SUPPORTING INFORMATION

Selective opening of nanoscopic capped mesoporous inorganic materials with nerve agent simulants; an application to design chromo-fluorogenic probes.

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Chemicals

The chemicals tetraethylorthosilicate (TEOS) (98%), *n*-cetyltrimethylammonium bromide (CTABr) (≥99%), sodium hydroxide (≥98%), triethanolamine ($TEAH_3$) (≥99%), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($[Ru(bipy)_3]Cl_2\cdot 6H_2O$) (100%), 3-[Bis(2-hidroxyethyl)amino]propyltriethoxysilane (HET) (65% in Ethanol), diethyl(2-cyanoethyl)phosphonate (**DCPP**) (95 %), diethyl 1-phenylethyl phosphonate (**DPEPP**) (98%), dimethyl chlorothiophosphate (**DCTP**) (97%), diethyl(methylthiomethyl)phosphate (**DMTMPP**) (96%), diethyl chlorophosphate (**DCP**) (97%), diethyl(2-oxopropyl)phosphonate (**DOPPP**) (96%), diisopropyl fluorophosphate (**DFP**) (99%) and diethyl cyanophosphate (**DCNP**) (≥90%) were provided by Aldrich and used as received. Analytical-grade solvents were acquired from Scharlab (Barcelona, Spain). All the reagents were used as received.

General Techniques

Powder XRD, TG analysis, elemental analysis, EDX microscopy and N_2 adsorption-desorption techniques were employed to characterise the prepared materials. UV-visible and fluorescence spectroscopy were used to study the controlled release behaviour of synthesised materials. Powder X-ray diffraction measurements were performed on a Philips D8 Advance diffractometer using Cu K_α radiation. The 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 programme consisting in a heating ramp of 10ºC per minute from 393 K to 1273 K, and an isothermal heating step at this temperature for 30 minutes. The elemental analysis was performed in a CE Instrument EA-1110 CHN Elemental Analyser. The SEM analysis was performed with a JSM-6300 scanning microscope. TEM images were obtained with a 100 kV Philips CM10 microscope. N_2 adsorption-desorption isotherms were recorded on a Micromeritics ASAP2010 automated sorption analyser. Samples were degassed overnight at 120ºC in vacuum. The specific surface areas were calculated from the adsorption data in the low pressures range using the BET model. Pore size was determined following the BJH method. UV-visible spectroscopy was carried out with a Lambda 35 UV/vis spectrometer (Perkin-Elmer Instruments). Fluorescence spectroscopy was carried out on a Felix 32 Analysis Version 1.2 (Build 56) PTI (Photon

Technology International). MAS ^{31}P-NMR spectra were measured in a Bruker AVIII, 400 MHz WB, equipped with a 4 mm DVT-CPMAS probe.

Synthesis of the mesoporous silica support

The molar ratio of the reagents in the mother liquor was fixed to 7 TEAH$_3$: 2 TEOS: 0.52 CTABr: 0.5 NaOH: 180 H_2O. In a typical synthesis leading to the MCM-41 pure silica, 4.67 g of CTABr (*n*-cetyltrimethylammonioum bromide) were added at 118ºC to a solution of TEAH$_3$ (25.76 g) containing 0.012 mol of NaOH and 0.049 mol of a silatrane derivative (e.g., 11 mL of TEOS were added at 70ºC to TEAH$_3$, e.g., in the form of Si(TEA)(TEAH$_2$), where TEA is the fully deprotonated ligand). Then, 80 mL of deionised water were added with vigorous stirring at 70ºC. After a few minutes, a white suspension resulted. This mixture was aged at room temperature overnight. The resulting powder was collected by filtration and washed with water. Finally, the solid was dried at 70ºC (MCM-41 as synthesised). To prepare the final porous material (MCM-41), the as-synthesized solid was calcined at 550ºC for 5 h to remove the template.

Synthesis of S1

In a typical synthesis, 0.9 g of template-free MCM-41 and 0.8 mmol/g MCM-41 (0.54 g) of [Ru(bipy)$_3$]Cl$_2$·6H_2O were suspended in 50 mL of acetonitrile in a round-bottomed flask. To remove the adsorbed water, 10 mL of acetonitrile were distilled using a Dean-Stark set-up. After stirring 24 h at room temperature, 10 mmol/g MCM-41 of Bis(2-hidroxyethyl)aminopropyltriethoxysilane (1.27 ml) were added and the mixture was stirred for 5.5 h at room temperature. The obtained solid was filtered, washed with acetonitrile and dried overnight (38ºC).

Material Characterisation

MCM-41 as-synthesised, MCM-41 and **S1** materials were characterised by standard techniques. Figure SI-1 shows the powder X-ray patterns of the solid MCM-41 as-synthesised (without calcination), calcined MCM-41 and **S1**. Powder XRD of siliceous MCM-41 as-synthesised shows four low-angle reflections that are typical of the hexagonal ordered array, which can be indexed as (100), (110), (200), and (210) Bragg peaks. A significant shift of the (100) reflection and a broadening of the (110) and (200) peaks in the XRD powder of the MCM-41 calcined sample are clearly seen. This corresponds to an approximate cell contraction of ca. 6-8 Å during the calcination step. Despite this clear partial order loss, the observation of the overlapped (100) and (200) reflections indicates that certain relative mesopore symmetry is preserved after calcination. Figure SI-1 also depicts a curve that corresponds to **S1**. For this solid, reflections (110) and (200) are lost, most likely because of a reduction of contrast because of the pore voids becoming filled with the ruthenium complex. Nevertheless, the clear presence of the (100) peak in this pattern suggests that the loading process with the [Ru(bipy)$_3$]$^{2+}$ complex, and the additional functionalisation with dialcohol, have not substantially modified the mesoporous MCM-41 support. Preservation in the final functionalised solids of the mesoporous structure was also confirmed by the TEM analysis (see Figure 1b in the manuscript) in which the typical hexagonal porosity of the MCM-41 matrix can be clearly observed as alternate black and white stripes.

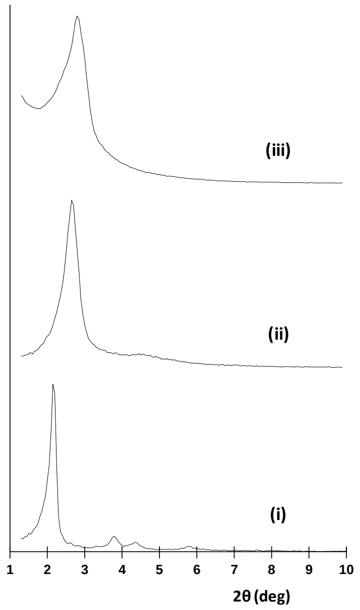

Figure SI-1. Powder X-Ray diffractograms showing X-Ray patterns of the MCM-41 scaffolding as synthesised (i), MCM-41 after the calcination process (ii) and of final solid **S1** (iii).

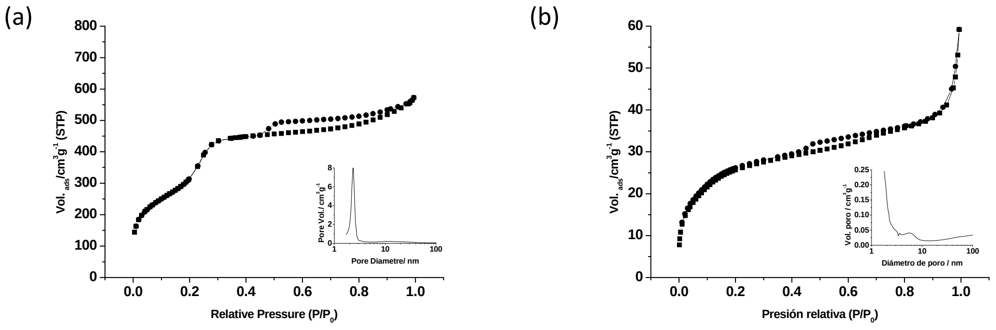

Figure SI-2. Nitrogen adsorption-desorption isotherms for (a) **MCM-41** mesoporous material (b) **S1**.

The N_2 adsorption-desorption isotherms of the MCM-41 calcined material show a typical curve for these mesoporous solids; i.e., an adsorption step at the intermediate P/P_0 value (0.2-0.35). This curve corresponds to a type IV isotherm in which the observed step can be related to the nitrogen condensation inside the mesopores through capillarity (see Figure SI-2). The mentioned isotherms present a slight hysteresis loop in a wide pressure range, which could probably be attributed to a textural-like porosity among particles. The application of the BET model resulted in a value for the total specific surface of 1140 m^2/g. From the XRD, porosimetry and TEM studies, the a_0 cell parameter (3.85 nm), the pore diameter (2.8 nm) and a value for wall thickness of 1.05 nm can be calculated. The N_2 adsorption-desorption isotherms of **S1** (see again Figure SI-2) are typical of mesoporous systems with filled mesopores, and the adsorbed N_2 volume significantly decreased. In fact, these solids present flat curves when compared (on the same scale) to those of the MCM-41 parent material, indicating significant pore blocking and the subsequent absence of appreciable porosity. This result was as expected considering that these solids have a high dye content filling the pores. The specific surface values, pore volumes and pore sizes for MCM-41 and **S1** are presented in Table SI-1.

Table SI-1. BET-specific surface values, pore volumes and pore sizes calculated from the N_2 adsorption-desorption isotherms for selected materials.

	S_{BET} (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore Size (nm)
MCM-41	1139	0.98	2.8
S1	96	0.07	-

The content of $[Ru(bipy)_3]^{2+}$ complex and bis(2-hidroxyethyl)aminopropyltriethoxysilane in the prepared solid **S1** was determined by elemental and thermogravimetric measurements and amounts to 0.163 mmol/g SiO_2 and 0.653 mmol/g $SiO_{2,}$ respectively. The heating ramp used to perform the thermogravimetric analysis consisted in a heating ramp of 10ºC per minute from 120ºC to 1000ºC, and an isothermal step at this temperature for 30 minutes.

Examination of the thermogravimetric curve and its first derivative shows four weight loss steps (see Figure SI-3). One weight loss of 9.08% corresponding to solvents elimination (T < 200ºC); another weight loss of 7.04% due to decomposition of the organic groups anchored on the siliceous surface (200 < T < 380 ºC); a third weight loss of 7.77 % that can be assigned to the decomposition of the ruthenium complex (380 < T < 520 ºC); finally, a loss of a 2.25 % owing to the condensation of silanols on the siliceous surface (T > 500ºC).

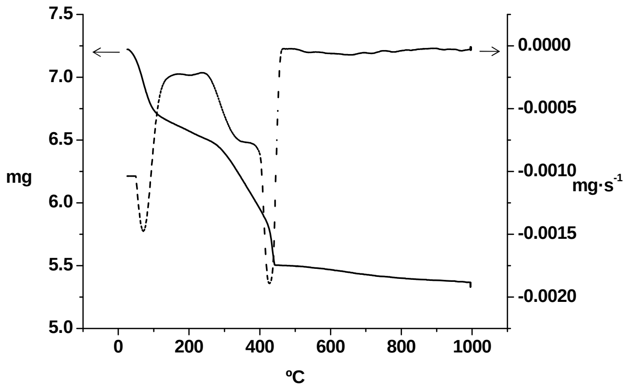

Figure SI-3. Thermogravimetric curve (straight line) and its derivative (dashed line) obtained from the thermogravimetric analysis of **S1**.

The amount of ruthenium complex in solid **S1**, measured by the SEM analysis using an energy dispersive X-ray spectroscopy (EDX, 5000x magnification, 20 kV), was 0.157 ± 0.018 mmol/g SiO_2. This value well matches the content obtained by the thermogravimetric measurements (0.163 mmol/g SiO_2).

The Chromogenic Response Mechanism

The sensing mechanism in the presence of nerve agent simulants relies on the breaking of the hydrogen bond network in solid **S1** upon the phosphorylation of the hydroxyl groups. In order to prove the proposed sensing mechanism, **S1** was reacted with an excess of DCP to obtain the corresponding solid **S1-e**.

This solid (**S1-e**) was studied by SEM analysis using energy dispersive X-ray spectroscopy (EDX, 20 kV). EDX measurements indicated the presence of a significant amount of phosphorus atoms on the surface of **S1-e** material, suggesting an efficient reaction between DCP and the hydroxyl moieties of the HET groups. As seen in Table SI-2, the OH content in **S1-e** determined by the thermogravimetric analysis is 1.30 mmol / g SiO_2, whereas the phosphorus content measured by SEM-EDX is 1.02 mmol / g SiO_2. By bearing in mind these contents, the reaction between DCP and HET offers an 80% yield. Furthermore, MAS ^{31}P-NMR of solid **S1-e** shows a broad singlet centred in the 1-2 ppm range, which is a typical signal for phosphate groups (see Figure SI-4).

Table SI-2. Phosphorous content (from the SEM-EDX analysis) and OH groups content (from the thermogravimetric analysis) for solid **S1-e**.

	mmol P/g SiO_2	mmol OH/g SiO_2
SEM-EDX	1.02 ± 0.08	-
TGA	-	1.30

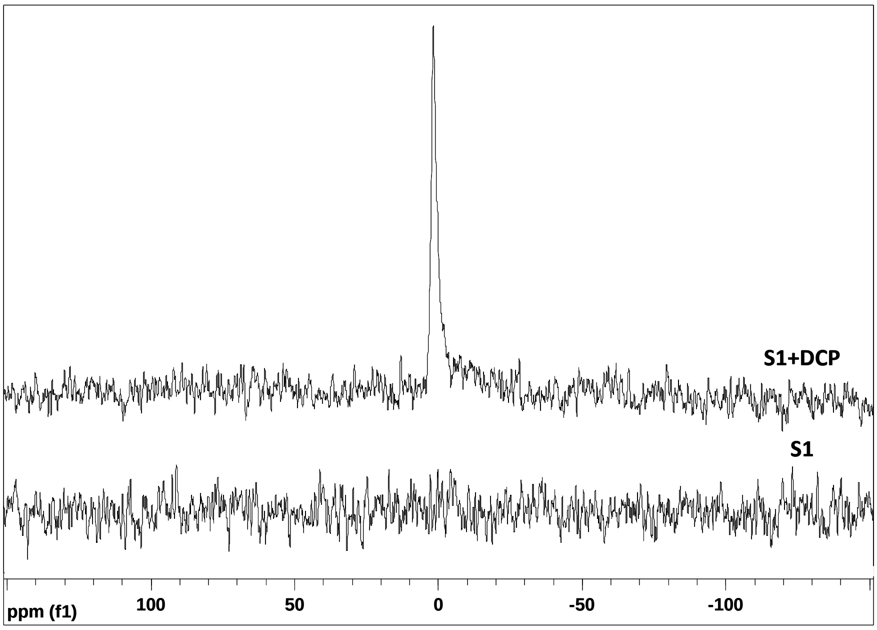

Figure SI-4. MAS ^{31}P-NMR spectra of solid **S1** and solid **S1** in the presence of DCP.

As regards the sensing process steps' efficiency, EDX and MAS ^{31}P-NMR spectra show an 80% yield for the reaction between the hydroxyl moieties in the HET groups and the DCP, whereas 50% of the ruthenium complex (measured by UV-visible) was released at 5 minutes after DCP addition.

Dye release studies

The release of the $[Ru(bipy)_3]^{2+}$ complex to the solution in the presence of several nerve agent simulants (see Scheme 2 in the paper) was studied. In a typical experiment, 5 mg of **S1** were suspended in 12.5 mL of the corresponding simulant solution in acetonitrile. This suspension was used to evaluate the gate-like effect by studying the dye release from the pore voids of the functionalised material. The delivery of the $[Ru(bipy)_3]^{2+}$ complex from the pore voids to the solution was easily monitored via the d-π metal-to-ligand charge transfer (MLCT) transition band of this complex centred at 451 nm (see Figure 2 in the paper).

Detection limit studies

In addition, the detection limit of **S1** solid in the presence of DFP, DCP and DCNP was measured. In order to carry out these measurements, 1.5 mg of solid **S1** were suspended in 11.25 mL of different solutions at increasing concentrations of the corresponding simulants (1, 2, 5, 11, 15, 20, 25, 35, 40, 50 and 60 ppm). Different aliquots (2 mL) were taken and filtered after 15 minutes. The delivery of the

$[Ru(bipy)_3]^{2+}$ complex from the pore voids to the solution was easily monitored via the d-π metal-to-ligand charge transfer (MLCT) transition band of this complex centred at 451 nm (see Figure SI-5-a). To perform further fluorescence studies, 1.5 mg of **S1** were suspended in 11.25 mL of different solutions at increasing concentrations of DCP (0.025, 0.05, 0.1, 0.2, 0.3, 0.5 and 0.7 ppm). Different aliquots (2 mL) were taken and filtered after 15 minutes. The dye release was monitored via the emission band of the $[Ru(bipy)_3]^{2+}$ complex centred at 610 nm (excitation at 451 nm) (see Figure SI-5-b).

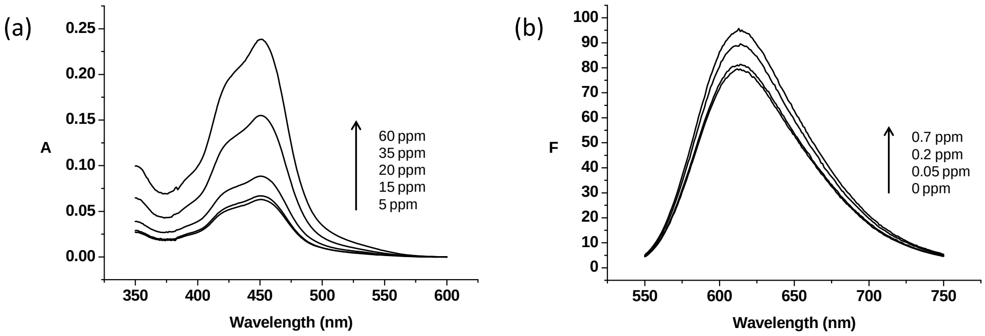

Figure SI-5. (a) Absorption spectrum of acetonitrile suspensions of **S1** in the presence of increasing concentrations of DCP. (b) Fluorescence emission spectrum (excitation at 451 nm) of acetonitrile suspensions of **S1** in the presence of increasing concentrations of DCP.

Dye release studies in the presence of other organophosphorous compounds

The followed procedure is analogous to that described in the dye release studies. Briefly, 5 mg of **S1** were suspended in 12.5 mL of a solution (10^{-3} mol dm^{-3}m in acetonitrile) of the following organophosphorous compounds (see Scheme 2 in the paper for their chemical structures): diethyl(2-cyanoethyl)phosphonate (**DCPP**), diethyl 1-phenylethyl phosphonate (**DPEPP**), dimethyl chlorothiophosphate (**DCTP**), diethyl(methylthiomethyl)phosphate (**DMTMPP**) and diethyl(2-oxopropyl)phosphonate (**DOPPP**). Different aliquots (2 mL) were separated and filtered after 15 minutes. The dye delivery from the pore voids to the solution was monitored via the d-π metal-to-ligand charge transfer (MLCT) transition band of the $[Ru(bipy)_3]^{2+}$ complex centred at 451 nm. Figure SI-6 shows the absorbance of the ruthenium band centred at 451 nm in the acetonitrile suspensions of **S1** upon addition of selected organophosphorous compounds. As seen, only DCP induced pore opening release the ruthenium complex, whereas the other organophosphorous compounds induced a negligible release.

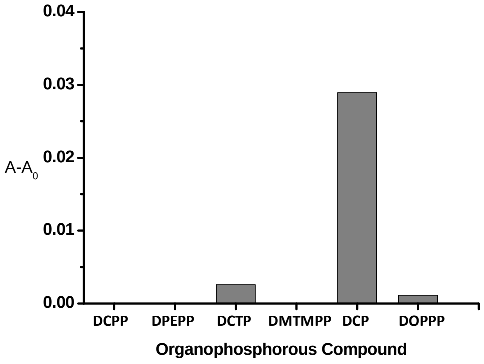

Figure SI-6. Absorbance at 451 nm (ruthenium complex band) of the acetonitrile suspensions of **S1** in the presence of organophosphorous compounds (1 mM).

Vapour phase studies

Solid **S1** was also tested as a chromogenic material for the sensing of nerve agent simulants in the vapour phase. For this purpose, acetonitrile suspensions **S1** (5 mg / 12.5 mL) were exposed to air containing 50 ppm of DCP for 30 minutes. In this situation, the vapours of DCP partially dissolved in the acetonitrile suspension of **S1,** inducing the release of the $Ru(bipy)_3^{2+}$ dye, which indicates the presence of DCP in the gas phase.