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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 $m^2\,g^{-1}$ measured by Brunauer-Emmett-Teller (BET) surface area analysis. Covalent grafting of silylated ruthenium(II) complexes [Ru(bpy)$_2$1]Cl$_2$ and [Ru(bpy)$_2$2]Cl$_2$ 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.

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, photodegradation, 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 ^{29}Si 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(propyltriethoxy-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 $[Ru(bpy)_2(\mathbf{1})]Cl_2$ (designated **Ru1**) and $[Ru(bpy)_2(\mathbf{2})]Cl_2$ (designated **Ru2**); *cis*-$RuCl_2(bpy)_2$ 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. N_2 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 ^{29}Si MAS (Magic Angle Spinning) Nuclear Magnetic Resonance (NMR) spectra of mesoporous silica were recorded on a Varian Unity Inova (59.59 MHz for ^{29}Si) spectrometer. NMR spectra were decomposed 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

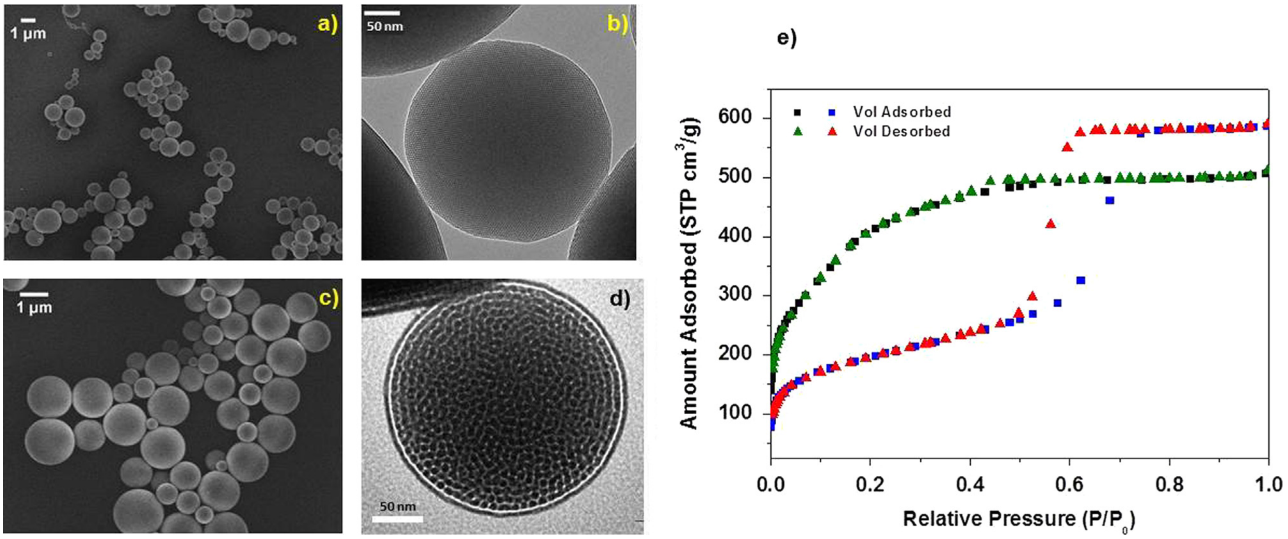


Fig. 1. SEM and TEM images of the materials **MS1** (a and b) and **MS2** (c and d); (e) N_2 adsorption isotherms for the **MS1** (green and black) and **MS2** (red and blue) particles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Grafting ratios, in mmol of ruthenium(II) complex g^{-1} of silica, and amount of ruthenium(II) complex nm^{-2} of silica for the hybrids

	EA (mmol g^{-1})	TGA (mmol g^{-1})	Complexes/nm^2
SiO_2-**MS1**-**Ru1**	0.11	0.11	0.05
SiO_2-**MS1**-**Ru2**	0.09	0.09	0.04
SiO_2-**MS2**-**Ru1**	0.10	0.10	0.09
SiO_2-**MS2**-**Ru2**	0.07	0.07	0.07

solution in the final powder, and the samples displayed an ordered hexagonal array of pores with average diameter of 2.0 and 5.2 nm for **MS1** and **MS2**, respectively, as observed by TEM (Fig. 1).

Fig. 1e shows the N_2 adsorption isotherms obtained for **MS1** and **MS2**. The specific surface areas of these materials were 1420 and 678 $m^2\ g^{-1}$, respectively; the pore volume values were calculated as 0.62 and 0.84 $cm^3\ g^{-1}$, respectively. **MS2** presented type IV isotherm with a type H1 hysteresis loop according to the IUPAC classification, which is characteristic of mesoporous materials [14]. In turn, **MS1** presented type I isotherm, which is typical of microporous materials. These different features were a consequence of the pore size of **MS1** particles 2 nm, as characterized by TEM which lies at the borderline between microporous and mesoporous materials [15]. Therefore, a simple change in surfactant (directing agent) determined production of micro- or mesoporous materials.

3.2. *Characterization of the luminescent hybrids MS-Ru*

Upon reaction of silylated ruthenium(II) with mesoporous silica, residual OH groups present on the surface of the mesoporous particles were the target for grafting of the ruthenium(II) complex. Mesoporous structures make interesting grafting platforms because it is possible to control the architecture of the pores and to produce different multifunctional systems. The FTIR spectra (not shown) confirmed grafting of ruthenium(II) complex on mesoporous silica. However, the small concentration of ruthenium(II) complex in the material gave rise to only some bands in the FTIR spectra. These bands were attributed to CH_2, CH_3 asymmetric vibration (2927–2970 cm^{-1}) and axial deformation of C=C and C=N bonds (1600 and 1400 cm^{-1}) [16–18]. It was not possible to assign the bands characteristic of the covalent binding of ruthenium complexes on silica because they overlapped with the bands due to the silica matrix (υ (Si-O-Si)) [18,19].

The grafting ratio (amount of ruthenium(II) complex per gram of mesoporous silica) displayed in Table 1 was determined by elemental analysis based on the nitrogen content, according to previous works [6–8], and by the TGA and BET data (Fig. 2).

Analysis of the data presented in Table 1 showed higher grafting ratios for **Ru1** as compared with **Ru2. Ru1** contains three ethoxy groups (see structure illustrated in Fig. 3), which favored reaction between the OH groups in the silica and the alkoxy groups in the ruthenium(II) complex. The methodology employed here provided coating of a porous surface with a monolayer of ruthenium(II) complex.

Despite their different surface areas, the micro- (**MS1**) and

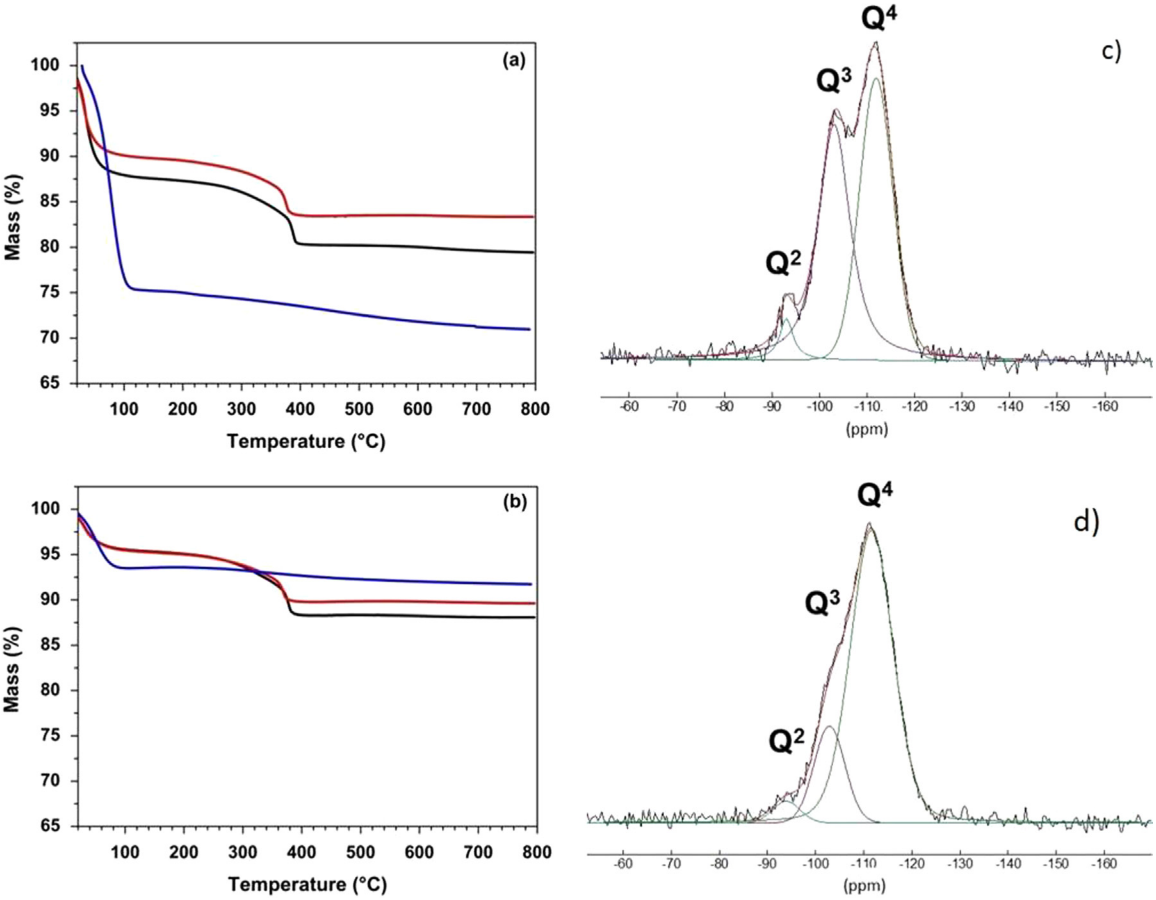
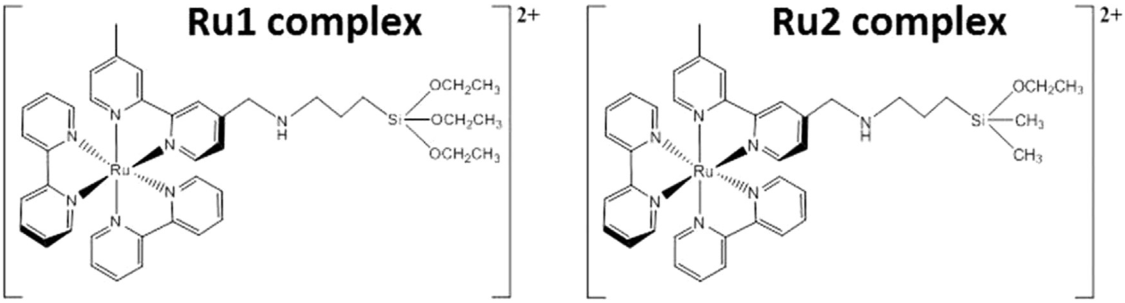


Fig. 2. Thermogravimetric analysis (TGA) of pure and grafted hybrids. (a) **MS1** (blue line) and hybrids **MS1-Ru1** (black line) and **MS1-Ru2** (red line); (b) **MS2** (blue line), hybrids **MS2-Ru1** (black line) and **MS2-Ru2** (red line). ^{29}Si MAS NMR spectra and their respective deconvolution to (c) **MS1** and (d) **MS2**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



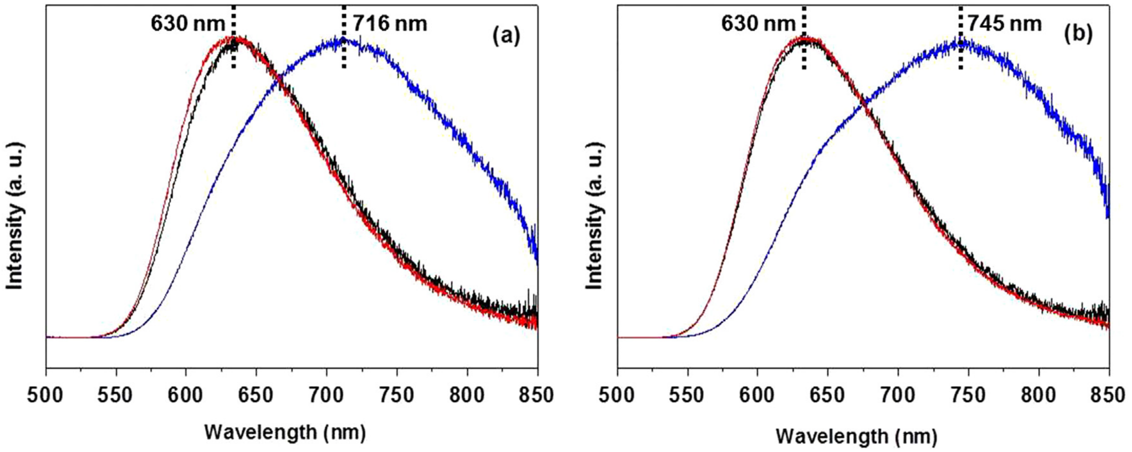


Fig. 3. (a) Emission spectra of **Ru1** (blue line), **MS1-Ru1** (red line), and **MS2-Ru1** (black line) (Excitation: 455 nm); **(b)** emission spectra of **Ru2** (blue line), **MS1-Ru2** (red line) ,and **MS2-Ru2** (black line) (Excitation: 455 nm). (For interpretation of the references to color in this figure legend,the reader is referred to the web version of this article.)

mesoporous (**MS2**) systems had similar grafting ratios. Elemental analysis results agreed with thermal analysis data. A larger amount of solvent adsorbed on the **MS1** surface (Fig. 2a), probably due to the relationship between the pore diameter of the material and the heating rate applied during pyrolysis [3,8].

The characteristic emission band of the **Ru1** and **Ru2** complexes emerged at lower energy than 550 nm, and it was centered at 716 and 745 nm, respectively (Fig. 3), as a result of the transition from the triplet MLCT (metal-to-ligand charge transfer) excited state to the ground state. These results are quite different from Ru (bpy)3(2+) complex, and it was consequence of the new symmetry imposed by the alkoxysilyldipyridine ligands 1 and 2. The emission band of all the hybrids significantly shifted toward the blue. This shift toward higher energy was related to the rigidochromism phenomenon [20,21] due the interaction between the complexes and the silanol groups of the rigid network avoid the spatial reorientation of complex. When the ruthenium(II) complexes were grafted onto the mesoporous surface, the solvent present into the pores was unable to reorient around the excited complex. As a consequence, the Franck-Condon excited state was not completely stabilized, and emission occurred from a higher energy level than free complex.

The different pore diameters of **MS1** (2.0 nm) and **MS2** (5.2 nm) did not modify the emission spectra substantially. The high concentration of grafted complex per nm^{-2} in the **MS2** materials (Table 1) probably minimized the effect of pore size.

4. Conclusion

Potential multifunctional systems based on mesoporous silica particles and silylated ruthenium(II) complexes were obtained. The ordered hexagonal arrays of the mesochannels proved to be an excellent host for luminescent complexes: the final system presented intense photoluminescence emission for both studied complexes. The high surface area of the materials added to the hydroxyl group remaining on the silica walls constituting the pores shall allow for further functionalization of the hybrids, to produce luminescent systems tailored for drug delivery and biomolecular identification. The physicochemical behavior of the silica surface could also be tuned from hydrophilic to hydrophobic, to give new luminescent platforms for investigation and therapy in biological systems.

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