Self-Assembled Tin-Based Bridged Hybrid Materials

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Hybrid materials where an organic and an inorganic component are combined on the nanometer scale gave access to a new field of research with promising applications in optics, electronics, membranes, coatings, etc.[1] In this context, bridged hybrid materials prepared from silylated precursors received considerable attention for their unique structural and morphological properties, which can be modified by making simple changes in the precursor or preparation conditions.[2] In this fashion, materials with very high surface area and varying porosity could be obtained. On the basis of earlier findings on templated synthesis of highly ordered mesoporous of silica (MCM 41),[3] the use of surfactants allowed the organization of bridged hybrid materials with both meso- and molecular-scale periodicity, to give hierarchical porous structures.[4] Organized networks can also form spontaneously. The presence of urea groups in the bridges, able to associate the organic moieties by formation of H-bonds, leads to self-organized hybrids with long-range ordered structures.[5] Well-organized structures can also be generated by solid-state hydrolysis/polycondensation of disilylated compounds. In this case, the architecture of the precursor, which is not preserved, serves as a template.[6]

Very few hybrid materials prepared from tin derivatives have been described previously. Known examples involve materials where cohesion between organic and inorganic networks relies on the presence of tin−oxygen bonds binding oxo−hydroxo organotin clusters and α,ω-dicarboxylic acids.[7] Hybrid materials where organic and inorganic networks are linked through carbon−tin bonds could find interesting applications for the preparation of mesoporous tin oxide with high surface area or as catalysts. The research reported here describes the preparation and the characterization of new hybrid materials based on an inorganic network of tin oxide and where the organic and the inorganic network are linked through tin−carbon bonds. With this aim, suitable precursors, labile alkynides instead of hardly accessible alkoxides,[8] have been designed and synthesized.[9]

Alkylene-bridge hybrid material **4** (Scheme 1) was prepared using precursor **1**[9] in neutral medium under microemulsion conditions.[10] In a typical procedure, **1** (2 g, 3.8 mmol) in toluene (7 mL) was added to a solution of sodium dodecyl sulfate (2%) (2 mL) and Igepal[11] 520 (1 g). Next, 200 mL of a 15% solution of Igepal 720 was added. A transparent oil-in-water microemulsion was obtained. After 15 days at room temperature, the suspension that formed was treated with 200 mL of acetone and centrifuged. The hybrid **4**[12] was washed with acetone (100 mL), THF (3 × 100 mL), and diethyl ether (2 × 100 mL) and dried at 120 °C for 3 h under vacuum

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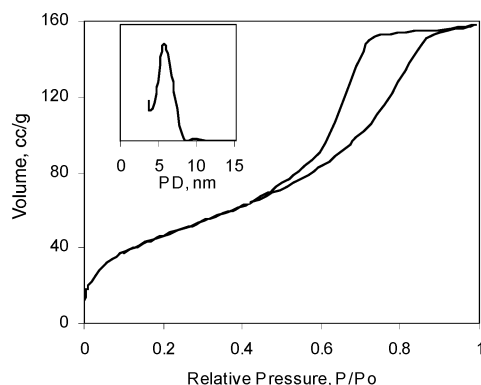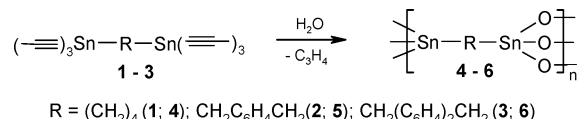[§] Centre de Recherche Paul Pascal.
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Figure 1. Nitrogen isotherms and pore size distribution (inset) for **4**.

Scheme 1. Synthesis of Hybrid Materials **4**−**6** from the Hydrolysis of Organotin Precursors **1**−**3**

R = (CH$_2$)$_4$(**1**; **4**); CH$_2$C$_6$H$_4$CH$_2$(**2**; **5**); CH$_2$(C$_6$H$_4$)$_2$CH$_2$ (**3**; **6**)

(yield: 1.1 g). Samples without surfactant were prepared as control experiments. The total disappearance of the peak at 2160 cm^{-1} in the IR spectrum of **4**, characteristic of the triple bond absorption, indicated clearly that the hydrolysis of the tin−propynyl bonds was complete. Microanalysis data and TGA/MS measurements were in agreement with the presence of two tin atoms per bridge. Thus, tin−aliphatic bonds were not cleaved under hydrolysis conditions.

N$_2$ adsorption measurements of **4** exhibited a type IV isotherm shape with a H$_2$ hysteresis loop, typical of mesoporous solids. The BET[13] surface area and the total pore volume were 173 m^2 g^{-1} and 0.25 cm^3 g^{-1}, respectively. The pore size distribution was rather narrow, with a mean pore diameter estimated to be 5.6 nm (BJH[14] model applied to the desorption branch) (Figure 1).

When hydrolysis of **1** was conducted under different conditions, i.e., under HCl catalysis, in THF, or without microemulsion, the corresponding hybrids showed surface areas lower than 12 m^2 g^{-1}. The formation of nanodroplets (diameter: 12 nm as measured by DLS) of a solution of **1** highly dispersed in water prevented the condensation of nanoparticles of hybrid, which led to a high surface area for **4**. The powder X-ray diffraction (PXRD) of hybrid **4** showed a broad peak at a low angle (8.1°), corresponding to a distance of 1.09 nm between scattering planes (Figure 2). This is consistent with the presence of tin oxide walls separated by organic bridges. This value is in the range of that calculated from the tin−tin separation found in 1,4-bis(trichlorostannyl)butane,[9] assuming a fully condensed network of tin oxide, without coordinated water.
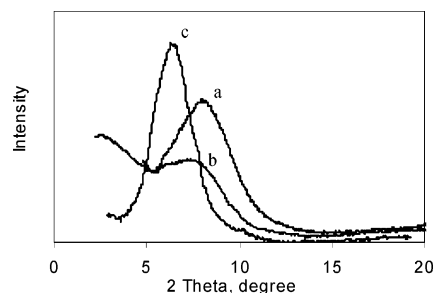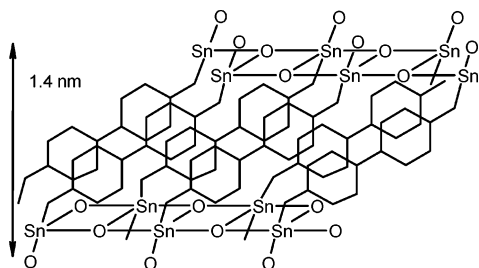
Figure 2. Powder X-ray diffraction patterns of **4** (a), **5** (b), and **6** (c).

Scheme 2. Structural Model for Hybrid **6**

The size of the ordered domains lies between two and three layers. Without surfactant, the hybrid material obtained from **1** was amorphous. The hydrolysis of distannylated compounds with a more rigid spacer, to favor self-assembly, was then studied without surfactant. In a typical procedure, **2** (2.18 g, 3.8 mmol) in THF (10 mL) was added to a solution of water (5.13 mL, 290 mmol) and HCl (1N, 0.51 mL) in THF (10 mL). After 3 days the mixture was gelified. After aging for 12 days, hybrid **5** was filtered, washed with THF (3 × 10 mL), and dried at 120 °C for 3 h under vacuum. Its PXRD analysis showed a broad peak at 7.3°, corresponding to a distance of 1.22 nm. This result suggested the use of a longer spacer to increase the interactions between the chains that would result in a higher order. Hydrolysis of **3** (under the same conditions as for **2**), lengthened by an extra phenylene ring with respect of **2**, gave hybrid **6**. Its PXRD pattern indeed showed a sharpened signal, indicative of a higher order (ordered domains ∼3 layers), corresponding to a larger interlayer distance, 1.4 nm. The calculated value from the tin−tin distance in 4,4′-bis(tricyclohexylstannylmethyl)biphenyl was 1.48 nm. The comparison between calculated and measured data suggests the existence of tilted organic chains with a tilt angle of 19°, smaller than the value of 30° reported for ordered silicon-based hybrid materials (Scheme 2).[6]

In summary, hybrid materials where layers of tin oxide alternate with layers of hydrophobic organic chains are accessible from the hydrolysis of distannylated compounds containing an organic chain α,ω-disubstituted by tripropynylstannyl groups. In the case of an aliphatic chain, hydrolysis under microemulsion conditions is necessary to organize the corresponding hybrid. These hydrolysis conditions also induce a high surface area and a defined mesoporosity in the hybrid. When a mixed aromatic−aliphatic spacer is used, weak hydrophobic interactions between the spacers are sufficient to favor the organization of the corresponding material.

Supporting Information Available: Infrared spectra of **1**, **3**, **4**, and **6**; microanalysis and TGA-MS data of **4**−**6**; and the crystal structure of 4,4′-bis(tricyclohexylstannylmethyl)biphenyl (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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