

## Chromo-fluorogenic sensing of pyrophosphate in aqueous media using silica functionalised with binding and reactive units.

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### General methods.

TG analysis, IR spectroscopy, elemental analysis, and UV-visible spectroscopy techniques were employed to characterize the materials obtained. Thermo-gravimetric analyses were carried out on a TGA/SDTA 851e Mettler Toledo balance, using an oxidant atmosphere (Air, 80 mL/min) with a heating program consisting of a ramp of 10 °C per minute from 393 K to 1273 K. IR spectra were recorded on a Jasco FT/IR-460 Plus between 400 and 4000 (cm<sup>-1</sup>) diluting the solids in KBr pellets. UV-visible spectroscopy was carried out with a Lambda 35 UV/Vis Spectrometer (Perkin Elmer Instruments). Nonporous amorphous Fumed silica, with a surface area of ca. 200 m<sup>2</sup>/g was provided by Aldrich. The organosiloxane derivatives 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane and 3-mercaptopropyltrimethoxysilane for the synthesis of the solids **S1** and **S1-SH** were provided by Aldrich.

### Synthesis of S1.

In a typical synthesis, 1.00 g of activated Silica Fumed was suspended in 50 mL of anhydrous acetonitrile inside a round-bottomed flask connected to a Dean–Stark (trap) apparatus in an inert atmosphere. The suspension was refluxed (110 °C) in azeotropic distillation collecting 20 mL in the trap in order to remove the adsorbed water. After this, 0.94 mmol of 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (**N3TS**) and 14.06 mmol of mercaptopropyltriethoxysilane (**MPTS**) were added to the silica suspension at room temperature. The mixture was stirred for 5.5 h. Finally, the solid **S1** was filtered off, washed with 30 ml of CH<sub>3</sub>CN and dried at 70 °C for 12 h.

### Squaraine-solid interaction studies.

9 mg of **S1** were suspended in 13.5 ml of water:acetonitrile 90:10 v/v mixtures containing a certain concentration of a given anion and then to the mixture 1.5 mL of a solution of squaraine **I** ( $C_{\text{squaraine}} = 5 \times 10^{-5} \text{ mol dm}^{-3}$ ) was added. After 15 minutes the mixture was filtered and the absorbance in the solution of the squaraine band measured. The reaction of the squaraine dye with the solid was monitored via changes in the squaraine band centered at 641 nm.

### Materials characterization.

Solid **S1** was characterized using standard procedures. The infrared spectra of the solid **S1** shows expected features for functionalised silica derivatives, i.e., intense bands due to the silica matrix (1250, 1087, 802, 462 cm<sup>-1</sup>), vibrations of water molecules (3420 and 1620 cm<sup>-1</sup>) and vibrations of C–H bonds at 2954–2850 cm<sup>-1</sup> from the anchored organic moieties.

The degree of functionalization was determined by elemental analysis and thermogravimetric studies for **S1**. From elemental analysis of C, H, N, S it is possible to determine the amount of thiol and amine groups contained in the materials calculated in millimole per gram of SiO<sub>2</sub> (mmol g<sup>-1</sup> SiO<sub>2</sub>) using equation 1:

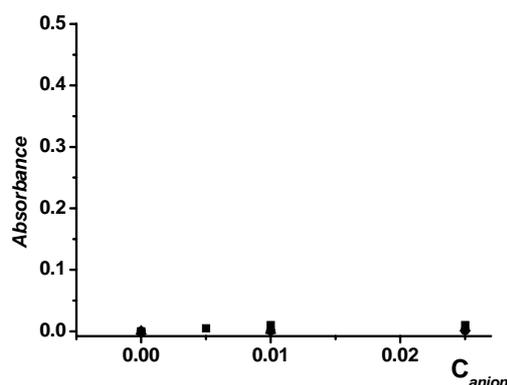
$$\alpha_A = \frac{\Delta W_i \% \times 1000}{\Delta W_{SiO_2} \% \times n M_i} \quad (1)$$

where  $\Delta W_i\%$  ( $i = C, N, S$ ) are the weight percentages of carbon, nitrogen or sulfur,  $M_i$  is the corresponding atomic weight and  $n$  is the number of the corresponding atom type in one molecule.  $\Delta W_{SiO_2}\%$  is the inorganic  $SiO_2$  content in weight percentage. The values of organic content as millimole of thiol (**MPTS**) and tri-amine (**N3TS**) per gram of  $SiO_2$  for the solids **S1** were found to be 0.089 and 0.343, respectively.

Taking into account these contents and the value of the specific surface of the silica fumed support ( $200 \text{ m}^2 \text{ g}^{-1}$ ), the average coverage ( $\beta_A$  in groups per  $\text{nm}^2$ ) of the surface of the solids **S1** by thiol and triamine groups was calculated by equation (2)

$$\beta_A = \alpha_A \times 10^{-3} \times S^{-1} \times 10^{-18} \times N_A = \alpha_A \times S^{-1} \times 602.3 \quad (2)$$

In which  $\alpha_A$  is the thiol or the triamine content ( $\text{mmol g}^{-1} \text{ SiO}_2$ ),  $S$  the specific surface ( $200 \text{ m}^2 \text{ g}^{-1}$ ) of the non-functionalized silica support and  $N_A$  Avogadro's number. From these data and equation 2 a surface coverage of  $1.20 \text{ molecules nm}^{-2}$  was calculated for the **S1** solids resulting in an average distance between anchored molecules of ca.  $9.15 \text{ \AA}$ . In more detail, for instance solid **S1** contains  $1.20 \text{ molecules nm}^{-2}$  of which 0.95 and 0.25 are of **N3TS** and **MPTS** respectively.



**Figure S1.** Absorbance at 643 nm (squaraine band) vs concentration of pyrophosphate, phosphate, sulfate, nitrate, chloride and perchlorate at pH 7 for solid **S1** in water/acetonitrile 90:10 v/v.