



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Molecular transport in thiacalix[4]arene-modified nanoporous colloidal films

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ARTICLE INFO

Article history:

Received 24 May 2009

Received in revised form 18 December 2009

Accepted 25 January 2010

Available online 1 February 2010

Keywords:

Nanoporous colloidal film

Thiacalix[4]arene

Controlled diffusion

Transport mechanism

ABSTRACT

The surface of nanopores in colloidal films assembled from 200 nm silica spheres was modified with thiacalix[4]arene moieties and transport of two redox-active species, ferrocene dimethanol and iron tris(bipyridyl) hexafluorophosphate, through the films has been studied using cyclic voltammetry. Evidence for two different molecular transport mechanisms was observed. Ferrocene dimethanol is transported via a simple diffusive mechanism while iron tris(bipyridyl) is transported via a surface-hopping mechanism. The difference in transport mechanisms is believed to result from different interaction strength between the diffusing species and the surface-bound organic moieties, and sheds light on transport mechanisms in nanoporous systems.

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1. Introduction

Nanoporous systems are attracting attention in fundamental research and technology [1–3] because they enable controlling transport of molecules and ions at a nanoscale. Recently, we introduced colloidal films as nanoporous systems with controlled molecular transport. Colloidal films possess a number of attractive features, including formation via self-assembly of sub-micron-sized silica spheres [4], highly ordered arrays of three-dimensional interconnected nanopores whose size can be controlled by changing the size of the silica spheres used to assemble the films, and facile surface modification [5]. We demonstrated that transport selectivity in colloidal films can be: (i) based on electrostatic interactions with chargeable surface-bound functional groups [6–8], (ii) utilize polymer brushes grown inside the nanopores [9,10], and (iii) based on hydrogen bonding and π – π stacking non-covalent interactions with surface-immobilized organic receptors [11,12]. In the latter case we were able to demonstrate that the transport through the chiral colloidal films occurs on the surface of the nanopores in a way similar to that demonstrated in porous polymer membranes [13,14] and surface-modified nanotubes [15–24]. Such transport relies on the non-covalent binding between the permeant molecules and the surface receptors.

Calix[n]arenes are known to be selective receptors for a variety of anions and neutral molecules. Recently reported replacement of the methylene bridges between the aromatic units in calixarenes

by sulfur atoms leads to thiacalix[n]arenes [25]. The presence of four sulfur atoms results in many novel features compared with “classical” calixarenes, such as different complexation ability with sulfur contribution, different size and different conformational behavior [25–30]. For instance, derivatives of *p*-tert-butylthiacalix[4]arene efficiently complexes various metal ions [31–33]. Thus, we decided to modify the surface of the nanoporous colloidal films with these receptors in order to study the transport mechanism in such systems. We expected that upon the coordination of metal cations the colloidal nanopore surfaces will become positively charged thus allowing electrostatic control of transport through the films. However, we discovered that non-covalent interactions with a transition metal complex lead to a surface-facilitated transport mechanism rather than a simple diffusive mechanism. The results of our study are described below.

2. Experimental

2.1. Materials and reagents

Sulfur (powder, 99.98% trace metals basis), 4-*tert*-butylphenol (99%), tetraethylene glycol dimethyl ether (99%), alkali metal carbonates (Cs_2CO_3 , K_2CO_3 , Na_2CO_3 , $\geq 99\%$) and hydroxides (NaOH , LiOH , $\geq 98\%$), ethyl bromoacetate (98%), thionyl chloride ($\geq 99\%$), tetraethyl orthosilicate (TEOS, 99.999% trace metals basis), (3-aminopropyl)triethoxysilane (APTES, 99%), pyridine ($\geq 99\%$), hexafluorophosphate salts (of potassium and tetra-*n*-butylammonium, $\geq 99\%$) and 1,1'-ferrocenedimethanol (98%) were obtained from Aldrich and used as received. Iron trisbipyridine hexafluorophosphate $\text{Fe}(\text{bpy})_3(\text{PF}_6)_2$ was synthesized according to literature

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