

## Hybrid materials with nanoscopic anion-binding pockets for the colorimetric sensing of phosphate in water using displacement assays.

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### Chemicals

The products tetraethylorthosilicate (TEOS), *n*-cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), triethanolamine (TEAH<sub>3</sub>) and all the anions used in this manuscript were provided by Aldrich and used as received.

### Synthesis of the mesoporous UVM-7 support (MCM41-type material).

The synthesis strategy we have used to prepare UVM-7 and hybrid related organosilicas is an application of the so-called “atrane route”, a simple preparative technique based on the use of complexes that include triethanolamine(TEAH<sub>3</sub>)-related ligands (i.e. in general “atranes” and silatranes for the silicon containing complexes) as hydrolytic inorganic precursors and surfactants as porogen species. Then, the molar ratio of the reagents in the mother liquor was fixed to 7 TEAH<sub>3</sub>:2 TEOS:0.52 CTAB:180 H<sub>2</sub>O for the synthesis of **UVM-7**. The mixture was heated to 140 °C to remove ethanol formed during the formation of the atrane complexes by distillation. Then the mixture was cooled to 90 °C and cetyltrimethylammonium bromide (CTAB) was slowly added. Finally the corresponding amount of water was added and the mixture was subsequently aged at room temperature for 24 h. The resulting powder was collected by filtration, washed with water and ethanol and dried in air. The surfactant was removed by calcination at 550°C for 5 hours.

### Synthesis of the amine derivative S1.

The calcinated material (UVM-7) was first activated in a ethanol/HCl 1M solution. 3 g of templated-free **UVM-7** activated material was suspended in 300 ml of anhydrous toluene and heated at 110 °C in a Dean-Stark in order to remove the adsorbed water by azeotropic distillation under inert atmosphere (Ar atmosphere). Then a large excess of 3-(aminopropyl)triethoxysilane (10-5 ml, 44.7 mmol) was added to the suspension at room temperature and stirred for 16 hours at 100 °C in reflux system. The final solid (**S1**) was filtered off, meticulously washed with toluene and acetone and dried at 60 °C for at least 12 hours.

### Synthesis of the dye-containing solids S1-2, S1-2 and S1-3.

The amine-functionalised solid **S1** (1 g) was suspended in 100 ml of water at pH 7.5 and the corresponding dye added (0.69 g, 0.4 g or 0.67 g of methyl red, carboxyfluorescein, or methylthymol blue, respectively) at room temperature. The mixture was stirred for 24 hours to yield the corresponding solids **S1-1**, **S1-2** and **S1-3** that were isolated by filtration and exhaustively washed with water until no elimination of the dye was observed. The solids remained stable for at least two months without apparent degradation of the dyes.

For the sake of comparison, and as a control solid, a similar material was prepared using as support a non-mesoporous silica (fumed silica). The procedure was the same as described above but using in this case silica gel and carboxyfluorescein as dye. The final product (**SG-2**) was filtered, washed and dried at 70 °C for 12 hours. This solid consists of a “flat” surface (i.e.

without the presence of mesopores) with anchored amine groups and a certain amount of adsorbed dye.

### **General Techniques and characterization**

XRD, TG analysis, IR spectroscopy, elemental analysis, TEM microscopy, N<sub>2</sub> adsorption-desorption, UV-visible spectrophotometer techniques were employed to characterize the materials. X-ray measurements were performed on a Seifert 3000TT diffractometer using Cu K $\alpha$  radiation. Thermo-gravimetric analysis were carried out on a TGA/SDTA 851e Mettler Toledo balance, using an oxidant atmosphere (Air, 80 mL/min) with a heating program consisting on a heating ramp of 10 °C per minute from 393 K to 1273 K and an isothermal heating step at this temperature during 30 minutes. 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. N<sub>2</sub> adsorption-desorption isotherms were recorded on a Micromeritics ASAP2010 automated sorption analyser. The samples were degassed at 120 °C in vacuum overnight. The specific surfaces areas were calculated from the adsorption data in the low pressures range using the BET model. Pore sized was determined following the BJH method. UV-visible spectroscopy was carried out with a Lambda 35 UV/Vis Spectrometer Perkin Elmer Instruments.

The thermal analysis of the **S1-1**, **S1-2** and **S1-3** solids showed three well defined steps; (i) a first weight loss between 25 and 150 °C related with the elimination of solvent molecules, (ii) a second step, between 150 and 800 °C due to the combustion of the organics groups (the propyl-amino groups and the corresponding dye) and (iii) a final weight loss in the ca. 800 - 1000 °C range attributed to the condensation of the silanol groups.

The powder X-ray diffraction patterns of the obtained for these solids (see Figure 1 in the paper) show the characteristic intense peak at ca.  $2\theta = 2^\circ$  (indexed to the (100) reflection assuming the existence of a MCM-41-like hexagonal cell) of a surfactant-assisted mesoporous material, indicating that the different synthetic steps did not affect to a large extent the structure of the silica matrix. In addition to this intense peak, we can observe in those structures with better contrast (lower amount of organics) a wide and small signal that could be assigned to the overlapped (110) and (200) reflections of the typical hexagonal cell. This feature can be associated to an intraparticle porous topology characteristic of MCM-41-like disordered hexagonal silicas. The bimodal pore array of **UVM-7**-like solids is additionally appreciated through TEM images (see Figure 2 in the paper) and porosimetry measurements (see below).

The N<sub>2</sub> adsorption-desorption isotherm of the **S1** material shows a typical curve for these mesoporous solids and it is similar to the curve observed for the parent **UVM-7** material. The isotherm is characterised by two adsorption steps at intermediate and high  $P/P_0$  values related with the bimodal pore system. The first step corresponds to the nitrogen condensation inside the mesopores by capillarity (pore size: 2.4 nm and pore volume 0.72 cc/g), whereas the second one corresponds to the nitrogen condensation inside the interparticle pores (textural porosity, pore size: 41.1 nm and ore volume 0.68 cc/g). The application of the BET model resulted in a value for the total specific surface of 870 m<sup>2</sup>/g for **S1**. Additionally, the interaction of the dyes with **S1** to yield the sensory materials **S1-1**, **S1-2** and **S1-3** resulted in a considerable reduction of the total specific surface to ca. 300 m<sup>2</sup>/g as consequence of the inclusion of the dyes into the pores.

The infrared spectrum of **S1-1**, **S1-2** and **S1-3** solids show strong bands due to the silica matrix (c.a. at 1250, 1087, 802 and 462 cm<sup>-1</sup>) and relatively medium and small bands due to the organic loaded molecules (the methyl red, carboxyfluorescein, or methylthymol blue dyes) such as for instance at ca. 1620 and 1400 cm<sup>-1</sup> assignable to the carboxylate groups.

Several **S1** and **S1-1**, **S1-2**, **S1-3** materials were prepared and their content in amine groups and imidazolium groups and methyl red, carboxyfluorescein, or methylthymol blue dyes were determined from elemental analysis and thermal analysis. From the different prepared solids an

average value of 0.175 mol amine/mol SiO<sub>2</sub> and dye contents in the 0.05 - 0.1 dye/SiO<sub>2</sub> mol/mol range were determined.

### *Competitive adsorption of dyes on S1*

In order to better understand the different displacement observed for 5-carboxyfluorescein and methylthymol blue (see article), competitive assays of adsorption of these dyes on the amine-functionalised material **S1** were carried out. In a typical assay, 100 mg of solid **S1** were suspended in 100 mL of an aqueous solution at pH 7.5 (HEPES 0.01 mol dm<sup>3</sup>) containing a mixture of both dyes; 5-carboxyfluorescein and methylthymol blue at a concentration of  $2 \times 10^{-5}$  mol dm<sup>3</sup>. Adsorption of the dyes on **S1** was followed by simple monitorization of the corresponding visible band of the dyes in the solution. Under these experimental conditions, the percentages of adsorption on **S1** of 5-carboxyfluorescein and methylthymol blue were 21 % and 55 % respectively. This shows that methylthymol blue is preferentially adsorbed on the amine-functionalised **S1** material. In additional experiments (not shown) the adsorption constants (K) for 5-carboxyfluorescein and methylthymol blue were determined using a Langmuir adsorption model and values of log K of 3.57 and 4.74 were obtained respectively. The stronger interaction of methylthymol blue with the mesoporous-functionalised surface is in agreement with the experimental data that shows that 5-carboxyfluorescein (solid **S1-2**) is displaced more efficiently than methylthymol blue (solid **S1-3**) in the presence of phosphate.