



Luminescent multifunctional hybrids obtained by grafting of ruthenium complexes on mesoporous silica

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ABSTRACT

This work evaluates the luminescent properties of new hybrids obtained by covalent grafting of ruthenium complexes on mesoporous silica particles. Spray pyrolysis afforded the mesoporous silica particles in one step; two different types of structure-directing agents were employed. Scanning and transmission electron microscopy (SEM and TEM, respectively) analyses confirmed that the particles had spherical morphology and ordered hexagonal mesoporosity (2 and 5 nm), which justified the high surface area up to 1420 m² g⁻¹ measured by Brunauer-Emmett-Teller (BET) surface area analysis. Covalent grafting of silylated ruthenium(II) complexes [Ru(bpy)₂1]Cl₂ and [Ru(bpy)₂2]Cl₂ on the mesoporous particles gave monolayered hybrids, characterized by fourier transform infrared spectroscopy (FTIR), TEM, and photoluminescence. Results highlighted the formation of new luminescent platforms containing an estimated 0.11 mmol of ruthenium(II) complex per gram of silica, which corresponded to 0.09 ruthenium(II) complex nm⁻² of silica.

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1. Introduction

Multifunctional mesoporous silica particles are potentially applicable in catalysis and separation systems, and they constitute good platforms to develop luminescent markers or probes [1,2]. Mesoporous silica particles combine unique properties such as high surface area and ordered porous structure with well-defined pore size. In addition, these particles can undergo well-controlled chemical modification, which makes them interesting hosts to prepare new luminescent systems. Porous network tuning is possible and consists of an original way to control the environment around the luminescent center, in addition to providing a protective effect against intermolecular interactions, photo-degradation, and leaching. Rocha et al. [3] have described spray pyrolysis as the best way to achieve mesoporous particles with controlled pore size and organization in one rapid step. The residual silanol groups allow covalent grafting of luminescent complexes to the silica by means of an alcoxysilylated agent. Several complexes have been grafted on mesoporous silica particles, but ruthenium(II) compounds bearing polypyridine ligands are

noteworthy for their chemical stability, redox properties, excited-state reactivity, luminescence emission, and excited-state lifetime [4–6]. Some authors [6–8] have used silylated ruthenium(II) complexes to functionalize dense silica particles. Here, we propose a multifunctional platform obtained by monolayer grafting of ruthenium(II) complexes on ordered mesoporous silica particles with controlled pore size. After modification of the particle surface with thiol or amino groups, which would make the particles available for additional coupling reactions with biomolecules, this platform could act as a specific luminescent marker for cancer cells [9]. Moreover, the ordered array of mesochannels could be an efficient approach to produce smart drug-release systems.

2. Experimental details

2.1. Preparation of mesoporous silica particles by spray pyrolysis

Mesoporous silica particles, designated **MS1** and **MS2**, were synthesized by the spray pyrolysis methodology as described in a previous work [3]; cetyltrimethylammonium bromide (CTAB) or the block copolymer Pluronic F-68 was used as structure-directing agent, respectively. TEM, SEM, FTIR, TGA (thermogravimetric analysis), BET, and ²⁹Si NMR (nuclear magnetic resonance

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spectroscopy) aided characterization of the morphology, chemical structure, and physicochemical properties of the mesoporous silica materials.

2.2. Synthesis of ruthenium complexes containing ligands modified by silylated groups

The silylated ligands 4-methyl-4'-[methylamino-3(propyl-triethoxy-silyl)]-2,2'-dipyridine (labeled **1**) and 4-methyl-4'-[methylamino-3(propyldimethyl-ethoxy-silyl)]-2,2'-dipyridine (labeled **2**) were obtained as described by Menu et al. [6]. These two ligands were used to synthesize the corresponding ruthenium(II) complexes $[\text{Ru}(\text{bpy})_2(\mathbf{1})]\text{Cl}_2$ (designated **Ru1**) and $[\text{Ru}(\text{bpy})_2(\mathbf{2})]\text{Cl}_2$ (designated **Ru2**); *cis*- $\text{RuCl}_2(\text{bpy})_2$ was the starting complex as described in [7]. Addition of acetone and dichloromethane led the complexes to precipitate, to afford **Ru1** and **Ru2** in 76% and 90% yield, respectively. The EA (elemental analyses), FTIR, and UV-vis characterization of the ruthenium(II) complexes agreed with data published in [7].

2.3. Grafting of the ruthenium(II) complexes on mesoporous silica particles

Two types of mesoporous silica particles (**MS1** and **MS2**) were modified with the **Ru1** and **Ru2** complexes, to give four luminescent hybrids denoted **MS1-Ru1**, **MS1-Ru2**, **MS2-Ru1**, and **MS2-Ru2**. Briefly, 200 mg of mesoporous silica (**MS1** or **MS2**) suspended in ethanol (20 mL) was reacted with 100 mg of the ruthenium(II) complex (**Ru1** or **Ru2**) and stirred at 295 K for 72 h, in inert atmosphere. The resulting suspensions were dialyzed for 72 h, and the solids were isolated by centrifugation at 10,000 rpm for 15 min. The solids were washed with water, acetone, ethanol, and diethyl ether, which was followed by drying *in vacuo* for 4 h. Elemental analysis allowed us to calculate the grafting ratio (R, see below), represented as the average of three experiments:

MS1-Ru1, %, found (calc.): R=0.11 mmol g⁻¹, C 5.55 (5.55), H 1.62 (0.54), N 1.05 (1.08); **MS2-Ru1**, %, found (calc.): R=0.10 mmol g⁻¹, C 4.82 (4.92), H 1.34 (0.50), N 1.00 (1.00); **MS1-Ru2**, %, found (calc.): R=0.09 mmol g⁻¹, C 4.58 (4.05), H 1.59 (0.39), N 0.85 (0.85); **MS2-Ru2**, %, found (calc.): R=0.07 mmol g⁻¹, C 4.13 (3.49), H 1.45 (0.34), N 0.73 (0.73).

2.4. Characterization methods

The MS particles were characterized by transmission electron microscopy (TEM) on a Philips CM20 microscope. Scanning electron microscopy (SEM) was conducted on a JEOL JSM 7500F microscope. N₂ isotherms were measured on a Micromeritics ASAP (Accelerated Surface Area and Porosimetry System) 2010 Sorptometer; specific surface areas were determined by the BET method [10], and pore size distribution was calculated as described in [11]. The relative errors associated with adsorption-desorption analysis were estimated as SBET, 5%; pore volume (Pv), 5%; and pore size (Ps) (DFT), 20%. FTIR spectra were acquired from 4000 to 400 cm⁻¹ with a Perkin-Elmer Spectrum 2000 (KBr dispersion) spectrometer. For all the samples, TGA was performed by using a TA Instruments SDT Q 600 thermal analyzer in oxygen, at a heating rate of 5 and 20 °C min⁻¹, from 25 to 800 °C. ¹H decoupled ²⁹Si MAS (Magic Angle Spinning) Nuclear Magnetic Resonance (NMR) spectra of mesoporous silica were recorded on a Varian Unity Inova (59.59 MHz for ²⁹Si) spectrometer. NMR spectra were de-composed to extract the proportion of the corresponding species; the DMfit software was employed [12]. C, H, and N elemental analyses were carried out for the ruthenium(II) complexes and hybrids on a Perkin Elmer 2400 series II and on a Fisons (EA 1108) analyzer, respectively. The amount of ruthenium(II) complex grafted on silica, in mmol of the complex per gram of silica, was determined by EA and TGA measurements as described by Menu and Co-workers [7]. Luminescence spectra were measured at room temperature on a Horiba Jobin Yvon Model Fluorolog FL3-22 spectrometer equipped with a DM-302 detector and a 450 W Xe excitation lamp.

3. Results and discussion

3.1. Characterization of the MS1 and MS2 materials

Spray pyrolysis is an elegant way to produce mesoporous silica in one fast step. Products obtained by spray pyrolysis are generally highly pure powders with spherical morphology [13]. SEM (Fig. 1) revealed that **MS1** and **MS2** had broad size distribution, particle sizes ranged from 100 nm to 2.5 μm, and the mean particle size was 580 and 745 nm for **MS1** and **MS2**, respectively. Spray pyrolysis retained the micelle organization present in the precursor

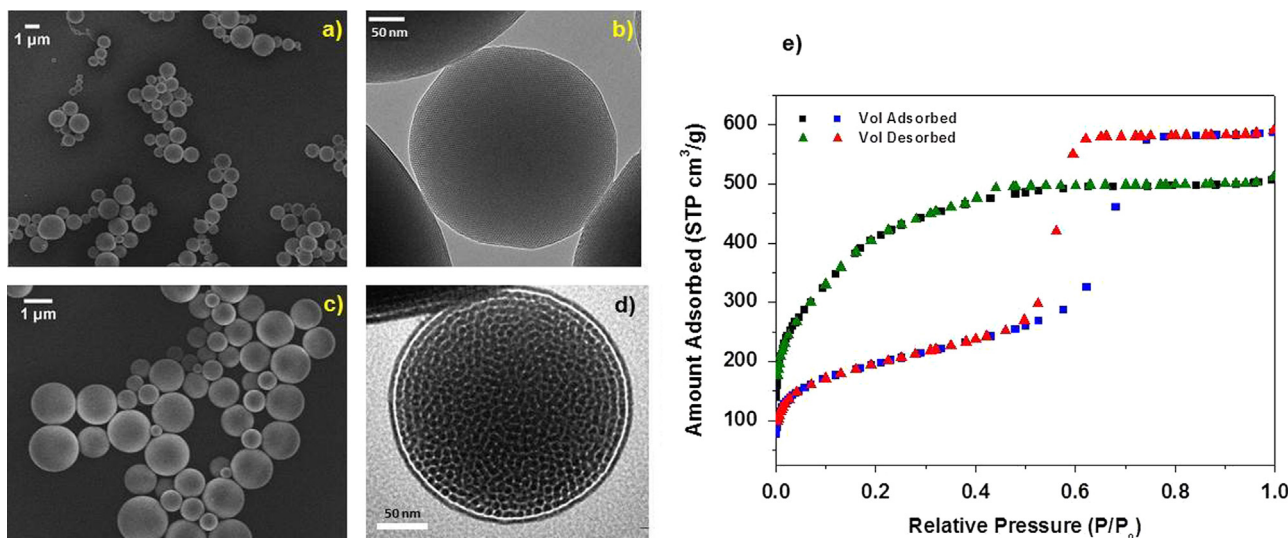


Fig. 1. SEM and TEM images of the materials **MS1** (a and b) and **MS2** (c and d); (e) N₂ adsorption isotherms for the **MS1** (green and black) and **MS2** (red and blue) particles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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