Supporting Information

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Chromogenic Detection of Nerve Agent Mimics by Mass Transport Control at the Surface of Bifunctionalized Silica Nanoparticles**

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Supporting Information

1. Experimental procedures

30 % suspension of ludox silica nanoparticles AS-30 Colloidal Silica were purchased from Sigma-Aldrich and were used without any further purification. The solvents were absolute grade and were purchased from Scharlab. Nerve agent simulants diisopropylfluorophosphate (DFP), diethylchlorophosphate (DCP) and diethylcyanophosphate (DCNP) and selected phosphonates and phosphates such as diethyl-(2-cyanoethyl)phosphonate (2-CN), diethyl-(1-phenylethyl)phosphonate (1-Ph), dimethylchlorothiophosphate (DCSP) diethyl-(methylthiomethyl)phosphate (DMSP) and diethyl-(2-oxopropyl)phosphonate (2-oxo) were purchased from Sigma-Aldrich. Mercaptopropyltriethoxysilane (MPTS) and 3-[bis-(2-hydroxyethyl)amino]propyltriethoxysilane (HPTS) were also purchased from Sigma-Aldrich and used as received.

TGA, Fluorescence spectroscopy and UV-visible spectroscopy techniques were employed to characterize the synthesized nanoparticles. Thermogravimetric analysis was carried out in a Mettler Toledo TGA/SDTA 851e. Transmission Electron Microscopy (TEM) images of the particles were obtained with a Philips CM10 operating at 20 KeV. Samples for TEM were prepared by spreading a drop of nanoparticles solution onto standard carbon-coated copper grids (200 mesh). Fluorescence spectroscopy was carried out on a Felix 32 Analysis Version 1.2 (Build 56) PTI (Photon Technology International) and UV-visible spectroscopy was carried out with a Lambda 35 UV/vis spectrometer (Perkin-Elmer Instruments).

2. Preparation of coated silica nanoparticles

Coated silica nanoparticles N1 were prepared using the corresponding trialkoxysilyl derivatives following reported procedures by Montalti and coworkers. Ludox silica nanoparticles AS-30, 20 nm average diameter, (5 mL) were added to a solution containing acetic acid (25 mL), water (25 mL) and ethanol (40 mL). Then a mixture of mercaptopropyltriethoxysilane (MPTS, 1.25 mmol) and 3-[bis-(2-hydroxyethyl)amino]propyltriethoxysilane (HPTS, 6.25 mmol) were added to the nanoparticle suspension. The crude reaction was heated at 80 ºC for 48 hours, the ethanol was evaporated and then the acetic acid solution neutralized with a saturated solution of sodium hydrogen carbonate. The functionalized nanoparticles (N1) were precipitated and isolated by filtration, washed with water and acetone and isolated by lyophilisation. This method would allow obtaining a uniform distribution of both functional groups on the silica surface.
Thermogravimetric analyses were carried out under a flow of air and with a heating rate of 10 °C/minute in the 30-1000 °C interval. The final solid was maintained at 1000 °C for 30 minutes. In the obtained thermograms of N1 three clearly defined zones are observed; (i) from 30 °C to 150 °C which was assigned to loss of water and organic solvents (11.69 %), (ii) from 150 °C to 800 °C which was assigned to the organic matter attached into the nanoparticle surface (26.9 %) and, finally (iii) from 800° to 1000° C a third step was assigned to condensation of silanol groups (0.57%). The silica residue amounts to 61.3 %. TEM images of N1 nanoparticles show a very homogenous particle size around 20 nm (see Figure S1).

Figure S1: TEM image of functionalized nanoparticles N1, average diameter = 20 nm.