Towards the development of ionically-controlled nanoscopic molecular gates.

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Supporting Information

Synthesis of the solids S1, S2 and S3.

**Synthesis of S1.** 2g of as-synthesized S3 solid (before removal of the template) was suspended in a solution containing 100 ml of toluene in an inert atmosphere. The solid was refluxed in azeotropic distillation using a Dean-Stark trap. Then (trimethoxysilyl)propyldiethylenetriamine (8.8 ml, 30 mmol) was added and the mixture was stirred for 2h at room temperature. The powder was filtered, washed with toluene, Soxhlet-extracted with acetonitrile overnight and dried at 343 K. The functionalization process was repeated. The ionic surfactant was removed by extraction with 0.17 M NaCl in ethanol. Elemental analysis: N, 3.31%; C, 14.55%; S, 4.73%; H, 1.03%.

**Synthesis of S2:** The UVM-7 solid was dried at 110°C overnight suspended in dry toluene (1 g of solid in 30 ml) and an excess of 3-aminopropyltriethoxysilane (3.0 ml, 13 mmol) added under inert atmosphere. The mixture was stirred at 110°C for one day. The resulting solid was filtered, washed with dichloromethane and ethanol, and dried at 70°C for 2h. Elemental analysis: N, 4.23%; C, 12.12%; H, 3.72%.

**Synthesis of S3**: The synthesis of S3 was achieved following the procedure in Chem. Commun., 2002, 330, using TEOS and mercaptopropyltrimethoxysilane as the silica source being the final molar gel composition 3.5 TEAH₃ : 0.85 TEOS : 0.15 MPTS : 0.26 CTAB : 90 H₂O (TEAH₃: triethanolamine, TEOS: tetraethylorthosilicate, MPTS: mercaptopropyl trimethoxysilane and CTAB: cetyl trimethylammonium bromide). The ionic surfactant was removed by extraction with 0.17 M NaCl in ethanol. Elemental analysis: N, 0.29%; C, 11.62%; S, 5.82; H, 2.71%.

**pH-controlled and anion-controlled gate effect.**

The pH-controlled and anion-controlled gate mechanism was monitored by using a colorimetric reaction consisting in the selective bleaching of a blue squaraine dye by reaction with mercaptopropyl groups. In the pH range studied, the used squaraine reacts selectively with thiols and not with amines (see Ros-Lis, J.V.; García, B.; Jiménez, D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J.; Gonzalvo, F.; Valldecabres, M.C. J. Am. Chem. Soc. 2004, 126, 4064. See also Figure 1 in the manuscript where the solid S1 (containing amines) is compared with solid S3 (containing thiols) at pH 5. A similar behaviour was found at pH 3 and pH 6). In a typical experiment, 3 mg of the corresponding solid were suspended in 13.5 mL of a 0.01 M water solution of certain anion (chloride, sulfate or ATP) and the pH adjusted to the desired value. Then, a solution of squaraine in acetonitrile was added to give water:acetonitrile 90:10 v/v mixtures with a total dye concentration of 5x10⁻⁶ mol dm⁻³. The mixture was placed in a spectrophotometric cuvette and stirred vigorously while the absorbance at 643 nm was measured vs. time.
In such experiments, the measured absorbance values are due to the absorption of the squaraine in the solution plus an additional “apparent absorption” due to the light dispersion by the colloidal solid. In order to “remove” the light dispersion effect, a blank suspension was also measured for each experience. Hence, 3 mg of the corresponding solid were also suspended in 13.5 mL of a 0.01 M water solution of the same anion (chloride, sulfate or ATP) and the pH was adjusted to the same value. Then, acetonitrile (without squaraine) was added to give water:acetonitrile 90:10 v/v mixtures and the absorbance at 643 nm was measured vs. time. Curves shown in Figures 1 and 2 of the manuscript were obtained by subtracting from each of the raw data curve its own light dispersion effect (blank curve). The values obtained with this method were in good accordance with those found after filtering the suspensions at a fixed time and measuring the absorbance at the 643 nm squaraine absorption band.

Characterization of the materials.

XRD, TG analysis, IR spectroscopy, SEM microscopy, elemental analysis, N₂ adsorption-desorption, and MAS NMR techniques were employed to characterize the functionalised materials S₁, S₂ and S₃. X-ray measurements were performed with a Seifert 3000TT diffractometer using Cu Kα radiation. Thermogravimetric analysis was carried out with a TGA/SDTA 851e Mettler Toledo balance, with a heating program consisting on a heating ramp of 10 °C per minute from 393 K to 1273 K. Scanning Electron Microscopy images were obtained on a Jeol JSM 6300 operated at 30kV. IR spectra were recorded on a Jasco FT/IR-460 Plus between 400 and 4000 (cm⁻¹) diluting the solids in KBr pellets. MAS NMR spectra were recorded on a Varian 300 Unity NMR spectrometer. For ¹³C CPMAS NMR the spectrometer operated at 75.43 MHz with delay time of 5 s and the sample was spun at 4.0 KHz. N₂ adsorption-desorption isotherms were recorded on a Micromeritics ASAP2010 automated sorption analyser.

In Figure I, powder X-ray patterns of the solids S₁, S₂, S₃ and UVM-7 are shown. The main features of a disordered MCM-41 phase typical for the UVM-7 material are clearly observed in all the patterns, evidencing that the structural order of the channels has not changed after the functionalization processes carried out.

TG curves for S₁, S₂ and S₃ are shown in Figure II. Apart from the different organic functionalization of each solid no meaningful difference in the TG profiles was observed. From the analysis of the curves the following weight loss regimes were found. For S₁, a weight loss of 3.0 % corresponding to solvents (T < 150 °C) and another weight loss of 27.7 % mainly due to the decomposition of the organic groups and to the condensation of residual silanols (150 °C < T < 700 °C) were recorded. For S₂, a weight loss of 2.7 % corresponding to solvents (T < 150 °C) and another of 19.4 % due to the decomposition of the organic groups and condensation of residual silanols (150 °C < T < 700 °C) were observed. And finally, TG analysis of the S₃ solid resulted in a decomposition curve with weight losses of 2.9 % (T < 150 °C) corresponding to solvents and 21.0 % (150 °C < T < 700 °C) to the decomposition of the organic groups and residual silanols.

Figure III shows a representative SEM image of the S₁ and S₃ solids where the particular topography of the UVM-7 materials can be observed: nanometric particles joined together into micrometric conglomerates giving rise to its characteristic textural porosity. S₂ solid also shows the same type of microstructure.

Infrared spectra of the three solids S₁, S₂, S₃, as well as that of the UVM-7 material, are shown in Figure IV. The dominant bands in every spectrum are due to the silica matrix (1250, 1087, 802 y 462 cm⁻¹) and those related to the vibrations of water molecules (3420 and 1620 cm⁻¹). Apart from that, small bands related to the vibrations of the organic moieties are also observed: 2954-2850 cm⁻¹ due to vibrations of carbon to hydrogen bonds in S₁, S₂ and S₃; and 3150 cm⁻¹ and 1573-1430 cm⁻¹ due to vibrations of nitrogen to hydrogen bonds in S₁ and S₂.
Figure V shows the $^{29}$Si NMR spectrum of S1. There is a high proportion of functionalised silicon centres, corresponding for the most part to $T^3$ centres, though some $T^2$ and $T^1$ are also detected. In addition, the signal due to non functionalised silicon atoms is mainly due to fully condensed $Q^4$ centres though it is also observed a small intensity related to silanol groups ($Q^3$ and $Q^2$ centres).

Figure VI shows the $^{13}$C CPMAS NMR spectrum of solid S1. Three different groups of signals can be observed. The signal centred at 16.3 ppm was assigned to CH$_2$ groups bonded to silicon and to carbon atoms. The signal centred at 45.3 ppm was assigned to CH$_2$ groups bonded to nitrogen, whereas the signal at 52.1 ppm was attributed to CH$_2$ groups bonded to sulphur.

In relation with the N$_2$ adsorption-desorption isotherms, the S1 solid shows (Figure VII) similar curves to those of the parent UVM-7 material: two adsorption steps (at intermediate and high $P/P_0$ values) related to their bimodal pore system. The first step corresponds to the nitrogen condensation inside the intra-nanoparticle mesopores (MCM-41 type, 2.6 nm, 0.42 cm$^3$g$^{-1}$) and the second one to the condensation inside the interparticle large pores (45.2 nm, 0.74 cm$^3$g$^{-1}$, textural porosity). The calculated pore size value must be considered with caution because of problems related with the use of the BJH method (see Kruk, M.; Jaroniec, M. Chem. Mater., 2001, 13, 3169-3183). Notwithstanding, dealing with MCM-41 related materials, BJH values result useful for comparative purposes. The application of the BET model resulted in a value for the total specific surface of 633 m$^2$g$^{-1}$.

**Calculation of the number of polyamine molecules on the surface of S1 solid.**

From the elemental analysis of the S1 solid the N:S molar ratio can be calculated as 1.60. Also, from elemental analysis and TG analysis, the S:Si molar ratio of the S3 solid is 0.15. From these two values it can be calculated the amount of amines that have been anchored onto S3 solid to get S1:

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1.60 \times \frac{N}{S} \times 0.15 \frac{S}{Si} = 0.24 \text{ mol of N anchored onto } S3 \text{ per mol of Si or 0.08 mol of amine anchored per mol de Si (onto S3 to give S1)}
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As the amine molecules are anchored onto S3 solid before surfactant had been extracted, we will use the data of mesostructured S3 solid: 0.9953 mol of Si/100g from TGA on mesostructured S3; external surface of 220 m$^2$/g, similar to that of solids in which mesopores have been completely blocked by the organic functionalisation (UVM-7 type materials, Adv. Mater. 2002, 14, 966-969); and a medium distance among pores of 4.2 nm from the main peak position in the X-ray pattern. Then, the number of amine molecules related to each pore can be calculated to be 30.33 amine molecules per pore.
**Figure I.** X-ray powder diffraction patterns for S1, S2, S3 and UVM-7 solids

**Figure II.** Thermogravimetric analysis curves for S1, S2 and S3 solids.
Figure III. Representative SEM image of the prepared solids (white bar is equivalent to 1µm).

Figure IV. Infrared spectra of solids S1, S2, S3 and UVM-7.
Figure V. $^{29}$Si MAS NMR spectrum of the solid S1.

Figure VI. $^{13}$C CPMAS NMR spectrum of S1 solid.
**Figure VII.** N₂ adsorption-desorption isotherms for S1 material (pore size distribution in the inset) and (b) a detail of the adsorption curve with enlarged adsorption axis.