SELECTIVE DETECTION OF FLUORIDE BASED ON A PYRIDINIUM N-PHENOLATE-CALIX[4]PYRROLE DISPLACEMENT ASSAY: AN UNDERGRADUATE LABORATORY EXPERIMENT

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Figure 1S. $^1$H NMR spectrum of compound 1 in CDCl$_3$ (400 MHz)

Figure 2S. $^{13}$C NMR spectrum of compound 1 in CDCl$_3$ (100 MHz)

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Figure 3S. $^1$H NMR spectrum of compound 4 in DMSO–d$_6$ (400 MHz)

Figure 4S. $^{13}$C NMR spectrum of compound 4 in DMSO–d$_6$ (100 MHz)

Figure 5S. $^1$H NMR spectrum of compound 5 in DMSO–d$_6$ (400 MHz)

Figure 6S. $^{13}$C NMR spectrum of compound 5 in DMSO–d$_6$ (100 MHz)
Figure 7S. $^1\text{H}$ NMR spectrum of compound 3 in DMSO–d$_6$ (400 MHz)

Figure 8S. $^{13}\text{C}$ NMR spectrum of compound 3 in DMSO–d$_6$ (100 MHz)

Figure 9S. (A) Solutions in acetonitrile and (B) UV–vis spectra of (a) 1, (b) 2, and (c) 1+2. The concentrations of 1 and 2 were $6.2 \times 10^{-5}$ and $4.1 \times 10^{-4}$ mol L$^{-1}$, respectively.

Figure 10S. (A) Solutions in acetonitrile and (B) UV–vis spectra of (a) 1, (b) 3, (c) 1:3 complex, and 1:3 complex in the presence of (d) $F^-$, (c anion) = $4.1 \times 10^{-4}$ mol L$^{-1}$. The concentrations of 1 and 3 were $4.1 \times 10^{-4}$ and $2.9 \times 10^{-4}$ mol L$^{-1}$, respectively.

Figure 11S. (A) UV–vis spectra of 3 ($4.0 \times 10^{-5}$ mol L$^{-1}$) in acetonitrile at 25 ºC after addition of increasing amounts of 1. The final concentration of 1 was $3.32 \times 10^{-5}$ mol L$^{-1}$. (B) Titration curve for 3 and 1 in acetonitrile at 25 ºC. Absorbance values were collected at 450.0 nm and the theoretical curve was used for the estimation of the binding constant following a procedure available in the literature$^{12,13}$.

Figure 12S. Mechanism for the synthesis of compound 4
Figure 13S. Mechanism for the synthesis of the pyrilium salt 5 (adapted from ref. 17)

Figure 14S. Mechanism for the synthesis of the protonated form of compound 3
SUGGESTED EXERCISES

1. Write a mechanism for the reaction involved in the formation of compound 1 from acetone and pyrrole in the presence of HCl (hint: pyrrole is extremely reactive towards electrophiles and the intermediate formed from an attack at the C2 position has a greater positive charge delocalization than that resulting from an attack at the C3 position).

2. Postulate the mechanism for the condensation of acetophenone with benzaldehyde in basic media to provide the chalcone 4.

3. Chalcone 4 is isolated as an E-isomer and this can be confirmed by the 'H NMR data. Explain.

4. Suggest a mechanism for the formation of the pyrylium salt 5.

5. Write a mechanism for the formation of the pyridinophenolates 2 and 3 from compound 5 and the corresponding amines.

6. Explain the intermolecular forces that are responsible for the formation of the complex formed between 1 and 3 and for the displacement of 3 from the site of 1 by the presence of fluoride.

7. Why did the interaction between 1 and 2 not occur?

8. Suggest molecular structures of other dyes that could potentially be used to construct an anionic chromogenic chemosensor with 1.