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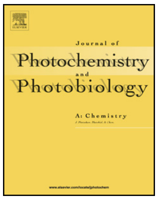

Ratiometric Hg^{2+} Sensor Based on Periodic Mesoporous Organosilica Nanoparticles and Förster Resonance Energy Transfer

Deli Lu [a,b], Hong Chen [a], Xuefeng Yan [a], Lingzhi Wang [a,*], Jinlong Zhang [a,*]

[a] Key Lab for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China
[b] School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, PR China

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ABSTRACT

A fluorescent resonance energy transfer (FRET) system was built for ratiometric sensing of Hg^{2+} in water with periodic mesoporous organosilica (PMO) nanoparticles (NPs) as the scaffold. The silylated rhodamine 6G with a spiro-ring (R6G) as the energy acceptor was covalently attached on the pore walls of anthracene (Anth) encapsulated PMO NPs, which played the role of energy donor. In the presence of Hg^{2+}, the fluorescence emission from R6G in the pore channel was observed by exciting Anth in the framework, which means the emission energy of Anth can effectively funnel into R6G and excite it. The successful FRET from Anth to R6G should be attributed to the shortened distance between them attributed to the nanometer-sized pore system of PMO matrix, which finally leads to the emission of original colorless R6G through a Hg^{2+}-promoted ring-opening process of R6G derivative. An extremely low detection limit for Hg^{2+} (6×10^{-9} M) can be achieved. These results demonstrate that fluorescent PMOs have great potential as supporting materials for enhanced fluorescence chemosensors.

1. Introduction

Heavy metal ions, widely distributed in the environment, are very harmful pollutants and would cause a series of diseases to beings [1,2]. Of these ions, mercury contamination is ubiquitous, and has been a global problem, which makes its sensing urgent and imperative [3]. Fluorescent sensor is effective and convenient when used for metal ions detection, and many fluorescent sensing systems for metal ions detection have been reported [4–10]. However, most of these metal ion fluorescent sensors are mainly based on the change of fluorescence intensity. Compared to the intensity-based fluorescent sensor, ratiometric fluorescent sensor based on two distinctly measurable signals in the presence or absence of the analyte exhibits some attractive advantages, such as, effectively minimizing influence from excitation back-scattering effects, and avoiding potential external interference from variations of sensor concentration and environment [11,12]. Up to now, more and more ratiometric fluorescent sensors have been reported, however, most of them still have some deficiency in practical applications including low detection sensitivity to target, complicated molecular design and synthesis process, and poor hydrophilicity [13–18]. Hence, how to overcome the shortcoming on preparation and accelerate the applications of ratiometric fluorescent sensor is still a huge challenge.

Recently, mesoporous silica has received much attention and has been proved to be an excellent host material for their special properties, such as, high specific surface area, ordered mesoporous pore, good optical transparency in the visible-light region and biocompatibility, making it ideal inorganic support for construction of optical sensing, bio-imaging system or light harvesting [19–21]. A variety of organic–inorganic hybrid materials based on mesoporous silica have been reported and applied for metal ions detection [22–26]. In our group, we have once found improved detection sensitivity from mesoporous silica based Cu^{2+} and Zn^{2+} fluorescent sensors [23,24]. Moreover, we also reported a sensing-range tuneable pH ratiometric sensor by incorporating commercially available dual-FRET pair into the pore channel of mesoporous silica [27]. However, it seems that the sensitivity of the dual dye system is partly discounted compared with the single dye modified mesoporous silica, which should be attributed to the sacrificed pore accessibility after the introduction of dual dye system into the pore channel. Recently, to make fluorescent mesoporous silica without sacrificing its pore volume and further modifiability, we have developed a convenient route for bis-silylation of different fluorephores and introduced them into the pore framework of mesoprous silica

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* Corresponding authors. Tel.: +86 21 64252062; fax: +86 21 64252062.
E-mail addresses: wlz@ecust.edu.cn (L. Wang), jlzhang@ecust.edu.cn (J. Zhang).

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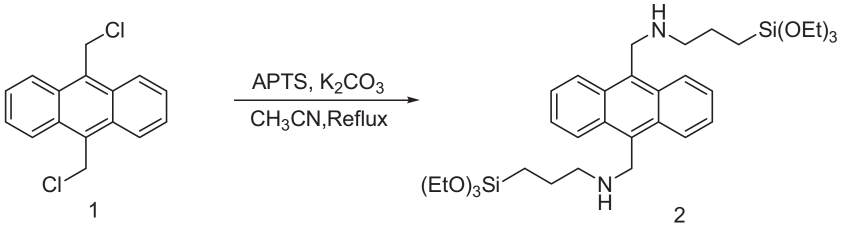
[28]. Various fluorephores can be alternatively encapsulated into the pore framework, leading to highly tuneable fluorescent performance applicable for the fabrication of different fluorescent sensor.

Herein, we first presented a novel FRET type ratiometric Hg^{2+} sensor based on fluorescent PMO nanoparticle by adopting our previously reported bis-anthracene as the reference unit, which was encapsulated into the pore framework, and taking R6G derivatives with spirolactam structure as reporting unit, which was introduced into the pore channel. Anth and R6G formed effective FRET after being assembled into mesoporous silica, which played the roles of energy donor and acceptor, respectively. The influence of pH value to Hg^{2+} detection, the detection selectivity and sensitivity to Hg^{2+}, and anti-interference to different metal ions were systematically investigated.

2. Experimentals



2.1. Materials

Chemicals for reactions were purchased from Sigma–Aldrich and are of A.R. grade. Solvents used in silica gel chromatography including ethyl acetate (EA) and petroleum ether (PE) were purchased from Sinopharm Chemical Reagent Co., Ltd. NMR solvent was purchased from J&K Chemical Ltd. All starting materials and solvents were used as received without further purification.

2.2. Experimental

2.2.1. Preparation of PMO nanoparticles (NPs)

Bis-silylated anthracene was prepared according to our previous report [28]. First, to a solution of 9,10-bis(chloromethyl) anthracene (1, 0.548 g, 2 mmol) and K_2CO_3 (1.09 g, 8 mmol) in anhydrous CH_3CN (40 mL) solution, aminopropyltriethoxylsilane (APTS, 0.96 mL, 4 mmol) was added dropwise. The mixture was then heated to reflux for 48 h under N_2 atmosphere. After the reaction was completed, the solvent was removed under reduced pressure. The crude product was then purified by chromatography on a silica gel column (ethyl acetate) to give target product bis-silylated anthracene (2) as a pale yellow liquid, isolated yield 15%.

PMO nanoparticles (NPs) were prepared by a mild and modified stöber system. First, cetyltrimethylammonium bromide (CTAB, 0.2 g, 5.5×10^{-4} mol) and NaOH (0.7 mL, 2 M) were added to 100 mL of double distilled water (DDW). The mixture was stirred for 15 min and then heated to 70 °C, which is followed by the addition of 1.0 mL (0.94 g, 4.5 mmol) of tetraethylorthosilicate (TEOS), 140 mg (0.225 mmol) of bis-silylated Anth and 0.1 mL APTS (0.427 mmol). After 1 min, 1.0 mL of ethyl acetate was added, and the resulting mixture was stirred at 70 °C for 30 s and then

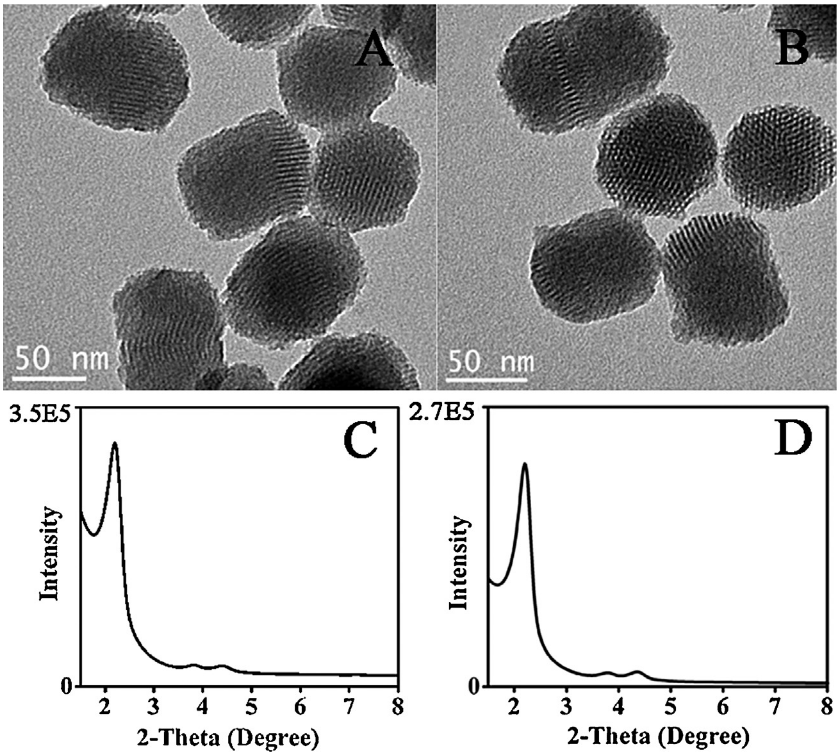


Fig. 1. TEM and low angle XRD patterns of PMO NPs before (A and C) and after (B and D) modified with sensor molecules.