Microporous and Mesoporous Materials 249 (2017) 157–164

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Novel family of periodic mesoporous organosilicas containing azobenzene within the pore walls

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ARTICLE INFO

Article history:
Received 10 March 2017
Received in revised form
21 April 2017
Accepted 30 April 2017
Available online 2 May 2017

Keywords:
PMO
Azobenzene
Mesoporous materials
Silica

ABSTRACT

Three new bis-silylated azobenzenes, differently substituted, having terminal triethoxysilyl groups attached directly to the para position of the phenyl rings without linker, namely bis(4-triethoxysilyl) azobenzene, bis(2,6-dimethyl-4-triethoxysilyl)azobenzene and bis(2,6-diisopropyl-4-triethoxysilyl)azobenzene, have been successfully synthesized by Lithium-Iodine exchange from its diiodoazobenzene-derivatives, and used to prepare three novel azobenzene-bridged periodic mesoporous organosilica materials (Azb-PMO-R, R= H, Me and *i*Pr). The synthesis of these materials from 100% of bis-silylated azobenzenes precursors was carried out under basic conditions using octadecyltrimethylammonium chloride (C18TMACl) as structure-directing agent. The successful synthesis was verified by N2 sorption measurements, solid state MAS-NMR spectroscopy, and IR spectroscopy. Materials with pore sizes between 3.7 and 4.6 nm and specific surface areas in the range of 400–700 m^2/g were obtained. UV–Visible spectroscopy shows that the prepared PMOs are formed by rigid combination of isomers *cis* and *trans* of azobenzene moieties, which do not exhibit a regular photochemical *trans*-to-*cis* isomerization of the azo group upon alternating UV–Visible irradiation. However, these materials probably exhibit a dynamic and local bending which could be useful for reversible gas adsorption and release with light.

1. Introduction

The synthesis of periodic mesoporous organosilica (PMOs) materials has attracted much interest since their discovery in 1999 [1–3]. These materials can be synthesized from alkoxysilyl precursors {R[Si(OR')3]n, n ≥ 2, R = organic group, R′ = Me, Et, *i*Pr or allyl} in the presence of surfactants such as tetraalkylammonium halides or nonionic copolymers acting as structure directing agents.

To date, several organic groups (R) such as ethylene [4], thiophene [5], benzene [6], biphenyle [7,8], naphthalene [9], anthracene [10], divinylbenzene [11], phenylpyridine [12], carbazole [13], acridone [14], divinylpyridine [15], bipyridine [13,16], porphyrin [17], and others [18] have been successfully incorporated in the framework of PMOs. By varying the organic linker group (R), mesostructured materials tailored towards specific applications can be prepared. Such applications include catalysis [19,20], adsorbents [20,21], optical [22,23] and electrical devices [24], and biomedical applications [25–29].

One potential application of mesoporous organosilica materials is their utilization as particle size-selective materials, allowing or impeding the passage through them of particles and species, depending on whether their dimensions are smaller or larger than the pores [20–39]. These materials of nanometric pores can even serve to separate molecules depending on their size and polarity.

A more developed categories of mesoporous organosilica materials called intelligent materials in which the permeability and pore diameter of the materials could be varied by applying an external stimulus [39–41]. An example of these intelligent materials is the photoactivable materials whose pore size could be switched between two states based on the photochemical interconversion between two isomers [26–29,42–53].

Photochemical *trans*/*cis* isomerization of azobenzenes adsorbed [42,49] or included in silicates [26–29,42–52], inorganic oxides [48,49] and membranes [31,54] has been widely used in order to have photoresponsive materials that exhibit some photochemical reversibility. Most of this reported work takes advantage of the remarkable changes in the molecular length when *trans*-

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http://dx.doi.org/10.1016/j.micromeso.2017.04.061
1387-1811/

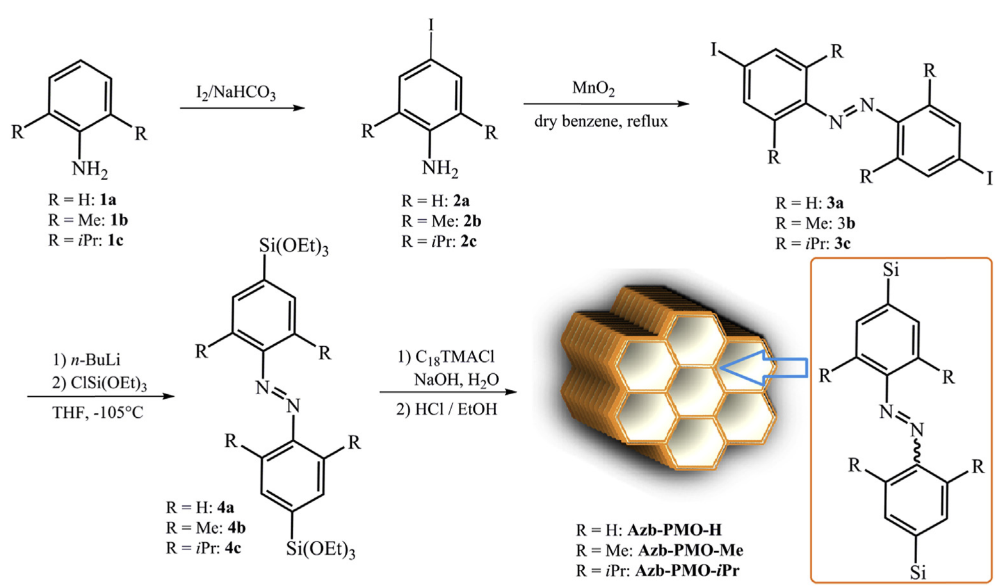
azobenzene (≈0.9 nm length) is transformed into *cis*-azobenzene (≈0.5 nm length) upon irradiation (coordinated *trans*: $\lambda_{max} \approx 350$ nm, *cis*: $\lambda_{max} \approx 450$ nm) [55,56], this drastic variation being responsible for the effect observed in the material. However, this isomerization in solid state requires a minimum flexibility around the azo group inside the solid material. Because, if both phenyl rings of an azobenzene group are attached directly, without any linker, to a trialkyloxysilane group, the exhibition of a real *cis/trans* isomerization of this azobenzene group within the corresponding PMO material seems impossible. Consequently, in the azobenzene-bridged PMOs which have been cited in the literature, the silyl groups are attached to the para-position of the phenyl rings by means of different linkers [46,48,52,57]. However, the incorporation of a linker makes the PMO softer and less ordered. Therefore, the addition of tetraethyl orthosilane (TEOS) or tetramethyl orthosilane (TMOS) was indispensable to assist the formation of more rigid and ordered material using such "long" and flexible precursors.

However, Lyndon et *al.* [58] have demonstrated that a bending about the azo group is recently observed where an azobenzene ligand is incorporated in a Metal-Organic Framework (MOF) wall. This bending occurs on a local scale in a dynamic fashion. The same authors have also reported the usefulness of these materials in gas capture and release area. Therefore, we are interested in the synthesis of new PMOs containing azobenzene groups without linker in the frameworks, from 100% of organosilane precursors, and the study of this bending property of azobenzene in the PMOs instead of MOFs.

Herein, we report the successful synthesis and characterization of three different azobenzene-bridged PMOs isomers, differently ortho-substituted, whose silyl groups are attached directly to the para-position of the phenyl rings. In this case, the azobenzene groups are part of the PMOs wall. Two of these three PMOs are 2,2′,6,6′-tetrasubstituted with methyl (Me) groups (Azb-PMO-Me) and isopropyl (Azb-PMO-*i*Pr) groups (Scheme 1). The synthesis of the 4,4′-bis-silylated azobenzene precursors 4a-c were based on the iodine-lithium exchange. These precursors were used as 100% organosilica source, in combination with C18TMACl as structure directing agents. The resulting Azb-PMO-R (R=H, Me, *i*Pr) systems were characterized by nuclear magnetic resonance (NMR) spectroscopy, nitrogen sorption, powder X-ray diffraction (XRD), UV–Visible, and FT-IR. The bending property of azobenzene groups within these new PMOs upon alternating UV–Visible radiation, and effect of the steric hindrance around the azo bond will be treated in further research.

2. Results and discussion

Scheme 1 describes the synthetic route employed in the synthesis of the three bis-silylated azobenzene precursors 4a-c. The azobenzene precursor 4a was prepared in two steps from a commercially available reagent 2a, while precusors 4b and 4c were prepared in three steps from 1b and 1c, respectively. Therefore, para-iodo-anilines 2b and 2c were easily obtained through iodination of 1b and 1c with I_2, following a reported procedure [59,60]. The 4,4′-diiodoazobenzenes 3a-c were obtained by oxydation of the corresponding anilines 2a-b with active manganese dioxide in benzene solution [61]. The resulting 4,4′-diiodoazobenzenes 3a–c were subjected to different silylation conditions, used in the literature to access to the 4,4′-bis-silylated azobenzene precursors, namely the palladium and rhodium-catalyzed carbon-silicon bond-forming reactions, between aryl halides and trialkoxysilanes $HSi(OR)_3$ (R = Me, Et) [62–66]. However, the synthesis of these precursors, with high purity, which is necessary for the synthesis of PMOs containing azobenzenes groups in the frameworks, from 100% of organosilane precursorss, was not possible using metal-catalyzed cross-coupling reactions. Therefore, we tried to find an alternative method, and after a thorough literature survey, we found only few examples reported an azobenzene group attached directly with a trialkoxysilane via a C–Si bond. The Si–C bond in these examples was created by an exchange Iodine-Lithium [52,67–70], using *n*-BuLi at low temperature (−105 °C), then Li–C bond was converted to Si–C, after transmetallation with chlorotrithoxysilane $ClSi(OEt)_3$. Using this method, with some modifications, we were able to prepare these three bis-silyated azobenzene precursors (4a-c), with high purity (Figs. S1–3 in the Supporting Information), and reasonable yield. Indeed, a stoichiometric amount of *n*-BuLi and $ClSi(OEt)_3$ was not sufficient to convert diiodo-azobenzene intermediates to their corresponding dilithio-azobenzene. An excess of *n*-BuLi was necessary to react all starting materials, followed by addition of an excess of $ClSi(OEt)_3$.



Scheme 1. Detailed synthesis of azobenzene-bridged periodic mesoporous organosilicas(Azb-PMOs).