## **Detection at ppt Level of Mercury Ions in Water Based in New NanoStructured Solid-Supported Systems**

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Heavy metal ions are highly toxic elements, which contamination, due to both natural and anthropogenic reasons, has become severe in some parts of the world, resulting in health damage to their inhabitants.<sup>1</sup> From all the chemical elements that integrate this group mercury is one of the more hazardous. Mercury ions can be transformed by some aquatic microorganisms into methylmercury, which subsequently bioaccumulates into the adipose tissues of fishes and marine mammals,<sup>2</sup> to be later spread out into the nutritional chain affecting, therefore, to the entire ecosystem. As a consequence mercury (II) ion levels in water are continually monitored by government agencies, and regulatory commissions are dictating increasingly stringent regulations for the maximum permitted limits of mercury ions in water. Therefore the developing of new sensors able to selectively and sensitively detect mercury ions on aqueous media is still a challenge.

In the literature, there are not many selective molecular mercury sensors, and the number of these, able to detect low levels of mercury supported on a solid substrate is limited. With this aim, herein we present two 1,4-disubstituted-2,3-diaza-1,3-butadiene derivatives (**1** and 2 Scheme 1) able to selectively detect mercury ions in aqueous media<sup>3</sup> that combined with different nanostructuration and analytical techniques allowed us to obtain highly sensitive solid-supported mercury probes matching the  $Hg^{2+}$  limit on potable water.

Specifically, we have obtained a new kind of sensing probes using the reprecipitation method<sup>4</sup> technique to fabricate hybrid cellulose membranes by means of the filtration of an aqueous suspension of nanoparticles of the compound **1** through a mixed cellulose acetate membrane (Figure 1) resulting a composite material able to perform the *in situ* selective fluorescent detection of mercury (II) ions<sup>5</sup> present on water sources up to the ppb ( $\mu$ g/l) level. This concentration matches the restrictions established by the *Environmental Protection*  Agency<sup>1</sup> for the presence of mercury on potable water.

 In order to continuously monitor and control the concentration of mercury ions the use of sensing probes may not be the best alternative. More recently, we have been able to perform the functionalization of gold surfaces using self-assembled monolayers<sup>6</sup> of the properly design compound **2**, allowing us to use evanescent wave techniques such as surface plasmon resonance<sup>7</sup> (SPR) for the development of a mercury (II) sensor, that works as highly sensitive and selective probe able to detect mercury ions continuously even down to the ppt (ng/l) level on aqueous media (Figure 2).

[1] a) United States Environmental Protection Agency Roadmap for Mercury, (2006); b) R. P. Mason, W. F. Fitzgerald, F. M. M. Morel. Geochim. Cosmochim. Ac*.* **58**, (1994), 3191; c) S. Díez, Reviews of Environmental Contamination and Toxicology **198**, (2009), 111.

[2] a) D.W. Boening. Chemosphere, **40**, (2000), 1335; b) H.H. Harris, I.J. Pickering, G.N. George Science, **301**, (2003), 1203; c) S. Jensen, A. Jernelov. Nature, **223**, (1969), 753.

[3] A. Caballero, R. Martínez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tárraga, P. Molina and J. Veciana, J. Am. Chem. Soc., **127**, (2005**)**, 15666.

[4] Y. Takahashi, H. Kasai, H. Nakanishi and T. M. Suzuki, Angew. Chem., Int. Ed., **45** (2006), 913.

[5] C. Díez-Gil, R. Martínez, I. Ratera, A. Tárraga, P. Molina, J. Veciana, J. Mater. Chem., **18**, (2008), 1997; b) C. Díez-Gil, R. Martínez, I. Ratera, A. Tárraga, P. Molina, J. Veciana, Patent WO2008077985-A1, (2008).

[6] Love, J. C., Estroff, L. A., Kriebel, J. K., Nuzzo, R G., Whitesides, G. M. Chemical Reviews, **105**, (2005), 1103.

[7] Homola, Jiri, Yee, Sinclair S., Gauglitz, Gunter, Sensors and Actuators, B: Chemical, **54** (1999), 3.

## **Figures:**



**2** R=  $-(CH_2CH_2O)_3(CH_2)_{11}SCOCH_3$ 



Scheme 1. Scheme 1. Scheme 1. Semi-mage of the mixed cellulose ester membrane after filtering the compound **1** nanoparticle suspension.



Figure 2. a) SPR sensogram for mercury (II) detection b) SPR mercury (II) calibration curve.