



Responsive hybrid inorganic-organic system derived from lanthanide luminescence



Zhan Zhou^b, Yuhui Zheng^{b,*}, Lasheng Jiang^b, Jinglian Yang^b, Qianming Wang^{a,b,c,*}

^a Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

^b School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

^c Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, Guangzhou 510006, PR China

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ABSTRACT

Terbium ions were incorporated into new organic-inorganic matrices to achieve intense green emissions. Hemoglobin (HB) interactions lead to dramatic changes in the luminescence emission intensities. Infrared spectra, morphological studies and photoluminescence give information for the speciation and process of hemoglobin additions. The porous material has a large specific surface area of 351 cm²/g and the detection limit for HB (0.7 μM) was much lower than its physical doped material (8 μM). This promising hybrid material will lead to the design of versatile optical probes that are efficiently responding to the external targets.

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1. Introduction

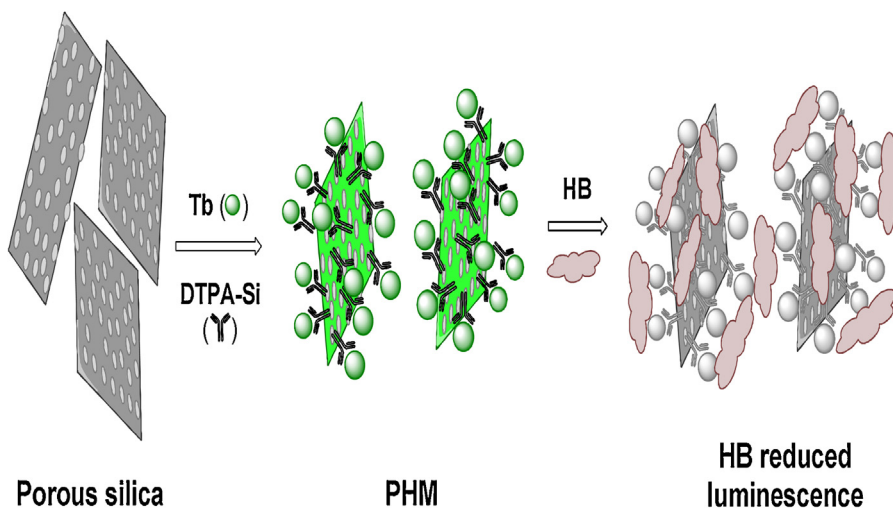
The modification of material interfaces has received extensive attention due to its technological importance [1]. Improving the properties on the surface based on its luminescence, electric or magnetic activities are hot topics in developing desired responses to the targets [2,3]. It serves a key issue to perform this surface modification in novel ways with the purpose to create functional surfaces that can be adjusted by stimuli controls. In this field, porous materials provide alternative strategies for potential applications because it is possible to realize the expected properties by loading the pores of the scaffold with organic structures or metal complexes. They have been defined as solids bearing empty spaces and interconnected pores. These highly flexible materials attracted enormous interests since multiple functions made them fascinating in numerous areas such as gas storage, catalysis, separation and adsorption [4,5]. In recent years, many typical microporous materials like zeolites, activated carbon, metal organic frameworks or cross linked polymers have been fully investigated [6,7]. However, the exploration of new candidates is still a real challenge. Here in this work, luminescent organic-

inorganic hybrid silica with intrinsic porosity has been designed and prepared.

As far as the analyte was concerned, the detection of hemoglobin has been considered to be very important in clinical diagnosis and metabolic processes. Several approaches to determine HB have been reported such as electrochemistry [8] electrophoresis [9] and high-performance liquid chromatography [10]. But the above mentioned methods still have several disadvantages with regard to stability of reagents, complexity and selectivity. Recently, many features make fluorometry one of the most powerful transduction ways to confirm the chemical recognition sites [11]. In contrast to pure organic molecules, lanthanide complexes have *f-f* forbidden transitions and the photophysical features are very unique such as long excited lifetimes, high color purity and large Stokes shifts [12–14]. The design of ideal building blocks has been of both fundamental and technological interests. In this article, we focused on the controllable syntheses of terbium containing hybrid porous nano-structures for the detection of hemoglobin (Scheme 1). In addition, physical doped material was fabricated and its physical properties were explored. In general, the sol-gel derived materials were obtained by incorporating emitting species directly into host gels and they belong to class I hybrid materials [15,16]. However, aggregation of emissive centers would frequently occur due to weak interactions between the organic and inorganic phases. Leaching problem of dopants was difficult to avoid during the

* Corresponding authors at: School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China. Fax: 86 20 39310187.

E-mail addresses: yhzheng78@scnu.edu.cn (Y. Zheng), qmwang@scnu.edu.cn (Q. Wang).



Scheme 1. Representation of the terbium hybrid material.

practical uses. Therefore, covalent linkage of the organic structure to the silica framework will allow us to circumvent the above drawbacks. The corresponding enhancement of thermal and photo-stabilities in the covalent grafting hybrid material would be expected. The structure control during the preparation of hybrid sensors will provide alternative routes in tailoring the optical properties of nano-size materials and offer more chances in the assembly of nano-devices.

2. Experimental methods

2.1. Materials

Tb₄O₇ (99.9%) was purchased from Shanghai Yuelong corporation. Terbium perchlorate was obtained by dissolving Tb₄O₇ in concentrated perchloric acid. Triton X-100, aminopropyltriethoxysilane (APS, 99%), diethylenetriaminepentaacetic acid (DTPA), diethylenetriamine pentaacetic acid dianhydride (DTPAda, 98%), human serum albumin (96–99% agarose gel electrophoresis, fraction V powder, remainder mostly globulins), hemoglobin, enzymes, proteins, and tris(hydroxymethyl) aminomethane hydrochloride (Tris-HCl, 99%), heme molecules were purchased from Aldrich company. Polyoxyethylene (20) cetyl ether (Brij 58), hydrazinehydrate (100%, hydrazine 80%), and tetraethyl orthosilicate (TEOS) were purchased from J&K Scientific. Pyropheophorbide-*a* methyl ester (chlorin 1) and 3-hydroxymethyl substituted pyropheophorbide-*a* methyl ester (chlorin 2) and were synthesized based on reported literatures [17]. DTPA-Si was prepared using procedures reported previously [18]. Graphene oxide was synthesized based on the literature [19]. All the other reagents were purchased from Guangzhou Chemical Reagent Factory and used without further purification.

2.2. Characterization

¹H NMR spectra were recorded at 293 K using a Varian 400 (400 MHz) with TMS as an internal standard, all chemical shifts were reported in the standard notation of parts per million. Fluorescence emission, excitation spectra and quantum yields were measured by using an Edinburgh FLS920 spectrometer (Great Britain), equipped with a 450 W lamp source. LC-MS was measured on a Thermo Finnigan LCQ Deca XP Max. FT-IR spectra were measured by using a Shimadzu Prestige-21. TEM was measured by using a JEOL JEM-2100HR transmission electron microscope. SEM and energy dispersive X-ray (EDX) analysis data

were measured using a Zeiss Ultra 55 scanning electron microscope. The adsorption desorption isotherms of nitrogen were measured at 77 K using the ASAP 2020 M system. TGA was carried out on a STA409PC system under air at a rate of 10 °C/min.

2.3. Synthesis of precursor DTPA-Si

Diethylenetriamine pentaacetic acid dianhydride (DTPAda) (1 g, 2.8 mmol) was dissolved in anhydrous pyridine (55 mL) under a steady flow of nitrogen, and APS (1.37 g, 6.2 mmol) was added with magnetic stirring. The mixture was stirred under nitrogen for 24 h at room temperature. The product was then precipitated with the addition of hexane to remove excessive amounts of APS, isolated by centrifuging, washed with additional aliquots of hexanes, and dried in a vacuum to obtain the target compound (DTPA-Si). MS (LCMS): 798.9 *m/z* [M – H][–]. NMR: ¹H (DMSO, ppm): 0.53 (*t*, 4H), 1.16 (*t*, 18H), 1.43(*p*, 4H), 2.83 (*t*, 4H), 2.91 (*t*, 4H), 3.05 (*q*, 4H), 3.21 (*s*, 6H), 3.36 (*s*, 4H), 3.69 (*q*, 12H), 8.11 (*t*, 2H).

2.4. Synthesis of Tb-DTPA-Si complex

DTPA-Si (0.52 g, 0.65 mmol) was dissolved in 5 mL DMSO in 50 mL round bottom flask. One equivalent of Tb(ClO₄)₃ (13 mL of a 0.05 M solution, 0.65 mmol) and ammonia (1 mL) were added. The mixture was stirred for 5 h at room temperature. The crude product was washed with ethanol and water and then dried in vacuo overnight. The resulting precipitate was collected to give the desired Tb-DTPA-Si as white powder.

2.5. Fabrication of porous hybrid material (PHM)

Graphite oxide was fabricated from natural graphite (SP-1) by Hummer's method with slight changes. 0.6 g graphite was added into a mixture of 5 mL 98% H₂SO₄, 1 g K₂S₂O₈, and 1 g P₂O₅, the solution was kept at 85 °C for 6 h. After the above preoxidized product was collected, it was added into 25 mL 98% H₂SO₄, then 3 g KMnO₄ was slowly added. The mixture was maintained at 30 °C for 2.5 h and 150 mL water was added. 3.5 mL H₂O₂ (30%) was also titrated. Finally, the resulting mixture was washed by HCl and H₂O twice. The obtained graphite oxide was dispersed in water and subsequently sonicated to give graphene oxide (GO). Silica support materials were prepared by using graphene oxide as a template [20]. 40 mL ethanol, 4 mL water, 0.5 mL ammonium hydroxide (28%), and 0.1 mL tetraethoxysilane were added to a 250 mL round bottomed flask. After 15 min, the GO solution (10 mL, 1 mg/mL) was

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