

## A new chromo-chemodosimeter selective for sulfide anion.

Diego Jiménez, Ramón Martínez-Máñez,\* Félix Sancenón, José V. Ros-Lis, A. Benito, and Juan Soto.

GDDS, Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, E-46071 Valencia (Spain).

### Supporting Information.

#### 1.- Synthesis and characterization of II and III:

Compound III. Compound III was isolated following a similar procedure to that in reference 11 by addition of Na<sub>2</sub>S and HClO<sub>4</sub> to acetone solutions of L<sup>1</sup> at room temperature that resulted in the precipitation of III.

NMR-<sup>1</sup>H (300 MHz, CDCl<sub>3</sub>): 3.18 (6H, s), 6.90 (2H, d, J = 9.3 Hz), 7.63 (6H, m), 7.91 (4H, m), 8.22 (2H, d, J = 9.3 Hz), 8.50 (2H, s). HRMS (EI) m/z calc for C<sub>25</sub>H<sub>22</sub>NS: 368.147297, found 368.147266. UV-vis (acetonitrile)  $\lambda_{\max}$  [nm] (log  $\epsilon$ ) 585 (4.72).

Compound II. The reaction of II to give III in organic solutions was found to be fast (in some few minutes a significant amount of III was found) and therefore II was not isolated but characterized by NMR after reaction of L<sup>1</sup> with the sulfide anion. <sup>1</sup>H NMR of II is fully consistent with the proposed formulation. NMR-<sup>1</sup>H (300 MHz, CDCl<sub>3</sub>): 3.00 (6H, s), 5.76 (1H, s), 6.78 (1H, d, J = 8.4 Hz), 6.99 (1H, s), 7.30-7.48 (1H, d, J = 7.8 Hz), 7.50 (1H, d, J = 8.4 Hz), 7.71 (1H, d, J = 7.8 Hz), 7.77 (1H, d, J = 7.8 Hz).

#### 2.- pH effect on the ability of the sensor.

L<sup>1</sup> could be used for the determination of the anion sulfide at pH higher than 7.5 – 8. For instance, addition of sodium sulfide to L<sup>1</sup> solutions buffered at pH 6 resulted in no color change. This is surely related with the protonation chemistry of the sulfide anion. At pH lower than ca. 7 the hydrogen sulfide anion suffers protonation to give the volatile and less nucleophilic sulfidric acid.

#### 3.- Competition assays using L<sup>1</sup>.

Compound I and similar derivatives have been reported by us to sense certain anions such as ATP, sulfate and tweezers-like carboxylates in acetonitrile:water mixtures because their ability to interact with the I-L<sup>1</sup> system and to induce cyclization from I to L<sup>1</sup>. Additionally, the reaction of L<sup>1</sup> with the sulfide anion probably takes place via a nucleophilic attack and therefore other potentially water present nucleophiles such as cyanide and amines were also tested as potential interfering species. The

competition assays were carried out in an individual fashion; different quantities (10, 20 and 30 equivalents) of the individual interfering species were added to a solution of receptor  $L^1$  (acetonitrile-water 1:1 v/v mixture buffered at pH 9.0) and then 30 equivalents of the sulfide anion and acid (30  $\mu$ L of  $H_2SO_4$  30%) were added. The anions, chloride, bromide, iodide, acetate, benzoate, phosphate, sulfate, nitrate, ATP, oxalate, cyanide and amines were tested in competition assays. Interference in the determination of sulfide was found in the presence of ca. 30 equivalents of ATP, oxalate or sulfate. Additionally, we found that cyanide also produced partial ring opening at pH 9 in acetonitrile:water solutions and gave color changes from magenta to yellow. In a similar manner, primary aliphatic amines partially transformed the pyrylium ring into a pyridinium one giving also color variation from magenta to yellow. In all those cases, the presence of the interfering species resulted in a less pronounced color change from magenta to blue in solutions containing the sulfide anion.