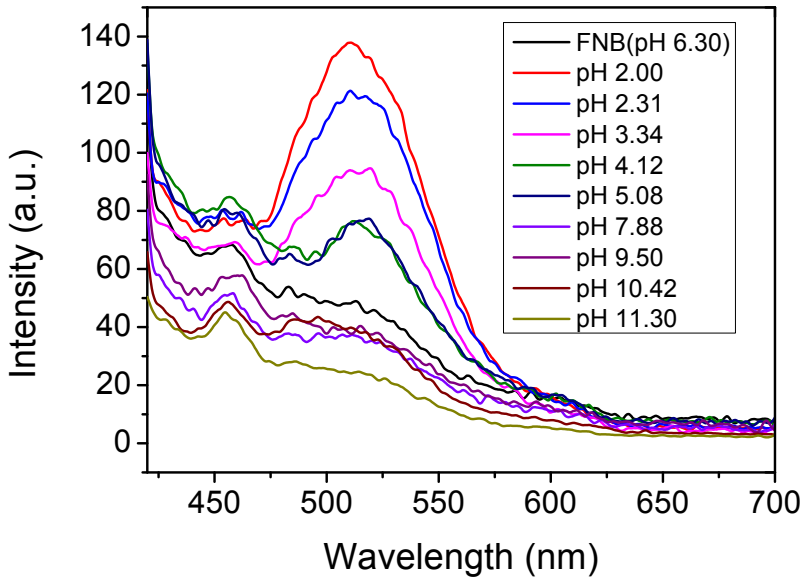


**Figure S10.** Fluorescent spectra of **FNB** (containing 52.1% methanol with 0.05 M NaCl in water solution, 10 μM, λex = 403 nm) at different pH.

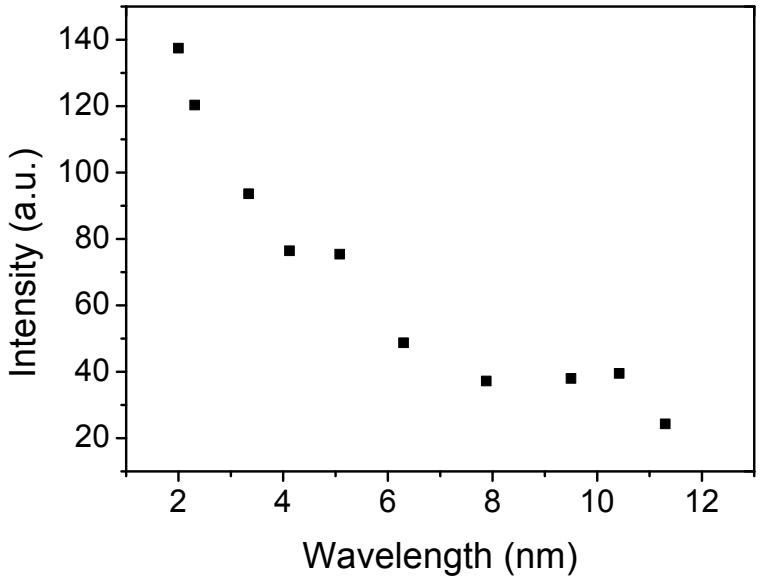


**Figure S11.** The values of intensity at 512 nm at different pH.

**10. pH titration of FNB with 50 mM fructose**

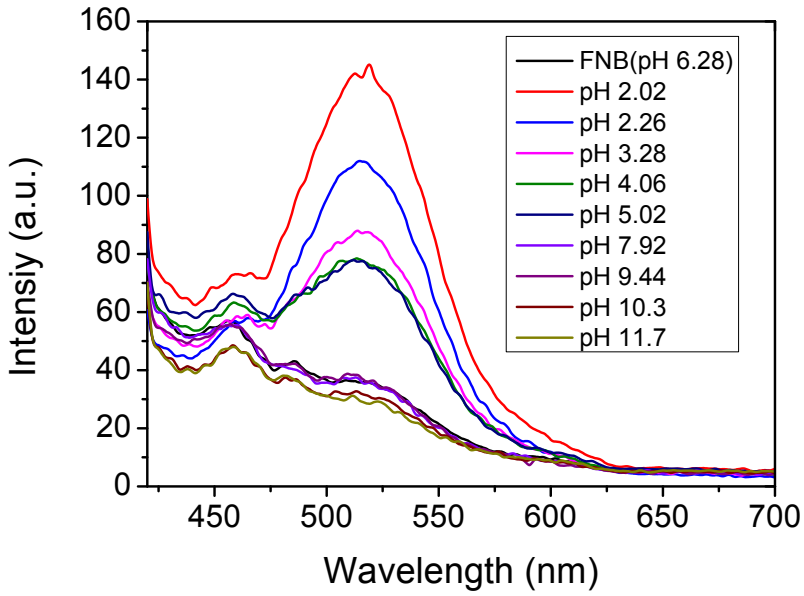


**Figure S12.** Fluorescent spectra of **FNB** (containing 52.1% methanol with 0.05 M NaCl in water solution, 10 μM, λex = 403 nm) with 50 mM fructose at different pH.

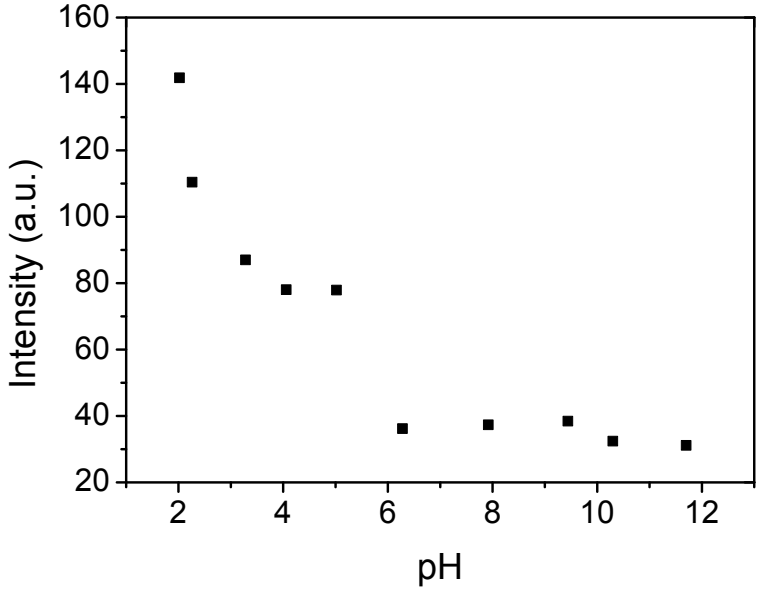


**Figure S13.** The values of intensity at 512 nm at different pH.

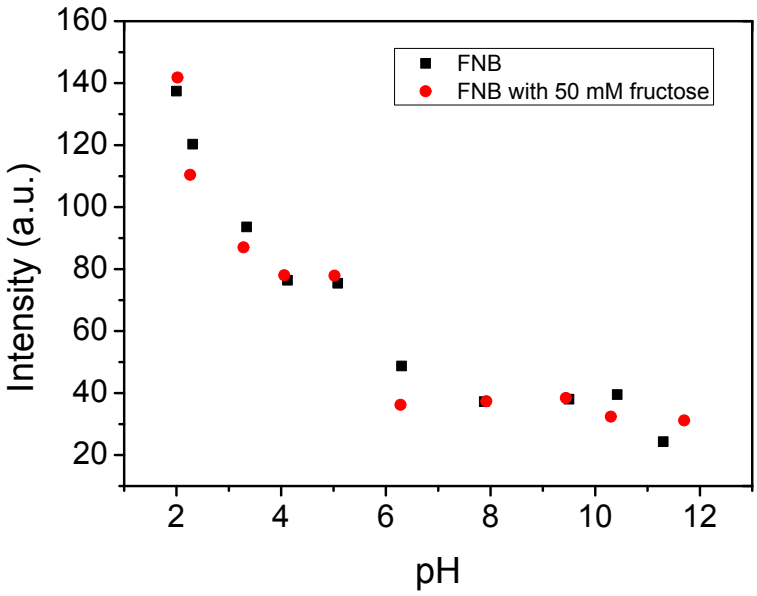


**Figure S14.** The Comparison of pH titrations of FNB without and with 50 mM fructose.

## 11. Electrochemical studies on detection of fluoride

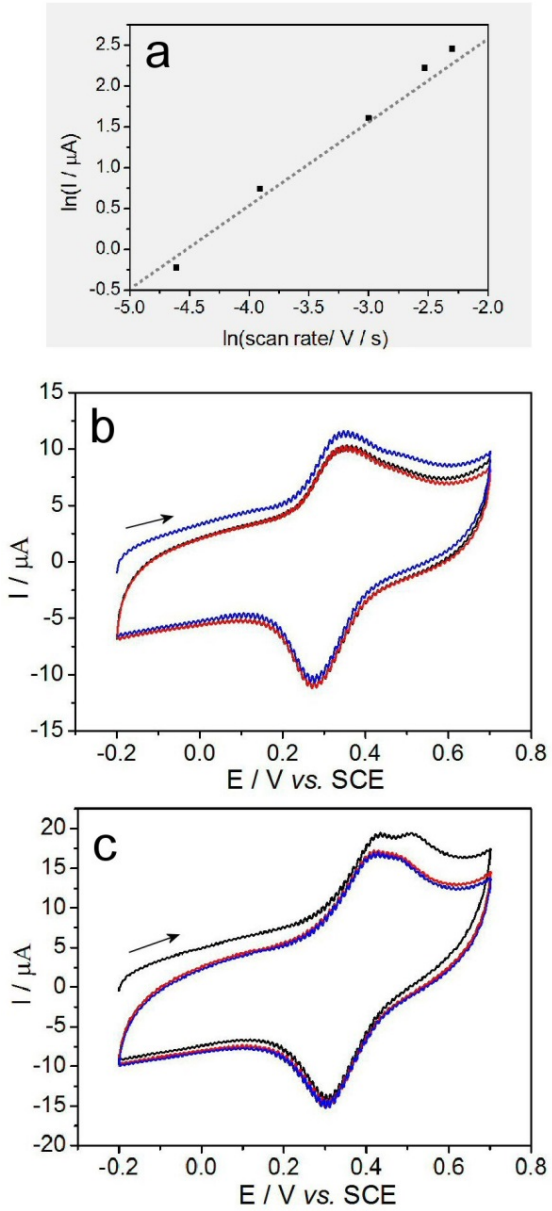


**Figure S15.** a) Plot of current peaks versus scan rates (10, 20, 50, 80, 100 mV s-1) for 0.36 μg FNB immobilised at a graphite electrode surface and immersed in 0.1 M $NaClO_4$; b) First three scans of cyclic voltammograms (scan rate 50 mV s-1) for 0.36 μg FNB immobilised at graphite electrode and immersed in 0.1 M $NaClO_4$; c) First three scans of cyclic voltammograms (scan rate 50 mV s-1) for 0.36 μg FNB immobilised at graphite electrode and immersed in 0.1 M $NaClO_4$ with the addition of 0.1 M NaF.

## 12. Electrochemical studies on different anions

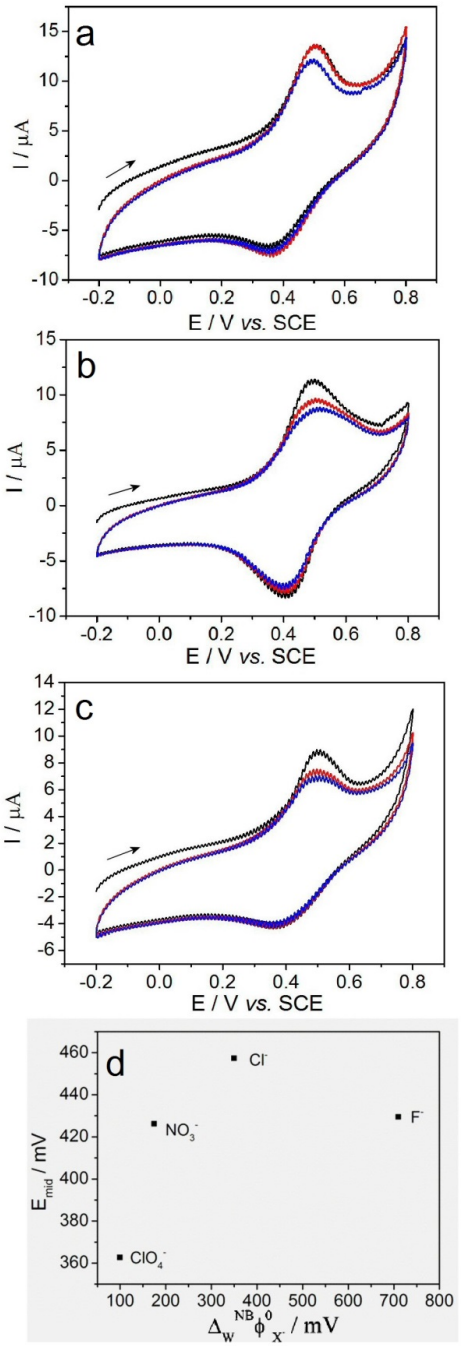


**Figure S16.** a)-c) First three scans of cyclic voltammograms (scan rate 50 mV s-1) for 0.36 μg FNB immobilised at graphite electrode and immersed in 0.1 M $NaNO_3$, NaCl, NaF solutons; d) Plot of formal potentials of the first oxidation step for FNB in the presence of different electrolyte anions versus the standard membrane potentials.

## 13. $^{1}$H NMR and $^{13}$C NMR spectra

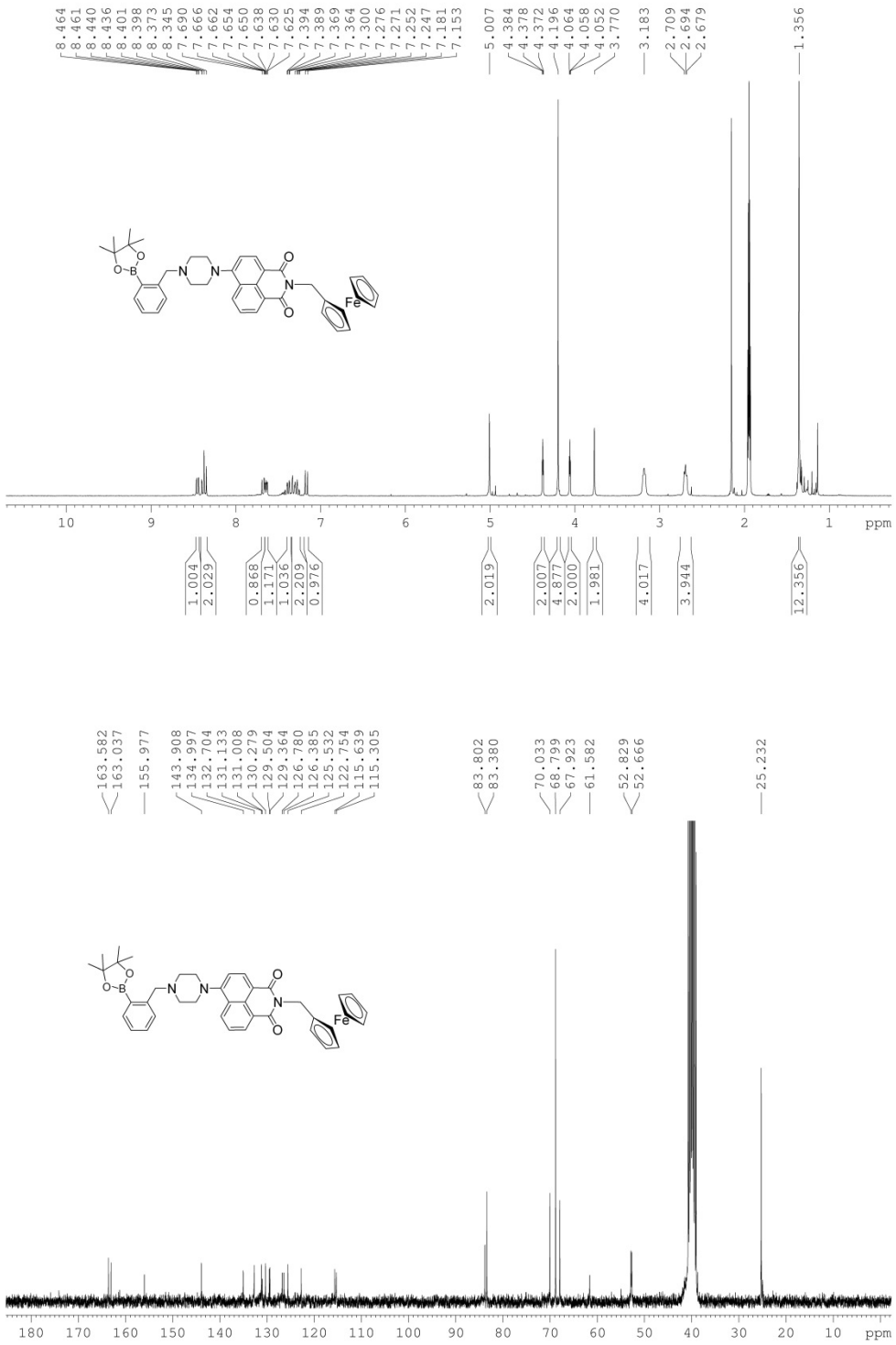


**Figure S17. $^{1}$H NMR and $^{13}$C NMR spectra of FNB**