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Covalent attachment of 4-amino-1,8-naphthalimides onto the walls of mesoporous molecular sieves MCM-41 and SBA-15

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ABSTRACT

This work describes the covalent grafting of 4-amino-1,8-naphthalimides, which are fluorescent dyes with very interesting optical properties, onto the walls of mesoporous molecular sieves. The mesoporous materials MCM-41 and SBA-15 were first treated with 3-aminopropyltriethoxysilane, generating amine-rich surfaces that were further reacted with 4-amino-1,8-naphthalic anhydride, resulting in yellow fluorescent solids. The success of the modification reactions was confirmed by elemental analysis, X-ray diffraction patterns, infrared spectroscopy, scanning electron microscopy and UV/visible and fluorescence spectroscopy. The emission spectra of the dye bound to MCM-41 was quite insensitive to solvent polarity, in contrast to dye-grafted SBA-15, which showed a high solvent sensitivity. These results suggest a tight fit of the dye molecules within the channels of MCM-41, leaving no room for the solvent molecules. In the case of SBA-15, the large pore size allows the invasion of the channels by solvent molecules, resulting in solvation of the encaged chromophore.

1. Introduction

Mesoporous molecular sieves are nanostructured materials obtained by surfactant-templated synthesis, resulting in highly ordered hexagonal arrays of one-dimensional, three-dimensional or wormlike channels, with large surface area and narrow pore size distribution [1,2]. Among the most well-known mesoporous molecular sieves are the MCM-41 [1] and SBA-15 [2] families, with pore sizes in the range 2–10 nm and 5–30 nm, respectively. Initially, researchers were interested in these materials as catalysts for the petroleum industry [3,4], in substitution for the zeolites. More recently, however, with the development of nanotechnology, it was acknowledged that these nanostructured materials have a great potential for novel applications in photonics and electronics, since they can incorporate large organic dyes [5,6]. Examples of organic dyes that have been incorporated into mesoporous silicates are porphyrins [7], phthalocyanines [8,9], methylene blue [10] and ferrocene [11]. The incorporation of fluorescent dyes is particularly interesting for the construction of optical devices, such as nanolasers and fluorescent nanoparticles for medical diagnosis [12–15], since the organized mesoporous framework usually prevents dye aggregation, increasing the fluorescence. Most studies on the incorporation of fluorescent dyes into mesoporous molecular sieves, however, have been restricted to rhodamine, fluorescein and coumarin derivatives [5,6,12–15]. Our group [16,17] and others [18] have recently reported on the incorporation of a different class of dyes, the 3,4,9,10-perylenediimides (PDI), into the channels of mesoporous materials MCM-41 and SBA-15. In a continuation to our efforts towards preparing new materials based on fluorescent aromatic imides, we report herein on the covalent grafting of 4-amino-1,8-naphthalimides (ANI) in the pores of MCM-41 and SBA-15. A recently published article described the encapsulation of a ANI derivative within the pores of MCM-41 [19], but in that case the dye was incorporated by sorption, and not by covalent bonding.

The 4-amino-1,8-naphthalimides (ANI) constitute a class of strongly fluorescent yellow dyes with very interesting photophysical properties [20–23]. Thank to these properties, the ANI have been used in several applications, ranging from electroluminescent devices [24] to sensors for cations and anions [25–29], molecular switchers [30,31], artificial photosynthetic systems [32–34] and thermochromic [35] and pH sensing [36] devices. The ANI are also useful as building blocks for the construction of supramolecular systems, such as rotaxanes, catenanes [37] and inclusion complexes with cyclodextrins [38,39].

In order to bind covalently the ANI chromophore to MCM-41 and SBA-15, we first modified the pore walls with 3-

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aminopropyltriethoxysilane (APTES), introducing amino functionalities [40,41] that were further reacted with the precursor molecule 4-amino-1,8-naphthalic anhydride, resulting in ANI-bound mesoporous materials (Scheme 1). The same method was used by our group to obtain PDI grafted MCM-41 and SBA-15 from the reaction of the surface bound amino groups with 3,4,9,10-naphthalenetetracarboxylic dianhydride [17]. Results obtained with a non-porous silica gel modified with ANI by the same method are also presented in this work, as a comparison. Recently, Leng et al. reported the use of a similar method to obtain ANI-grafted MCM-41 for use as a chemosensor for Hg^{2+} cations [42].

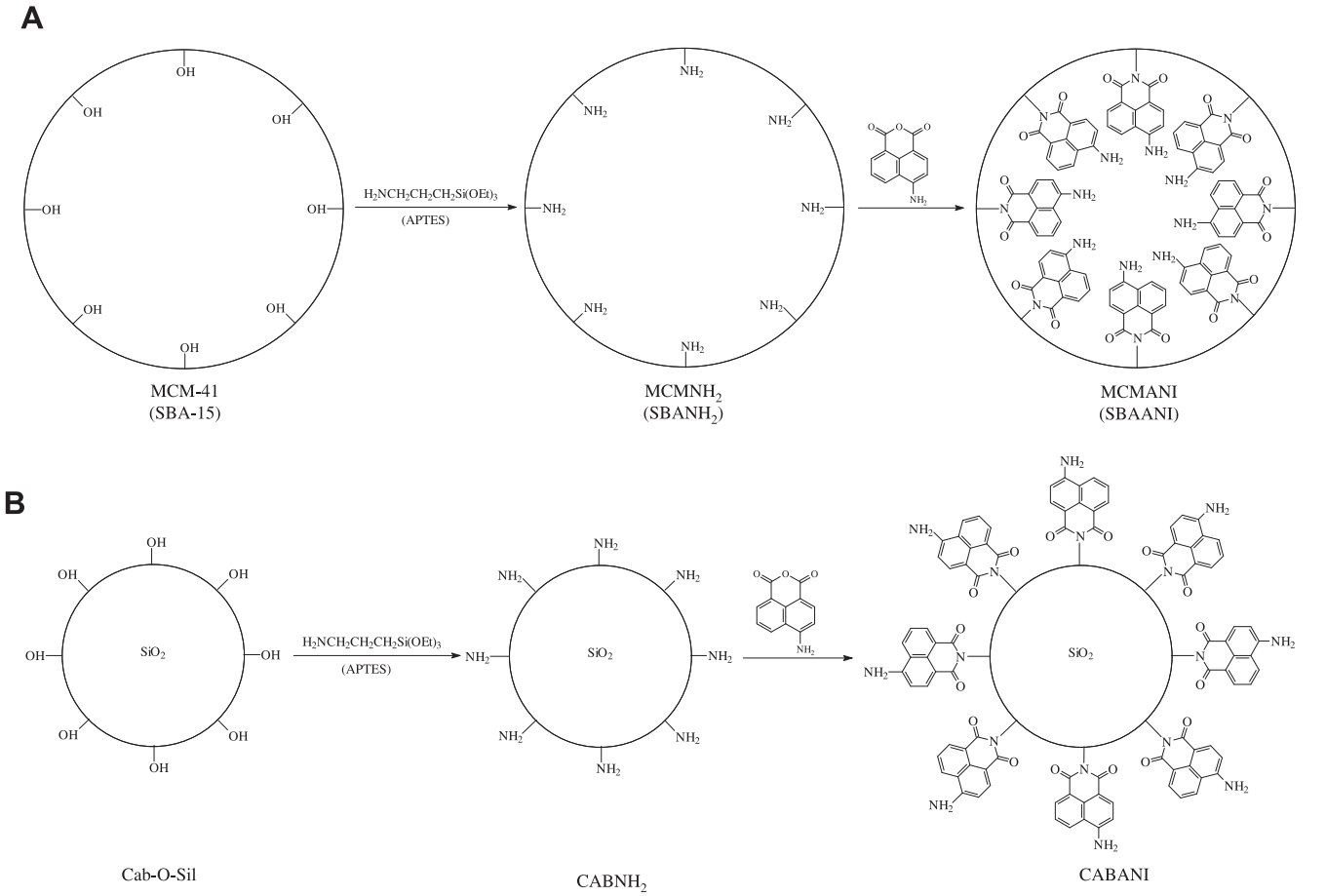
2. Experimental section

2.1. Materials

3-Aminopropyltriethoxysilane (APTES) and 4-amino-1,8-naphthalic anhydride were purchased from Aldrich, and used as received. The following HPLC grade solvents were obtained from Baker: chloroform, acetonitrile, toluene, *N*,*N*-dimethylformamide (DMF), ethanol (EtOH) and methanol. Deionized water (Barnstead easypure RF system) was used in all experiments. The mesoporous molecular sieves MCM-41 and SBA-15 were synthesized and characterized as described in our previous reports [16,17]. Silica gel Cab-O-Sil L-90 (supplier data: BET surface area 90 m^2/g, average particle diameter 20 nm) was a gift from Cabot Corporation, and was used as received.

2.2. Instruments

Elemental analysis of the samples were performed at the Chemistry Institute, São Paulo University. Infrared spectra were recorded with the samples in KBr pellets, using a FTIR Perkin-Elmer Spectrum One apparatus. Small angle X-ray scattering (SAXS) experiments were performed in a Rigaku Radiation Shield equipment using a rotating anode and CuK α radiation ($\lambda = 1.5418$ Å), with an image plate detector. The equipment was operated at 10 kW (50 kV and 200 μA), with a distance of 508 mm between the samples and the detector. The samples were placed inside a 1 mm diameter quartz tube and subjected to 2 h of beam exposure. The distance (a_o) between pore centers of the hexagonal structure was calculated with the formula $a_0 = \frac{2d_{(100)}}{\sqrt{3}}$. SEM images were recorded with a Supra 40 scanning electron microscope (Zeiss). Samples were gold coated prior to analysis. Absorption spectra were recorded with a Cary 50 spectrophotometer (Varian). Absorption spectra of the solid samples were taken using the solid sample support of the Cary 50, by pressing the powders in KBr pellets. Fluorescence spectra were registered with a Cary Eclipse fluorescence spectrophotometer (Varian), with the fluorescent powders either placed in a 5 mm NMR tube (for solid state measurements) or suspended in the appropriate solvent in a quartz cuvette (typically 2–3 mg of powder for 3 mL of solvent). After the measurements, the suspensions of the solid materials were filtered through 0.2 μm filters, and the absorption and emission spectra of the filtrates were measured. No detectable ANI absorbance or fluorescence was



Scheme 1. (A) Modification of mesoporous molecular sieves MCM-41 or SBA-15 with APTES followed by ANI on the inner surface. (B) Modification of non-porous silica gel with APTES followed by ANI on the outer surface.