

Photoluminescent and redox active periodic mesoporous organosilicas based on 2,7-diazapyrene

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Abstract

A novel redox-active, luminescent periodic mesoporous organosilica (PMO) based on 2,7-bis(3-trimethoxysilylpropyl)diazapyrium diiodide (BDAP) was prepared. A 2,7-diazapyrene grafted mesoporous material (DAP-DAM-1) was also synthesized. BDAP loadings as high as 2.3% were achieved in well ordered BDAP-PMO materials. The photoluminescence properties of BDAP-PMO and DAP-DAM-1, along with a PMO based on 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (BTEBp-PMO) were determined. The photoluminescence of BDAP-PMO, DAP-DAM-1, and BTEBp-PMO was quenched by nitrated explosive taggants including *o*-nitrotoluene, nitrobenzene, 2,3-dimethyl-2,3-dinitrobutane (DMNB), and nitromethane, suggesting the potential use of these PMOs as optical sensors for explosives. In the case of BDAP-PMO and DAP-DAM-1, exposure to nitrobenzene results in 81% quenching of fluorescence.

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1. Introduction

Periodic mesoporous organosilicas (PMO) as well as hybrid mesoporous materials have been widely reported in the literature [1,2]. These materials have either bridging or pendant organic groups in the pore walls. Historically, the mesoporous structure of all silica frameworks, such as MCM-41, SBA-15, and DAM-1 have been functionalized with a diverse range of organic groups [3–35,94]. These materials may have the organic functional groups incorporated in the framework during synthesis or by post-synthetic grafting. In 1997 we reported one of the first examples of MCM-41 decorated with organosilanes and metal complexes by post-synthesis modification [36]. This is typically accomplished using organosilanes which are either self-condensed or combined with silica precursors to form covalent linkages between the organics and the inorganic framework [1,2]. Potential problems with this

approach are low loadings, heterogeneous distribution and loss of pore volume. In contrast, PMOs are composed of bridging organosilanes which are incorporated into the pore walls and can make up as much as 100% of the framework. The accessible surface areas and density of organic groups in PMOs are much larger than for grafted materials. This provides more free volume in the pores, heterogeneous dispersion, as well as easier access to the organic groups.

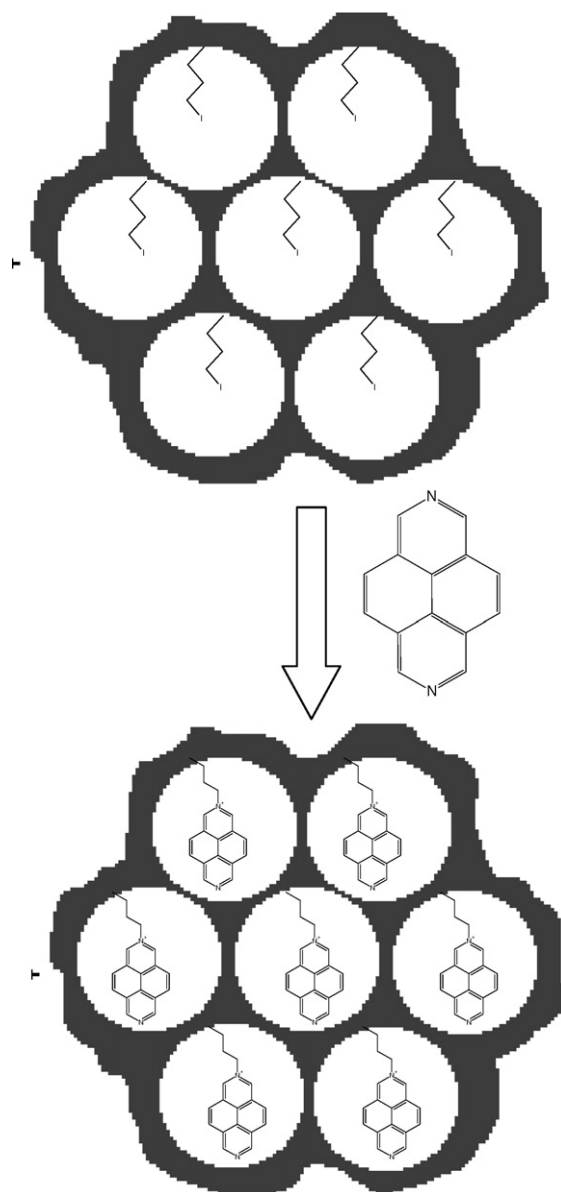
Theoretically, any organic compound that could be silanated might be incorporated into a mesoporous framework, provided it is stable under synthesis conditions. Most efforts to date have focused on acid/base groups or aromatic groups that impart specific surface properties, such as hydrophilicity/hydrophobicity or act as binding sites for metal ions. Ha and co-workers [19] incorporated a vanadyl Schiff base complex into a mesoporous framework which has the ability to catalyze the cyanosilylation of carbonyl groups, and Reye et al. used a cobalt Schiff base complex to absorb dioxygen [11]. There have also been other metal containing ligands co-condensed into

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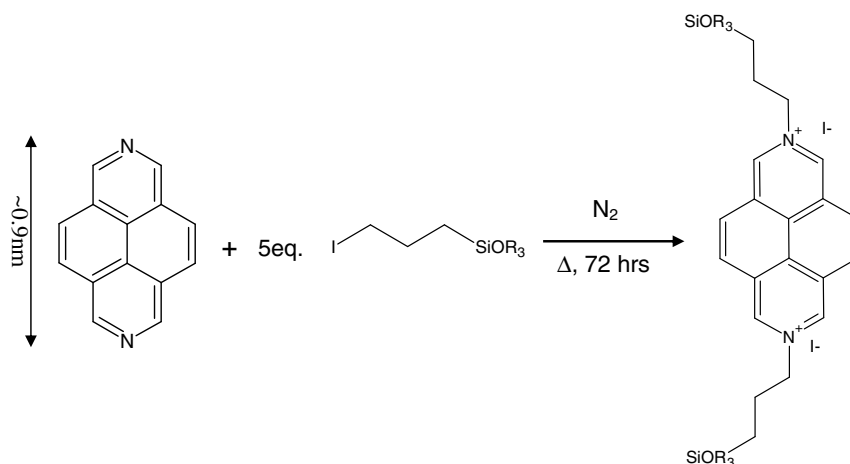
mesoporous materials such as a carbapalladacycle complex as a catalyst for Suzuki cross-coupling [9]. Also, various alkyl, aromatic, and sulfur containing groups have been disilinated and incorporated into mesoporous materials. Due to the ability to incorporate various organic compounds into the framework of mesoporous materials there is a potential for the application of PMOs as solid catalysts and sensors [1]. Some applications could benefit from a redox active framework; however, there are relatively few examples of such PMO materials. Recently a PMO was synthesized by co-condensing disilylated viologen (*N,N'*-bis(triethoxysilylpropyl)-4,4'-bipyridinium) with tetraethyl orthosilicate [32,35,37]. Upon irradiation, or mild heating (~ 100 °C) this PMO generates the radical cation. In related work, an electrochromic PMO was prepared using a viologen-modified periodic mesoporous nanocrystalline anatase [38].

Here we present the synthesis of a redox active, fluorescent di-silylated 2,7-diazapyrene mesoporous material (BDAP-PMO) shown in Scheme 1. Ordered BDAP-PMO was prepared with loadings up to $\sim 5\%$ with redox activity verified by cyclic voltammetry. For comparison, a tethered 2,7-diazapyrene (DAP-DAM-1) has been prepared from iodopropyl functionalized DAM-1 (Scheme 2).

The BDAP-PMO fluorescence can be quenched by certain molecules, which suggests this material might be exploited for optical sensing. A growing concern for homeland security is the detection of explosives. Explosives manufacturers add identification markers, called taggants, to their explosives to aid in detection and tracking. There are two types of taggants: detection taggants and identification taggants. Identification taggants are various types of materials that have been placed in the explosive which allow the explosive to be traced, post-detonation, to its point of origin and possibly determine how the explosive was acquired [40–42]. Because plastic explosives have low vapor pressures and are therefore difficult to detect through chemical means prior to detonation, detection taggants are added. These taggants are high vapor pressure compounds



Scheme 2. Synthesis of DAP-DAM-1.



Scheme 1. Synthesis of 2,7-bis(trimethoxysilylpropyl)diazapyrinium diiodide.

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