Mesoporous material containing Tb^{3+} complexes bonded to MCM-41 functionalized: Assembly, characterization and luminescence

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Abstract. Ligand N^2,N^6-bis(2-hydroxyethyl)pyridine-2,6-dicarboxamide (BHPC) was synthesized and used to construct lanthanide-based mesoporous material Tb-BHPC-MCM-41. In the structure of the luminescent material, BHPC was anchored into the forming MCM-41 host by the reaction between the hydroxyl group and active Si-OH, and Tb^{3+} ions were chelated by BHPC. The mesoporous material Tb-BHPC-MCM-41 was characterized by UV, IR, small-angle X-ray diffraction (SAXRD) patterns, nitrogen adsorption/desorption isotherms and fluorescence spectra. The results indicate that ligand and Tb^{3+} had been introduced into the MCM-41 host, and Tb-BHPC-MCM-41 exhibits characteristic luminescence of Tb^{3+}.

Introduction

In recent years, lanthanide complexes have received much attention because of their interesting photophysical properties such as sharp emission spectra for high color purity, broad emission bands covering the ultraviolet–visible–near infrared region, a wide range of lifetimes from the microseconds to seconds level, which have potential application in the luminescence probes for chemical or biological macromolecules and the active center for luminescent materials [1][2]. However, although the lanthanide complexes have good luminescence properties, its stability is poor, which limits its application. One feasible solution is to introduce the complexes in a stable rigid matrix, for example, a silica-based or titania-based material. Incorporation of a luminescent lanthanide complex into these matrices, so-called "organic–inorganic hybrid materials", has not only improved the photo- and thermal- stabilities of the lanthanide complex, but also avoided self-quenching because of the concentration effect [3].

Mesoporous silica materials (MCM-41, MCM-48, SBA-15, SBA-16, and so on) have interesting unique propertie, such like ordered pore structure, high surface area, varying morphology, and potentially are excellent host for lanthanide complexes to form functional mesoporous materials [4][5]. Recently, lanthanide-based luminescent mesoporous materials have been reported. To pre pare the mesoporous materials with covalent bonds between lanthanide complexes and mesoporous host, silane coupling agents are widely used [6][7][8]. Silane coupling agents have Si-OR group which is easy to form strong Si-O-Si bond with etraethoxysilane during a hydrolysis process. However, Si-OR group is not stable because of its hyper-moisture sensitive, and as a result, the intermediate ligands modified by silane coupling agents are hard to purify. Therefore, the purity of the lanthanide complexes and the final mesoporous materials cannot be guaranteed.

On the other hand, hydroxyl is a functional group that can react with active Si-OH to form a covalent C-O-Si bond. Based on this kind of reaction, the luminescent Tb-containing mesoporous material Tb-BHPC-MCM-41 was prepared in this work. The BHPC ligand can form a stable chelating structure with lanthanide ions, and the hydroxyl group can anchor the ligand to the forming MCM-41 host. In addition, the luminescent properties of the mesoporous material were investigated, and it exhibit characteristic luminescence of Tb^{3+}.

Experimental

Materials: The lanthanide oxide Tb_2O_3 was converted to its chloride by the treatments with concentrated hydrochloric acid. Other chemicals were obtained from commercial sources and used without further purification.

Synthesis of Pyridine-2,6-dicarbonyl Dichloride: To a mixture of pyridine-2,6-dicarboxylic acid (1.34 g, 8 mmol) in DMF (0.05 mL) was added $SOCl_2$ (15 mL). The mixture was refluxed under stirring for 2 h, during which time the insoluble powder gradually dissolved. The excess amount of $SOCl_2$ was then removed under reduced pressure by adding a small amount of toluene, and pale white solid (1.61 g) was obtained.

Synthesis of N^2,N^6-bis(2-hydroxyethyl)pyridine -2,6-dicarboxamide (L): To a ice-cooled solution of of 2-aminoethanol (1.22 g, 20 mmol) and triethylamine (3 mL, 20 mmol) in dichloromethane (20 mL) was added a solution of pyridine-2,6-dicarbonyl dichloride (1.61 g, 8 mmol) in dichloromethane (20 mL) over 10 min; a white precipitate was generated immediately. After stirring for 1 d at room temperature, $SOCl_2$ (15 mL) was added. The solution was cooled in an icebath and stirred at reflux for further 2 h until the white precipitate dissolved, and the color of the solution turned violent. The solution was then concentrated under reduced pressure, and the residual amount of $SOCl_2$ was removed under reduced pressure by adding a small amount of toluene. The resulting residue was triturated with dichloromethane (20 mL), and the solution was washed with saturated sodium hydrogen carbonate solution (12 mL), water (12 mL), and brine (12 mL), dried with sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography [silica gel, petroleum ether/ Ethyl acetate, 2:1 to 1:1] to give product as a white solid (1.37 g, 60%), . 1H NMR (400 MHz, DMSO): δ = 9.55 (t, 2 H), 8.25–8.19 (m, 3 H), 3.83–3.79 (m, 4 H), 3.72 (t, 4 H) ppm. Anal. Calcd. for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59; Found: C 52.31; H, 6.01; N, 16.44.

Preparation of MCM-41 host: in a typical synthesis process, cetyltrimethylammoniumbromide (CTAB) was used as a template. 1.0 g CTAB was first dissolved in 40 g of deionized water under heating at 60 ˚C. After the solution turned clear, then added subsequently 11 ml of $NH_3 \cdot H_2O$ and 5 ml of tetraethylorthosilicate (TEOS). The solution was further stirred for 3 h, and then was placed in a Teflon-lined vessel and heated at 110 ˚C for 120 h. The resulting white powder was filtered, thoroughly washed with deionized water and dried. CTAB surfactant molecules were then removed by calcination of the resulting white powder at 600 ˚C in air for 6 h.

Preparation of Tb-BHPC-MCM-41: Ligand N^2,N^6-bis(2-hydroxyethyl)pyridine -2,6-dicarboxamide was first dissolved in 20 ml ethanol / 3 ml H_2O / 0.1 ml HCl, and then MCM-41 was added (L:MCM-41 = 1:10). The mixture was stirred for 24 hours, and then filtered, washed by Soxhlet extraction with ethanol under reflux for 6 h to remove unreacted ligand. The resulting white solid was re-dispersed in 15 ml ethanol, and then added a solution of $TbCl_3 \cdot 6H_2O$ (L:Tb^{3+} = 3:1) in 5ml 95% ethanol. The mixture was refluxed for 6 h, and then filtered, washed with H_2O to remove access $TbCl_3$ in the system. The powder of product was dried at 60 ˚C, and this mesoporous material containing Tb^{3+} was denoted as Tb–BHPC–MCM-41.

Measurements: ^1H NMR spectra were recorded in DMSO on an INOVA2 400 spectrometer with tetramethylsilane (TMS) as internal reference. Elemental analyses (C, H, N) were carried out by the Elementar Cario EL elemental analyzer. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol/L, DMSO solution) were recorded with an Agilent 8453 spectrophotometer. IR spectra were measured with in the 4000–400cm^{-1} region on the Gangdong FTIR-650 infrared spectrophotometer with the KBr pellet technique. The X-ray powder diffraction (XRD) patterns of all samples were performed on a Rigaku D/max-rB diffractometer equipped with a Cu anode in a 2θ range from 0.6° to 5.994°. Surface areas and total pore volumes were performed on Quantachrome autosorb-iQ, and the instrument of N_2 adsorption/desorption isotherms using the BET and BJH methods. The luminescence (excitation and emission) spectra and lifetime for the solid sample were determined with a HORIBA FluoroMax-4 spectrophotometer.

Results and discussion

Ligand N^2,N^6-bis(2-hydroxyethyl)pyridine -2,6-dicarboxamide (BHPC) was synthesized by modification of 2,6-Pyridinedicarboxylic acid molecule. In the structure of BHPC, there are two hydroxyl groups in the structure. As the previous reports of Dr. Siovio quici et al., the hydroxyl group can react with active Si-OH to form a covalent C-O-Si bond under weak acidic addition, and this kind of reaction has been used to prepare lanthanide organic-inorganic materials[9][10][11]. In this work, the BHPC was introduced into a forming MCM-41 host by the reaction between the hydroxyl groups and the surface Si-OH from SiO_2 network. In addition, the unreacted BHPC in the system, such as the free BHPC and most of hydrogen bond forming BHPC, can be eluted off by Soxhlet extraction technique since the BHPC ligand has excellent soluble ability in ethanol.
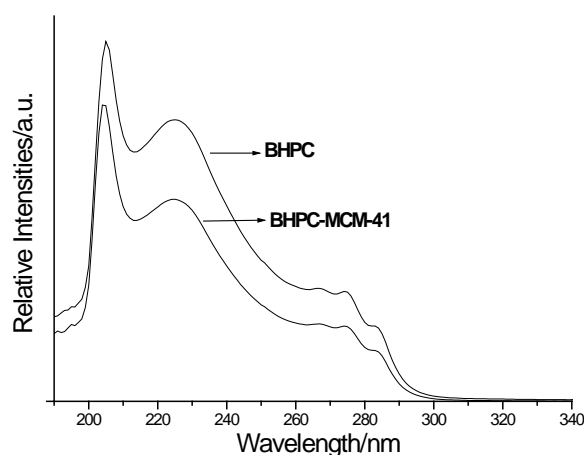

Fig. 1. UV spectra of free BHPC and BHPC-MCM-41.

The above resulting intermediate was donated as BHPC-MCM-41. Fig. 1 shows the ultraviolet absorption spectra (5×10^{-4} mol/L DMSO solution) of free BHPC and the BHPC-MCM-41. It can be observed almost the same absorption band of the major π-π^* electronic transitions of BHPC and BHPC-MCM-41, they all exhibit two large broad absorption band and the maximum absorption peaks are located at around 205, 225, 266, 275 and 284 nm. The results indicate that the BHPC ligand has been introduced into the mesoporous host. In addition, as the previous reports, the 2,6-Pyridinedicarboxylic acid derivatives by acylation reaction usually exhibit multi-dentate coordination modes toward metallic ions, so BHPC ligand can capture Tb^{3+} ions to form a complex component in the mesoporous material system, and then the luminescent material Tb-BHPC-MCM-41 was obtained. Scheme 1 shows the synthesis process of BHPC and the mesoporous material Tb-BHPC-MCM-41.
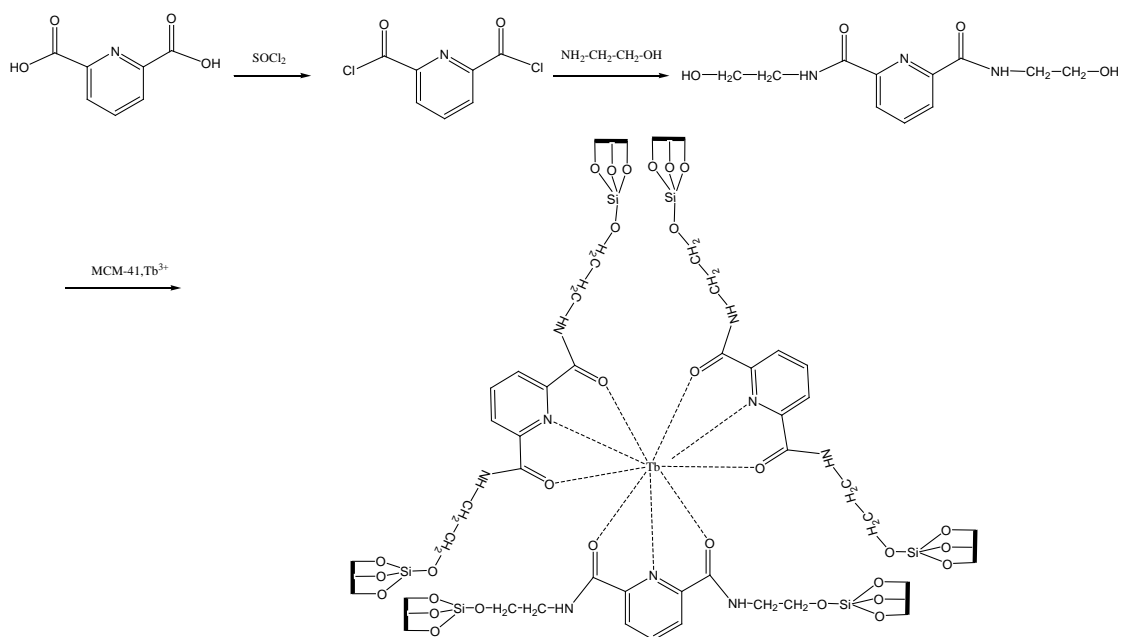
Scheme 1. Synthesis of BHPC and Tb-BHPC-MCM-41

Fig. 2 shows the IR spectra of preparing MCM-41 host and the mesoporous material Tb-BHPC-MCM-41. The MCM-41 host exhibits peaks at 3435 cm^{-1}, 1642 cm^{-1}, 1082 cm^{-1}, 958 cm^{-1}, 796 cm^{-1}, 552 cm^{-1}, 458 cm^{-1}, respectively. Among, the peak at 1082 cm^{-1} originate from the antisymmetric stretching vibration of Si-O-Si bonds; the peak at 458 cm^{-1} originates from the symmetrical stretching vibration of Si-O bonds; the peak at 1642 cm^{-1} originates from the bending vibration of H-O-H; the peak at 958 cm^{-1} originates from the bending vibration of Si-OH. Tb-L-MCM-41 shows the similar infrared absorption bands except one shoulder peak at 2949 cm^{-1} and 2964 cm^{-1}, which is the absorption band of -CH$_2$-CH$_2$- from ligand, indicating that ligand has been been grafted onto the wall of MCM-41 host. The absorption band of Si-O-C should appear in the 1000–1100 cm^{-1} range, however, it is covered by the absorption band of Si-O-Si bonds.
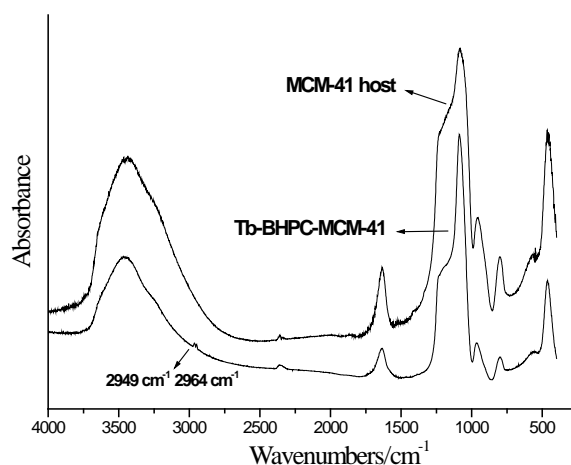

Fig. 2. IR spectra of MCM-41and Tb-BHPC-MCM-41.

The small-angle X-ray diffraction (SAXRD) patterns and nitrogen adsorption/desorption isotherms are popular and efficient methods to characterize highly ordered mesoporous material with hexagonal symmetry of the space group *p6mm*. The SAXRD patterns of preparing MCM-41 host and the luminescent material Tb-BHPC-MCM-41 are presented in Fig. 3. For the host, the pattern clearly shows the order of the hexagonal array of the MCM-41 structure and exhibit distinct

Bragg peaks in the 2θ range of 0.6–6°, which can be indexed as (100), (110), and (200) reflections. The Tb-BHPC-MCM-41 shows similar curve with that of MCM-41 host, only the diffraction intensity is lower, which is due to the presence of organic complex moieties inside the pore channels of the MCM-41 host, resulting in the decrease of the mesoporous order.
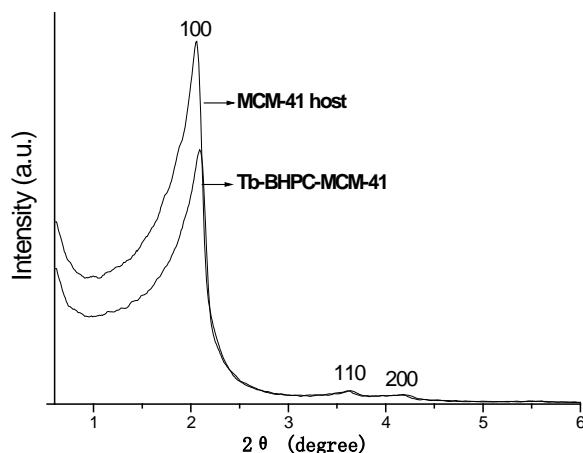

Fig. 3. SAXRD of MCM-41 host and Tb-BHPC-MCM-41.

Fig. 4 shows the N_2 adsorption–desorption isotherm for preparing MCM-41 host and Tb-BHPC-MCM-41. The two isotherms are quite similar and display Type IV isotherms with H1-type hysteresis loops at low relative pressure in accordance with the IUPAC classification, characteristic of mesoporous materials with highly uniform size distributions. For the two curves of adsorption–desorption isotherms, the presence of a sharp adsorption step in the P/P_0 region from 0.3 to 0.4 and a hysteresis loop at the relative pressure $P/P_0 > 0.45$ shows that all materials process a well-defined array of regular mesopores. By using BET and BJH methods, the surface area and the pore volume of the MCM-41 host were calculated to be 1081.3 m^2g^{-1} and 0.999 cm^3g^{-1}, respectively. Furthermore, the surface area and the pore volume of Tb-BHPC-MCM-41 were calculated to be 854.2 m^2g^{-1} and 0. 903 m^2g^{-1}, which are lower compared with that of MCM-41 host. The decrease might be due to the presence of Tb-complexes on the pore surface, which reduces the diameter of the micelles.
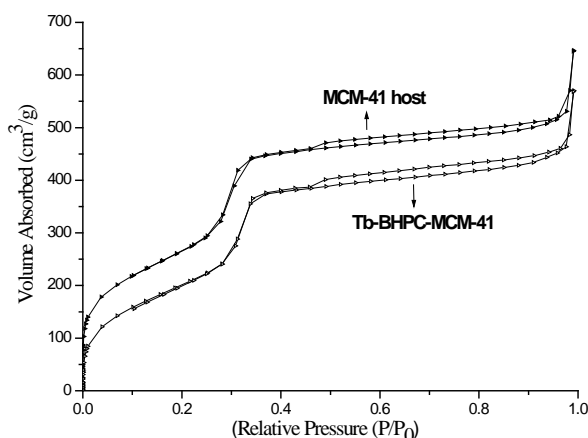

Fig. 4. N_2 adsorption/desorption isotherms of MCM-41 host and and Tb-BHPC-MCM-41.

The excitation (inner) and emission spectra of the luminescent mesoporous material Tb-BHPC-MCM-41 are shown in Fig. 4. The excitation spectrum of Tb-BHPC-MCM-41 monitored at 543 nm is dominated by one broad band with the main peak at around 339 nm. Upon excitation at 350 nm, the characteristic emission peaks of Tb^{3+} $^5D_4\rightarrow^7F_j$ (j = 6, 5, 4) transitions at 489 nm, 543 nm and 582 nm are observed, among the green luminescent intensity of $^5D_4\rightarrow^7F_5$ transition is the strongest, and the blue transition of $^5D_4\rightarrow^7F_6$ transition exhibits the second strongest intensity.
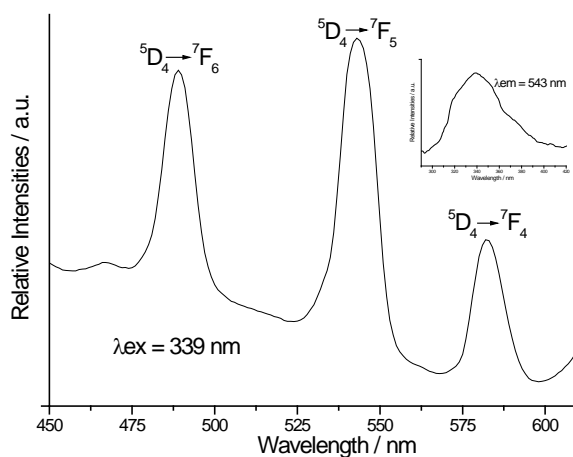

Fig. 5. Luminescence of Tb-BHPC-MCM-41.

Conclusions

In conclusion, the modification of pyridine-2,6-dicarboxylic acid, results in a ligand BHPC with a functional –OH group, which is useful to introduce the ligand to forming MCM-41 host based on the reaction between the hydroxyl group and active Si-OH. The prepared mesoporous material Tb-BHPC-MCM-41 was characterized by UV, IR, SAXRD and N_2 adsorp-tion/desorption isotherm. The results indicate that ligand was introduced into the MCM-41 host, and Tb-BHPC-MCM-41 exhibits characteristic luminescence of Tb^{3+}. In addition, there is no silane coupling agent in the preparation process, which is superior to the reported method since the intermediate ligand can be purified and then ensure the purity of product.

Acknowledgement

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