2021 ONLINE
February 17-18
sC SmallChem
Small Chem International Online Conference
February 17-18, 2021

CHROMOGENIC CHEMODOSIMETER BASED ON CAPPED SILICA NANOPARTICLES TO DETECT SPERMINE AND SPERMIDINE.

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INTRODUCTION

High levels of polyamines such as spermine (Spm), spermidine (Spd) and putrescine (Put) have proven to be interesting biomarkers in the detection of diverse pathological situations[1-3]. Therefore, the design and synthesis of new probes is a field of research in constant development and of great interest[4-5] since they can be used to detect the presence of these polyamines in biological fluids and tissues with no need of expensive instruments.

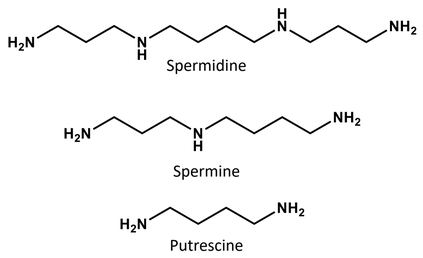
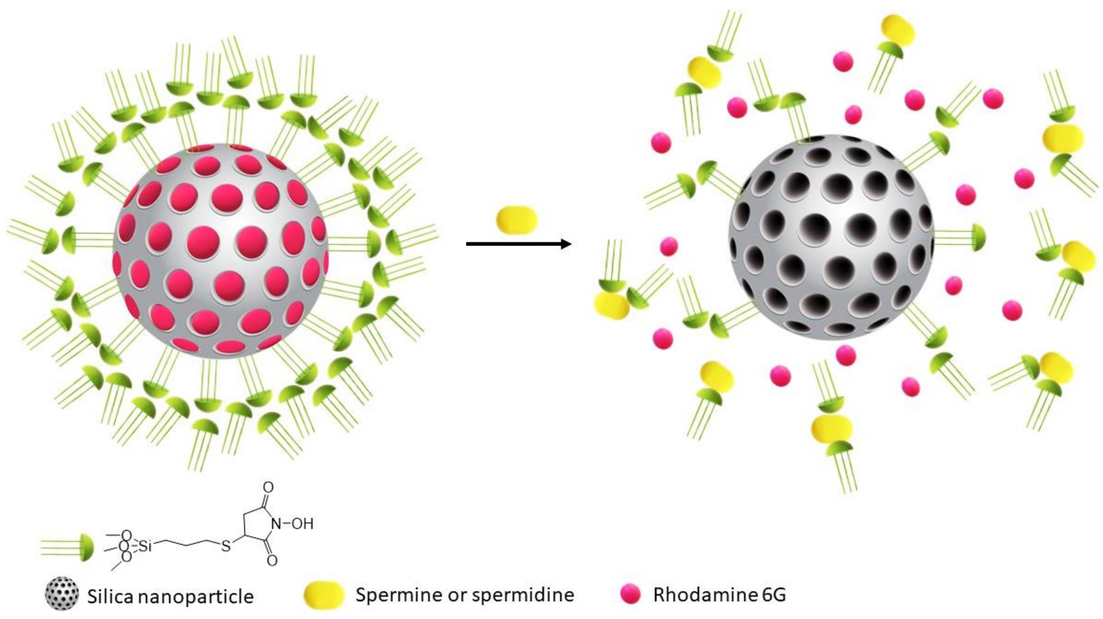


Figure 1. Structure of biological polyamines.

Hence, a new material based on MCM-41 functionalized with a N-hydroxysuccinimide derivative and loaded with rhodamine 6G has been developed for the sensing of Spm and Spd. The dye is kept inside the porous due to a double layer formation of organic matter. The inner layer is covalently bound to the silica nanoparticles and the external one is formed through hydrogen and hydrophobic interactions. Removal of the external coverage, in amine groups presence, opens the pores allowing the dye to release. The sensing protocol is described in **Scheme 1**. The release studies were performed through fluorimetric titrations, obtaining limits of detection of 2.7x10-5 M for Spm and 4.5x10-5 M for Spd. The sensor remains silent in the presence of other biologically important amines and can detect Spm and Spd in aqueous solution and in cells.

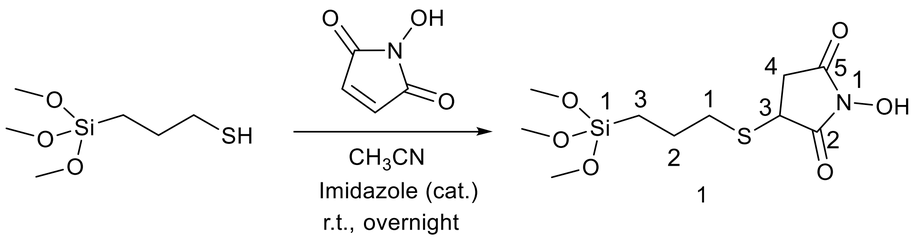


Scheme 1. Sensing protocol for detecting Spm and Spd.

METHODS AND MATERIALS

Preparation of S1

MCM-41 (200 mg) and rhodamine 6G (200 mg) were suspended in dry CH3CN (35 mL) and the mixture stirred under Ar atmosphere for 24 h, at room temperature. Compound **1** (**Scheme 2**) was dissolved in a mixture of CH3CN and DMSO (5:1) and then added to the reaction and the mixture was stirred for 24h. Finally, the material was washed with acetonitrile, water and ethanol and dried in the drying oven at 50 ºC.



Scheme 2. Synthesis of the molecular gate **1**.

RESULTS

Characterization of the prepared materials

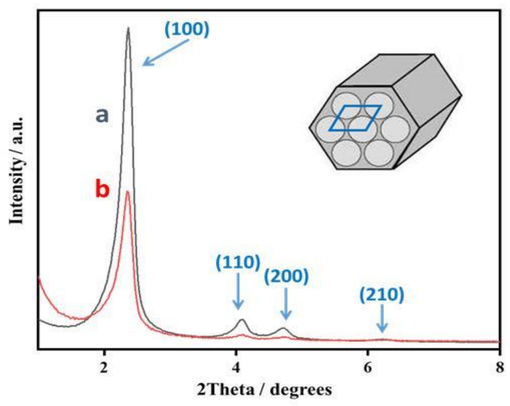


Figure 2. PXRD patterns of the starting MCm-41 (**a**) and the **S1** solid (**b**).

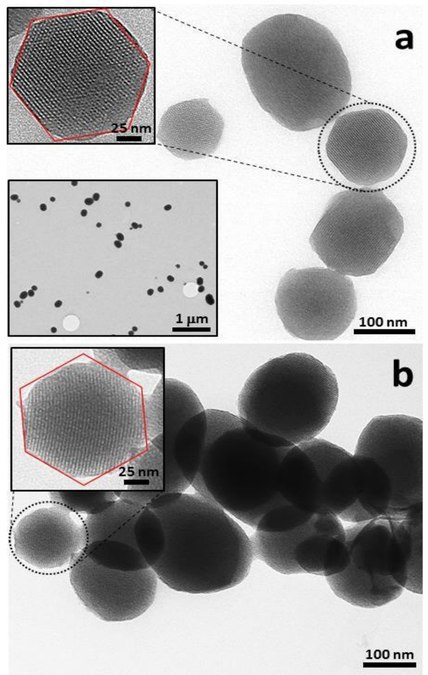


Figure 3. TEM images of the starting pure silica (**a**) and the **S1** solid (**b**).

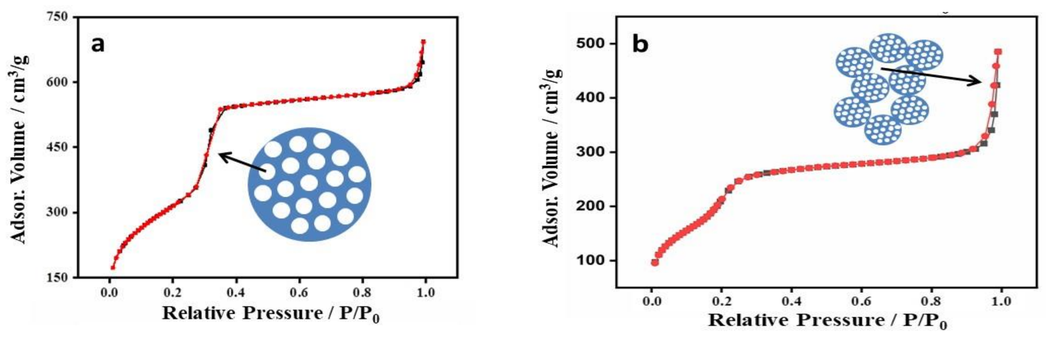


Figure 4. N_2 adsorption-desorption isotherms of the starting MCM-41 (**a**) and the **S1** solid (**b**).

Sensing studies

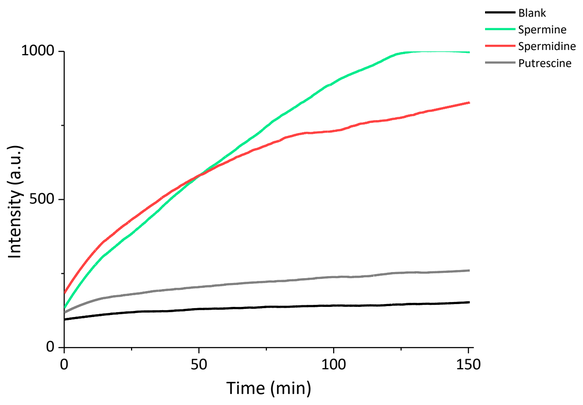


Figure 5. Rhodamine 6G (λ_{em} = 550 nm, λ_{ex} = 525 nm) delivery profiles from **S1** nanoparticles in the absence and presence of Spm, Spd and putrescine.

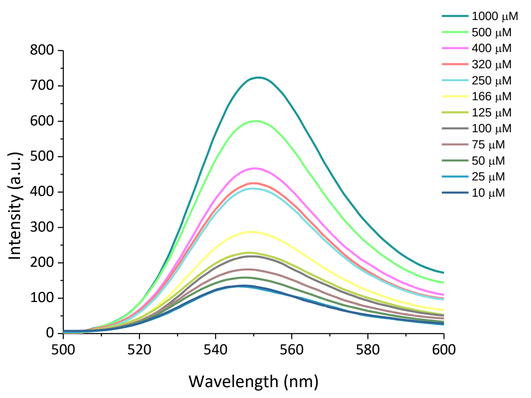


Figure 6. Fluorescence titration of S1 with Spm.

Cell Experiments

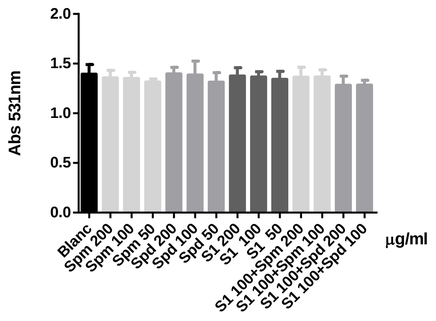


Figure 7. Cell viability determined by the MTT assay after 2h-incubation of RAW 264,7 macrophages with different concentrations of S1, Spm, Spd and the mixture.

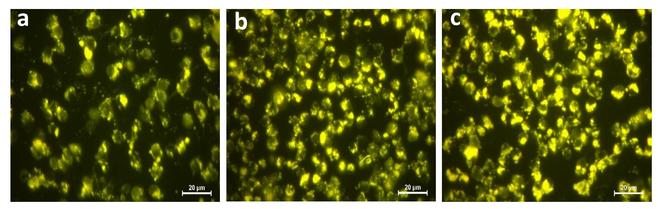


Figure 8. Fluorescence imaging of RAW 264.7 incubated with: (a) **S1** (100 µg/ml), (b) **S1** 359 (100 µg/ml) + Spd (100 µg/ml), (c) **S1** (100 µg/ml) + Spd (200 µg/ml).

CONCLUSION

- A new hybrid organic-inorganic material (**S1**) has been prepared and characterized.
- In the presence of Spm or Spd, the molecular gate is opened and the rhodamine 6G is released sensing the presence of the amines. Putrescine and other biologically important amines do not act as interferents.
- Detection has been carried out in solution and in RAW 264.7 macrophages.

ACKNOWLEDGMENTS

GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA E INNOVACIÓN
GENERALITAT VALENCIANA CONSELLERIA D'EDUCACIÓ, CULTURA I ESPORT

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