Supporting Information

# Solution and Fluorescence Properties of Symmetric Dipicolylamine-Containing Dichlorofluorescein-Based $Zn^{2+}$ Sensors

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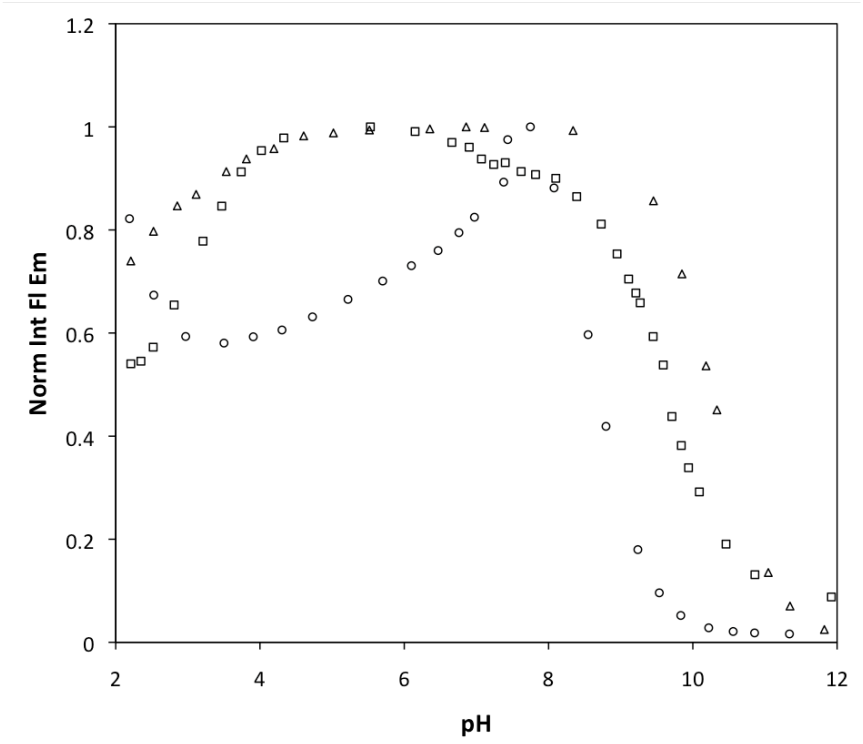


**Figure S1.** Normalized and integrated fluorescence emission of compounds **4** (circles), **5** (squares), and **6** (triangles) over the pH range 2-12. Each solution contains 1.0 μM of the fluorophore and 100 mM KCl as the electrolyte. The fluorescence "turns on" as the pH is lowered due to protonation of the quenching units. The decrease in fluorescence at the lower end of the pH scale is caused by formation of the non-fluorescent lactone isomer. The drop in emission from **4** below pH 8 is due to partial precipitation.

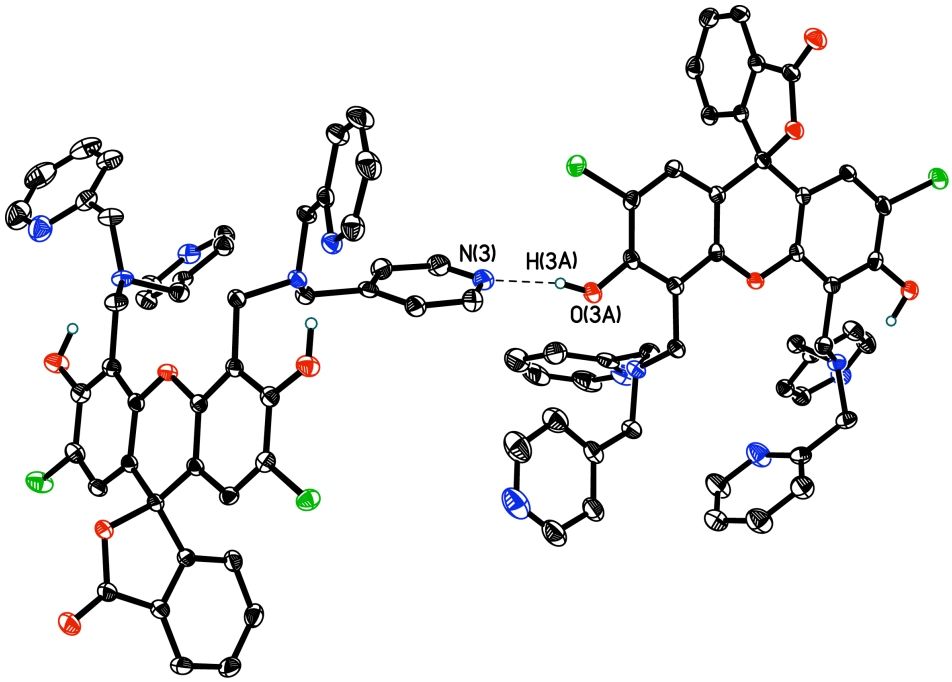


**Figure S2.** ORTEP diagram of the two independent molecules in the structure of **2** (40% probability thermal ellipsoids on all non-hydrogen atoms) showing intermolecular hydrogen bonding (O3A–H3A...N3 = 2.673(3) Å).

**Table S1.** Crystallographic parameters for **1**, **2**, and **6**

| | **1·MeCN·$H_2O$** | **2·MeCN·0.25$H_2O$** | **6** |
|---|---|---|---|
| Empirical formula | $C_{48}H_{41}N_7O_6Cl_2$ | $C_{48}H_{39}N_7O_{5.25}Cl_2$ | $C_{30}H_{32}N_2O_5Cl_2$ |
| Formula weight | 882.78 | 868.76 | 571.48 |
| Crystal System | Triclinic | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| a (Å) | 13.023(3) | 14.766(3) | 10.521(2) |
| b (Å) | 13.385(4) | 14.851(3) | 11.825(3) |
| c (Å) | 14.076(4) | 22.573(4) | 12.749(3) |
| $\alpha$ (deg) | 80.980(4) | 92.659(3) | 90.430(3) |
| $\beta$ (deg) | 86.683(4) | 105.087(2) | 111.283(3) |
| $\gamma$ (deg) | 61.886(3) | 117.641(3) | 111.419(3) |
| V (Å$^3$) | 2136.9(10) | 4152.4(14) | 1357.8(5) |
| Z | 2 | 4 | 2 |
| $\rho_{calc,}$ g/cm$^3$ | 1.372 | 1.390 | 1.398 |
| Temperature (K) | 110 | 110 | 110 |
| $\mu$ (Mo K$\alpha$), mm$^{-1}$ | 0.212 | 0.216 | 0.283 |
| $\theta$ range (deg) | 2.11 to 27.88 | 1.99 to 26.14 | 2.30 to 26.37 |
| Crystal size (mm) | 0.23 x 0.20 x 0.16 | 0.45 x 0.20 x 0.10 | 0.15 x 0.15 x 0.10 |
| Total no. of data | 36729 | 51063 | 21002 |
| No. of unique data | 10110 | 16307 | 5524 |
| Completeness to $\theta$ | 99.2 % | 98.5 % | 99.5 % |
| max, min peaks, e/Å$^3$ | 0.575 and -0.358 | 0.686 and -0.420 | 0.825 and -0.718 |
| Goodness-of-fit on $F^2$ | 1.052 | 1.039 | 1.061 |
| $R_1$ (%)[a] | 4.87 | 5.11 | 4.77 |
| $wR_2$ (%)[b] | 11.92 | 12.61 | 11.66 |

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = \{\sum [(F_o^2-F_c^2)/ \sum [w(F_o^2)^2]\}^{1/2}$

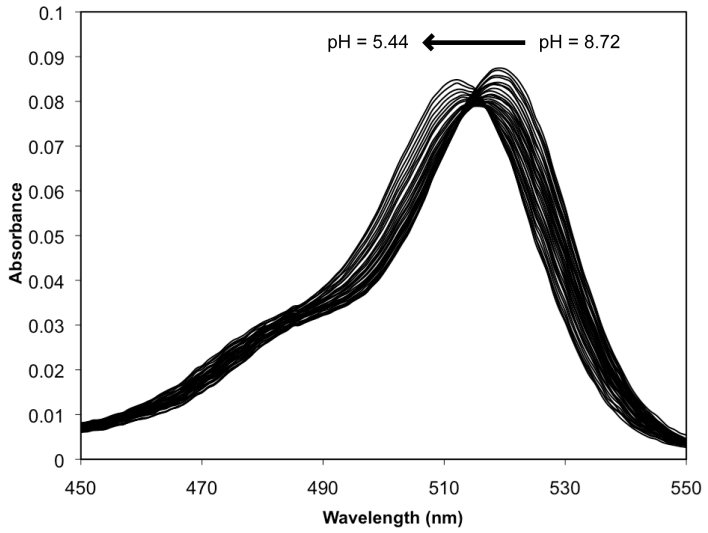


**Figure S3.** Absorbance spectra of a 1.0 μM solution of **2** containing 100 mM KCl over the pH range 8.72-5.44. A hypsochromic shift (519 nm to 512 nm) occurs as the pH is lowered due to protonation of the binding pockets, resulting in reduced conjugation through the π-system of the xanthenone group.

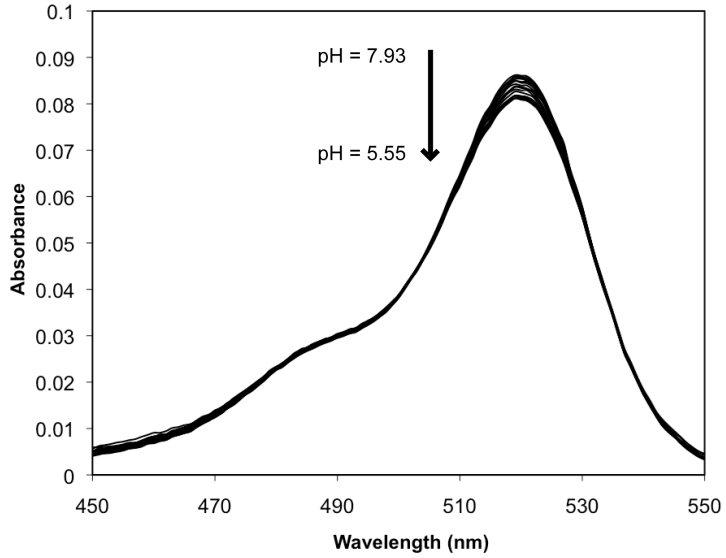


**Figure S4.** Absorbance spectra of a 1.0 μM solution of **3** containing 100 mM KCl over the pH range 7.93-5.55. No wavelength shift occurs as the pH is lowered, only a slight decrease in absorbance. The difference in first proton affinities between the fluorophore (p$K_{a6}$ = 7.02) and the parent amine (p$K_{a3}$ = 6.47) is not very large, therefore the hydrogen bonding interaction with the phenolic oxygen of the absorbing xanthenone moiety is not sufficient to perturb the absorption spectrum.

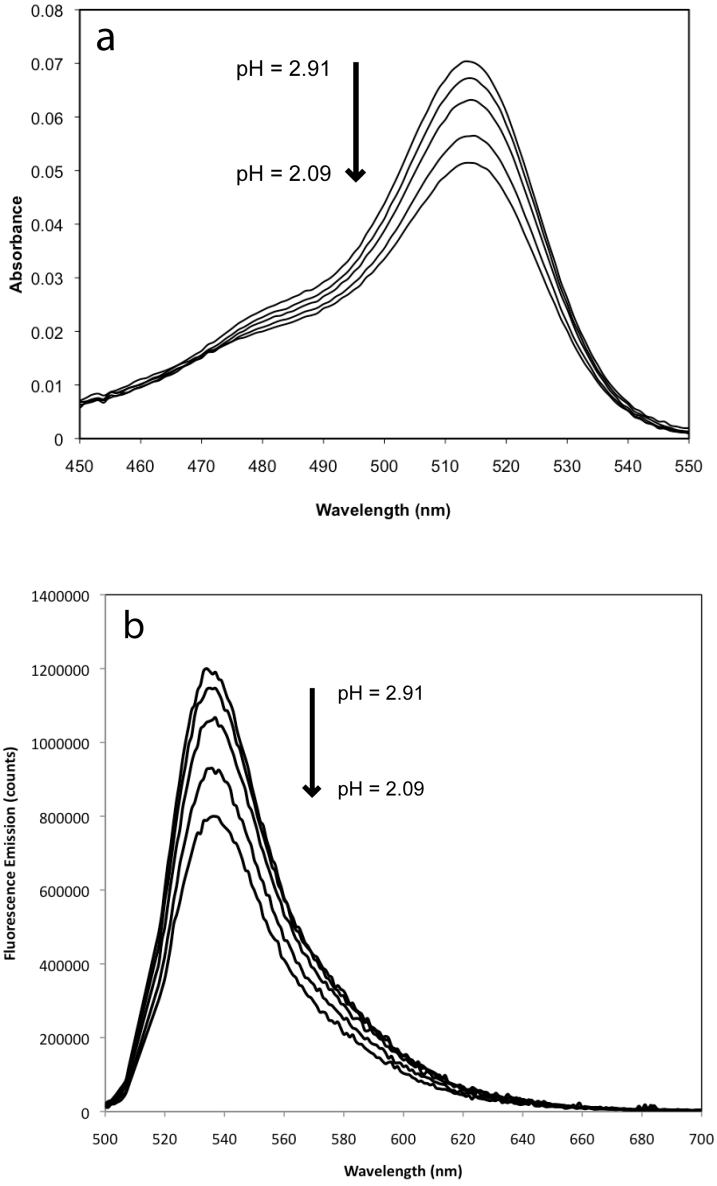


**Figure S5.** Absorbance (a) and fluorescence (b) spectra of a 1.0 μM solution of **1** containing 100 mM KCl over the pH range 2.91-2.09. Both absorbance and emission decrease in unison as the pH is lowered, suggesting formation of the ring-closed lactone isomer.

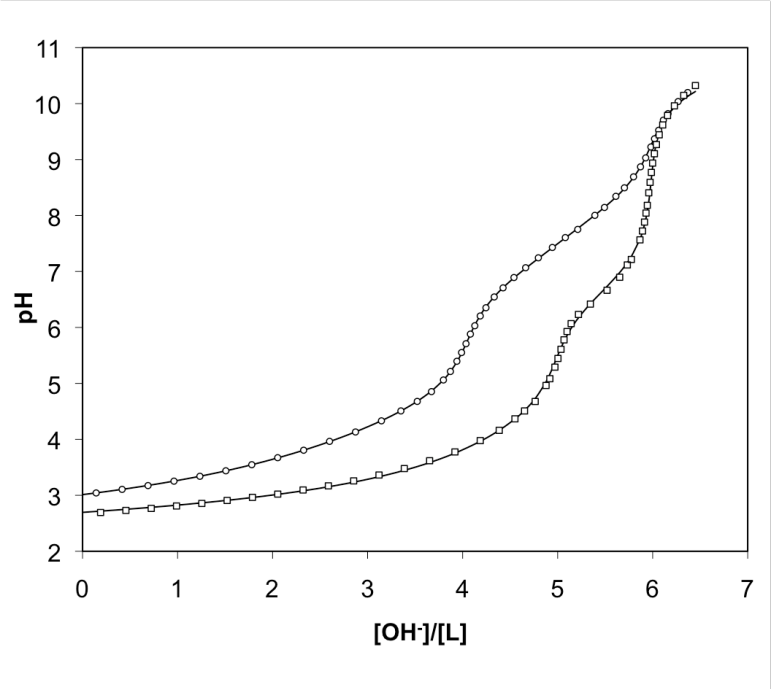


**Figure S6.** Potentiometric titration curves of **1** in the absence of $ZnCl_2$ (circles) and in the presence of 1 equivalent of $ZnCl_2$ (squares) in aqueous solution containing 100 mM KCl at 25 °C. Each trial started with 0.6 mM of the neutral molecule, dissolved in excess HCl. The abscissa is measured in equivalents of base added per mole of ligand. The solid lines overlaying the data points represent model curves from calculated $pK_a$ values.