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Mesoporous MCM-41 embeded with Ru(II)-based chemosensor: Preparation, characterization, and emission variation towards pH

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ABSTRACT

In this article, a pH sensing mesoporous MCM-41 material containing covalently bonded Ru(II) complex in the silicate network was prepared and named as Ru–MCM-41. The emission signal shows a tendency to decrease upon increasing pH values. The luminescent pH sensor can be explained by the protonation and deprotonation of the PIP ligand (PIP=2-phenyl-1H-imidazo[4,5-f][1,10]phenanthroline) and the fact that the mesoporousity of the MCM-41 matrix favors the –OH that diffused to the complex, resulting in quick emission quenching. It also shows a slight sensitivity towards dissolved molecular oxygen and varying temperatures, which, however, may not be too troublesome for actual applications. The sensing mechanism is also investigated.

1. Introduction

Recently, chemosensors are gaining more and more interests due to their implications in numerous fields, such as chemistry, biology, medicine and environmental studies [1,2]. A chemosensor can be defined as a compound that can detect analyte by invoking a change in one or more properties of the system, such as absorption, emission, or redox potential characteristics. Fluorescence detection, in particular, is considered to be the most effective tool for sensing applications owing to the high sensitivity, easy visualization, and short response time for detection [2]. Among all compounds used as fluorescent chemosensors, heavy-metal complexes with phosphorescent emission are particularly attractive due to their rich chemical structures, ease of chemical modification and high photoluminescence (PL) quantum yield.

At the same time, the development of pH chemosensors that can selectively recognize and signal the presence of specific guests has extensively been pushed owing to their potential in medical, biological, and environmental applications [3]. For example, covalent porphyrin monolayers have been tried as pH sensing candidates, where promising results have been obtained [4–6]. In general, this involves the incorporation of chemosensor molecules into a sol–gel matrix [3,7]. Physical entrapment and functionalization of organosilane monomers by sensor molecules are two common approaches for such incorporation. The latter method is considered more advanced, as it eliminates the problem of dopant leaching and improves the homogeneity of sensing units in the sol–gel matrix [8,9]. High sensitivity and ease of operation are two main features for the design and fabrication of a sensor. Fluorescence techniques can easily fulfill these requirements and fluorescence-based sensors are therefore particularly well suited to monitor the presence of interesting analytes [10–12]. However, to avoid the time-consuming synthesis and testing that govern the development of such devices, the construction of optical sensors for multianalyte detection is a real challenge, which should make full use of rational strategies available in the fields of organic and/or inorganic supramolecular chemistry, photochemistry and photophysics [13,14].

In this paper, we introduce a novel Ru(II) complex of Ru(Bphen)$_2$PIP, where Bphen=Bphen=4,7-diphenyl-1,10-phenanthroline and PIP=2-phenyl-1H-imidazo[4,5-f] [1,10]phenanthroline, into the framework of MCM-41, resulting in a composite material of mesoporous MCM-41 embedded with Ru(II)-based chemosensor, hoping to develop a new pH sensing material.

2. Experimental

The synthetic route for the composite material of mesoporous MCM-41 embedded with Ru(II)-based chemosensor, named as Ru–MCM-41, is shown in Scheme 1. Analytical grade solvents and compounds were used for preparations. TEOS (Tianjin Chemicals Co.), 3-(triethoxysilyl)-propyl isocyanate (ICPTES, Aldrich), CTAB (Aldrich). Anhydrous RuCl$_3$ (99.99%) was obtained from A1cros Organics (Geel, Belgium). All reagents were of analytical grade. The water used in our work was deionized.

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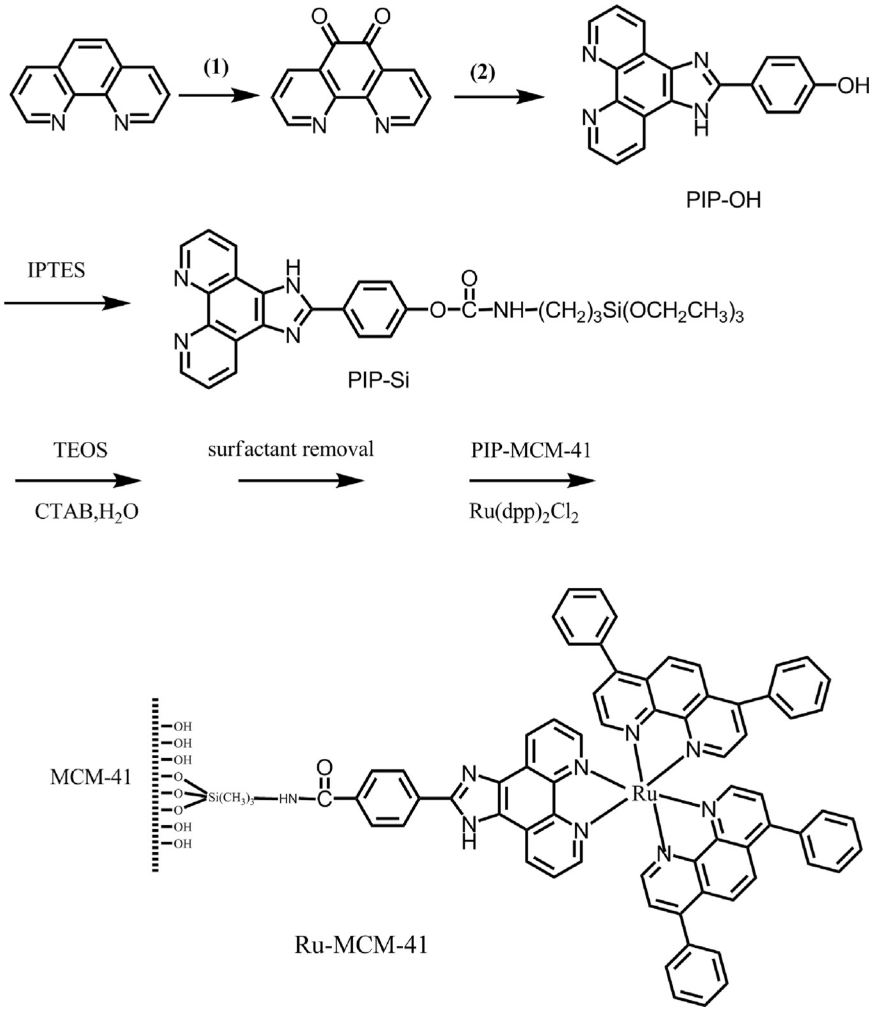

Scheme 1. The synthetic route to Ru–MCM-41.

2.1. Synthesis of hydrolyzable 1,10-phenanthroline functionalized PIP–Si ligand

The PIP–Si was prepared using 2-phenyl-1H-imidazo [4,5-f][1,10]phenanthroline (PIP-OH) and ICPTES as the staring materials. The synthesis of PIP-OH was performed by oxidation of 1,10-phenanthroline in a mixture of concentrated sulfuric acid and nitric acid, followed by condensation of 1,10-phenanthroline-5,6-dione and 4-hydroxy-benzaldehyde, according to a slightly modified imidazole ring preparation method [15–21]. The detailed synthetic procedure of PIP–Si is described as follows: PIP-OH (0.25 g) was mixed with an excess of ICPTES (1 mL) in a round-bottomed flask, then the mixture was kept under nitrogen in an ultrasonic bath for about 15 min. After having stirred under nitrogen at 80 °C for 72 h, the residual was added dropwise into about 30 mL of cold hexane to precipitate a white-yellow solid from the mixture. The final filtered-off precipitate was washed with several portions of cold hexane and then dissolved in absolute ethanol. The solution was filtered, and the ethanol was eliminated by evaporation to obtain a solid compound. The compound can be dissolved in a small portion of dichloromethane, which proves that the reaction between PIP-OH and ICPTES occurred since the starting PIP-OH was not soluble in dichloromethane. The solution was added dropwise into about 30 mL of cold hexane to re-precipitate the compound and dried in vacuum. The product obtained by the method described above is pure enough for use as a starting product for the preparation of hybrid materials.

2.2. Synthesis of phen-functionalized MCM-41 mesoporous material (PIP–MCM-41)

The synthetic procedure of intermediate mesoporous silica PIP–MCM-41 was similar to the previous publication with some minor modifications [15–17]. The synthetic procedure was described as follows: concentrated $NH_3 \cdot H_2O$ (4.5 mL) was mixed with deionized water (10 mL) and CTAB (0.41 g) at 35 °C. To this homogeneous solution TEOS (1.9 mL) and PIP–Si (0.11 g) were added under vigorous stirring. The molar ratio of the synthetic mixture was PIP–Si/TEOS/CTAB/NH_3H_2O/H_2O=0.02:1.0:0.139:3.76:66.57. The mixture was stirred for 10 h at room temperature and then transferred into a Teflon bottle sealed in an autoclave, which was then heated at 100 °C for 48 h. The solid product was filtered, washed with H_2O, and dried for 12 h at 60 °C. The surfactant was removed by acid/solvent extraction, using a solution of 1 M HCl in ethanol. This mixture was refluxed for 72 h, then filtered and washed with EtOH to remove the residual HCl. The product was dried at 60 °C for 12 h in vacuo to obtain the synthesized PIP–MCM-41.