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Luminescent Eu(III) hybrid sensors for in situ copper detection

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ABSTRACT

In this work we used the sol–gel technique to develop luminescent Eu(III) transparent films deposited on glass slides to build for sensor devices capable of monitoring transition metal ions in aqueous solutions. The films were obtained from a bis(trialkoxysilyl) organic precursor synthesized from the amide of the 2,6-pyridinedicarboxylic acid (DPA) with aminopropyltriethoxysilane (APTES) in the presence or absence of cetyl trimethyl ammonium bromide (CTAB) surfactant as templating agent and triethylethoxysilane (TEOS) as crosslinker. These sensor devices were used to perform in situ quenching experiments by Cu(II), Fe(III), Co(II) and Ni(II) ions. The results indicate that the templated films allow the detection and quantification of these metals down to ppb levels by means of the values of the Stern–Volmer constants. In particular, it was shown that Cu(II) acts as an extremely efficient quencher ($K_{SV} = 3.5 \times 10^5$ M^{-1}) when compared with the results obtained for the other metals, opening the possibility to use these devices as potential Cu(II) sensors for actual applications in aqueous media.

1. Introduction

The use of bridged silsesquioxanes $[(RO)_3Si]_n - R'$ $(n \geq 2)$ as precursors to include an organic functional group inside the inorganic framework of a mesoporous matrix itself gave rise, since the pioneering works in the early nineties, to the novel periodic mesoporous organosilicas (PMO) [1–3]. The development of luminescent PMO is in constant progress [4]. The functionalization of these matrices with different organic groups capable of emitting light efficiently is a key strategy. The increasing use of chemically modified bridged silsesquioxanes, to include lanthanides by the sol–gel technique into the frameworks and/or the pores of the hybrid matrices [5–7] in order to obtain lanthanide based luminescent organic–inorganic hybrid materials can be attributed to the high potential of these materials for several applications as sensors, organic light emitting diodes, phosphors, etc. [8,9].

Lanthanide ions display a well-defined luminescence characterized by narrow and highly structured emission bands arising from their parity forbidden intra f–f transitions. Their excited state lifetimes are in the millisecond timescale and are not quenched by molecular O_2 [10–13], in contrast to what is generally observed for organic dyes. Unfortunately, their low absorption coefficients ($\varepsilon < 10$ M^{-1} cm^{-1}) do not allow their use as such, but are useful when coordinated to an antenna chromophore capable of sensitizing the lanthanide emission mechanisms by populating the ion centered emitting states [14–16] through energy transfer. These unique properties focused the attention of many researchers in the design of different lanthanides complexes for potential applications as biological probes [17,18] or chemical sensors [19–21]. A recent review describes the latest developments in the use of lanthanides in a wide group of functional luminescent materials [22].

Europium based luminescent organosilica materials obtained by the hydrolysis and condensation of organoalkylsilanes from a sol–gel technique [23,24] have been widely used to immobilize organic or inorganic molecules [25–27] in a porous glass or film [28] or nanoparticles [29] to build optical sensors of pH [30], anions [21] and cations [31,32].

Transition metal ions are known to be efficient quenchers of the emission of lanthanide complexes being the electronic energy transfer the deactivating mechanism postulated to operate in these cases [33,34].

Among these metals, Cu (II) ions act much more efficiently than any other fourth period transition metal cation [35,36]. The sodium salt of the tris 2,6-pyridinedicarboxylic Eu(III) complex, $Na_3Eu(DPA)_3$, has the advantage that the DPA acts not only as an efficient coordinating ligand, but also as an antenna enhancing the emission intensity and therefore the sensitivity of the luminescent system towards the detection of cations. A recent

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publication reports the luminescence quenching of $Na_3Eu(DPA)_3$ and $Na_3Tb(DPA)_3$ in aqueous solution for the detection of Fe(III) [37]. Other authors synthesized a metal-organic framework (MOF) using a luminescent Eu(III)–3,5-pyridinedicarboxylic acid–dimethylformamide complex for which Cu(II) showed the most significant quenching effect [38].

The technology applied to the development of metal sensors is in constant progress with the purpose of attaining lower detection limits and higher specificity for the different analytes. Luminescence based analytical methods are known to be one of the most sensitive techniques and this advantage has been widely used to develop optical sensors for the detection of different analytes, including Cu(II) [39–41].

The use of expensive and generally sophisticated instrumentation makes the detection not suitable for an in situ or on-line monitoring, particularly if the sample needs special treatments such as preconcentration. In this work, we use the sol–gel technique to synthesize luminescent transparent Eu(III) films from a bis(trialkoxysilyl) organic precursor synthesized from the diamide of 2,6-pyridinedicarboxylic acid (DPA) with aminopropyltriethoxysilane (APTES) in the presence or absence of cetyltrimethyl ammonium bromide (CTAB) surfactant with triethylethoxysilane (TEOS) as crosslinker. The films were deposited on glass slices to build solid devices that operate by measuring the decrease in the emission signal of the $Eu(III)(DPA)_3$ complex in the presence of a transition metal. At this point it is worth mentioning that, contrary to what is usually reported, these devices were constantly immersed in the solution to be tested while simultaneously measuring the signal response. Therefore, the films deposited in the glass slides of these devices have the adequate mechanical robustness and chemical stability for in situ detection during long periods of time. The performance of these devices as potential sensors of Cu(II) was evaluated in terms of the values of the Stern–Volmer constant of the quenching experiments. This equation has been widely used to evaluate the relationship between the relative fluorescence intensity of an immobilized luminescent probe and the measured analyte concentration; coated fiber sensors, enzyme-mediated sensors, or gas sensors are representative examples [42]. These low cost simple devices are capable of sensing Cu(II) down to 50 ppb in aqueous systems for which neither pretreatment, degasification nor destruction of the sample are necessary.

2. Materials and methods

2.1. Chemicals

Copper(II) chloride-dihydrate, cobalt(II) nitrate hexahydrate, nickel(II) chloride hydrate, iron(III) nitrate nonahydrate, DPA (2,6-pyridinedicarboxylic) acid, APTES (3-aminopropyltriethoxysilane), TEOS, and CTAB (cetyltrimethylammonium bromide) were obtained from Aldrich. All compounds were analytical grade and were used without further purification. $Eu(NO_3)_3{\cdot}6H_20$ (99%) was obtained from Fluka Chemie AG and used as received. Water was from a Milli-Q system. $Na_3Eu(DPA)_3{\cdot}15H_2O$ was synthesized according to literature methods [43]. HCl(c) and NH_3(c) were from Mallinckrodt.

2.2. Spectroscopic measurements

Steady State emission spectroscopy: The steady state emission spectra were recorded on a PTI QuantaMaster QM-1 luminescence spectrometer. The excitation and emission wavelengths were 290 nm and 615 nm, respectively. Excitation and emission bandwidths were set to 8 and 4 nm, respectively. The experimental points plotted in the graphs of the quenching experiments were obtained from the emission intensity averaged over a period of 10 min. These average values were affected by an error not higher than 3%.

Infrared spectroscopy: IR spectra were obtained in KBr pellets using a Nicolet 8700 FTIR equipment.

2.3. Microscopic measurements

Scanning electron microscopy (SEM) was performed on a Zeiss Supra 40 microscope equipped with a field emission gun (CMA, FCEN-UBA). The images were taken with in-lens detector and 3 kV acceleration voltages. The samples were placed on an aluminum holder, supported on conductive carbon tape.

2.4. Synthesis of the compounds

A prehydrolized stock solution of TEOS, ethanol, water and HCl ($1{:}3.63{:}1{:}4.75 \times 10^{-5}$ molar ratio) was refluxed for 90 min at 60 °C. An organic hybrid N,N-bis(triethoxysilanepropyl)-2,6-pyridine dicarboxiamide ligand (SL, M = 573 g mol^{-1}) synthesized according to published procedures [44,45] was added to the stock solution (nSL:nTEOS = 1:15.5) in HCl 7 mM under stirring. After 45 min of ageing, the sol was diluted in ethanol (nSi:nEtOH = 1:26.5) to achieve the final molar ratio nSi:nEtOH:nwater:nHCl = 1:26.5: 5.23: 3.95×10^{-3} [46]. CTAB was added under stirring to half of the sol as a structuring agent in a 4.1% (w/w). $Eu(NO_3)_3$ was added to both sols with a molar ratio of nSL:nEu(III) = 1:2.9 (in the absence of CTAB added) and nSL:nEu(III) = 1:3.0 (for templated films with CTAB). The synthetic procedure is depicted in Scheme 1.

2.5. Fabrication of the sensors

The sensors were fabricated by dip-coating clean glass slides (0.8 cm × 3.8 cm × 1 mm) into the sols synthesized as described in Section 2.4, at a constant pulling rate of 10 cm/min to obtain transparent films which were left ageing at room temperature for 3 months in sealed boxes. A further heating at 95 °C for 24 h was performed for a better structuration. A sketch of the hybrid material is depicted in Scheme 2.

The CTAB was removed from the templated films by heating them with ethanol at 65 °C for 2.45 h. FTIR spectra of the films were registered to track the presence of CTAB until the ν_{CH2} bands located at 2800–3000 cm^{-1} were significantly reduced. Residual signals in this region are assigned to the methylene groups of the synthetic material. After the CTAB was withdrawn, the sensors were placed in an oven at 60 °C overnight. Hereafter, the films with and without CTAB will be named templated sensors (TS) and non-templated sensors (NTS) films, respectively.

2.6. Luminescence measurements with the sensors

The sensors were firmly fixed to a specially designed cuvette half cap. This cap keeps the sensor in a front face geometry (55° approximately) inside the cuvette which is filled with the solution of the test sample. The luminescent response was measured in situ, with the sensors always immersed in the solution and kept in the spectrofluorimeter in the same position. The sensor was allowed to equilibrate with water (hydration period) before recording the zero quencher intensity (I_o, no metal added). The addition of the metal quencher solution was performed from the top of the cuvette using a Hamilton microsyringe under stirring while keeping the cuvette with the sensor in the spectrofluorometer.

The steady state emission intensity of each sample was recorded at 615 nm after 500 s under stirring.