

A doubly folded spacer in a self-assembled hybrid material†

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The hydrolysis of a bridged α,ω -bis(trialkynylstannylated) compound leads to a hybrid material ordered by self-assembly where the spacer forms two six-membered [1,2]oxastanninane rings by intramolecular coordination.

The combination of organic and inorganic components bonded through a covalent bond at the nanometre scale leads to hybrid materials with promising applications in various fields such as coatings, membranes, electronics, optics, *etc.*¹ Silicon-based hybrid materials received considerable attention as minute changes in the structure of the starting materials or in the preparation conditions have a dramatic influence on their physical properties, specific surface, porosity, texture and morphology.² This is especially true for bridged hybrids which, moreover, show the remarkable property of self-assembly. Depending on the nature of the spacer between the silicon atoms and on their preparation conditions, the corresponding hybrids can self-assemble to give ordered materials with dimensions of up to hundreds of nanometres. This nanostructuration can be achieved by the use of surfactants and usually results from the properties of the structure directing agent.³ However, a double organization can be reached with a short scale one induced by the spacer and a medium scale one induced by the surfactant.⁴ Nanostructuration is also possible by running solid state hydrolysis/polycondensations where the starting materials are used as templates⁵ or by the association of the organic bridges by formation of hydrogen bonds.⁶ However, a precise picture of the organization of the organic spacer, as deduced from X-ray data which allow the measurement of the distance between the polysiloxane planes, could only be performed in the very rare cases where it corresponded to a fully extended organic spacer.⁶

The stability of tin–carbon bonds towards hydrolysis and the recent development of suitable starting materials,⁷ alkynides instead of the alkoxides usually employed in sol–gel chemistry, has recently allowed the preparation of tin-based hybrid materials.⁸ In addition, it was demonstrated that the use of distannylated precursors leads to organized materials where walls of polystannoxane units are separated by organic bridges of several

types: alkylene, arylene or mixed arylene–alkylene. This self-assembly occurred spontaneously, without the use of surfactants. The comparison of the tin–tin distances obtained from the crystal structures of suitable starting compounds and the distances between the polystannoxane walls showed that the latter corresponded to fully extended spacers, as was observed in the case of silicon-based hybrid materials with alkylene or mixed alkylene–phenylene spacers.⁶ The work reported here describes the preparation and a structural study of a bridged tin-based hybrid material with a particular focus on the conformation of the spacer which separates the metal atoms.

The synthesis of the precursor 4,4'-bis(5-(triprop-1-ynylstannyl)pentylloxymethyl)biphenyl **2** started from the etherification of 4,4'-bis(chloromethyl)biphenyl with but-3-enol, followed by the hydrostannation of the corresponding diether with tricyclohexyltin hydride. Electrophilic cleavage of the tricyclohexyltin groups with tin tetrachloride afforded 4,4'-bis(5-(trichlorostannyl)butyloxymethyl)biphenyl **1** in 96% yield. Compound **1** was characterized by ¹¹⁹Sn NMR giving a signal at –142.2 ppm indicative of strong coordination of the tin by the oxygen atom in solution. Dilution studies showed that the coordination was intramolecular and variable temperature experiments (δ –174 ppm at –80 °C, –95 ppm at 80 °C) revealed that the open form of the trichloride (a chemical shift of around –5 ppm is expected for uncoordinated linear alkyl trichloroorganotins) was in fast equilibrium with the cyclic form at room temperature (21% open form; 79% closed form). The CP-MAS ¹¹⁹Sn chemical shift (δ –163 ppm) was indicative of a closed form in the solid state. That was confirmed by the cyclic conformation of the methylene chains and the short distance (247 pm) between the tin and the oxygen atom in the crystal structure of **1**, which lies about inversion centers in the crystal lattice (see Fig. 1).‡ A similar distance was measured in the crystal structure of methyl 3-trichlorostannylpropanoate which shows the same conformation with a six-membered ring.⁹ The hexachloride **1** was then alkynylated with a slight excess of propynyllithium to give **2**. Subsequently, a solution of **2** in THF was added to a solution of water in THF. After 6 days at room temperature the mixture was gelated and was aged for 28 days. The hybrid **3** was filtered, washed with THF and dried at 120 °C for 3 h under vacuum.

The IR spectrum of **3** showed the total disappearance of the signal at 2166 cm^{–1} characteristic for the triple bond stretching. The hydrolysis of the tin–propynyl bonds in the starting compound was thus complete. Microanalysis data and TGA measurements were consistent with the presence of two tin atoms per organic bridge, confirming the expected structure of **3**. The BET specific area was low (<2 m² g^{–1}) and was only slightly increased (12 m² g^{–1}) when the hydrolysis of **2** was conducted

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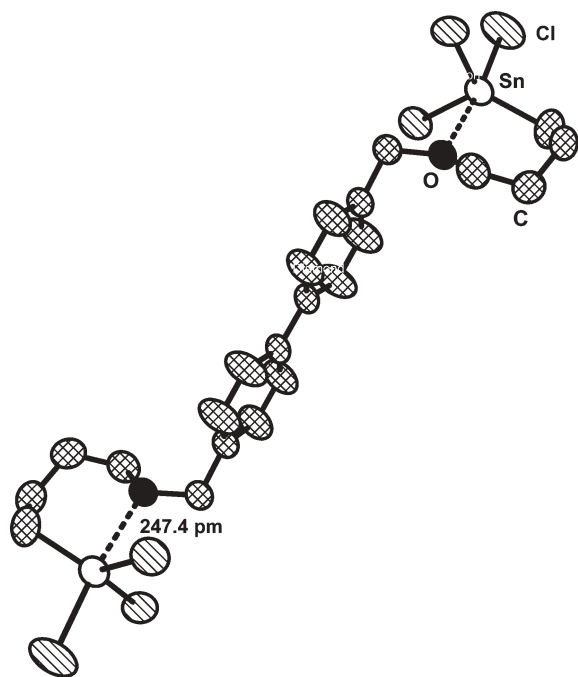


Fig. 1 ORTEP rendering of **1** with 60% probability displacement ellipsoids. Distances between tin and oxygen atoms are indicated, and highlighted with dashed lines.

under micro-emulsion conditions with Igepal 720 as a surfactant.⁸ The powder X-ray diffraction (PXRD) of hybrid **3** showed a peak at low angle ($2\theta = 5.2^\circ$) corresponding to a distance of 1.70 nm between refractive planes (see Fig. 2). This is assigned to the presence of polystannoxane walls separated by organic bridges. The size of the ordered domains was between three and four layers. The same result ($2\theta = 5.2^\circ$) was recorded when the hydrolysis of **2** was conducted in a biphasic medium (toluene solution of **2**–water), which shows that this phenomenon does not depend on the reaction conditions.

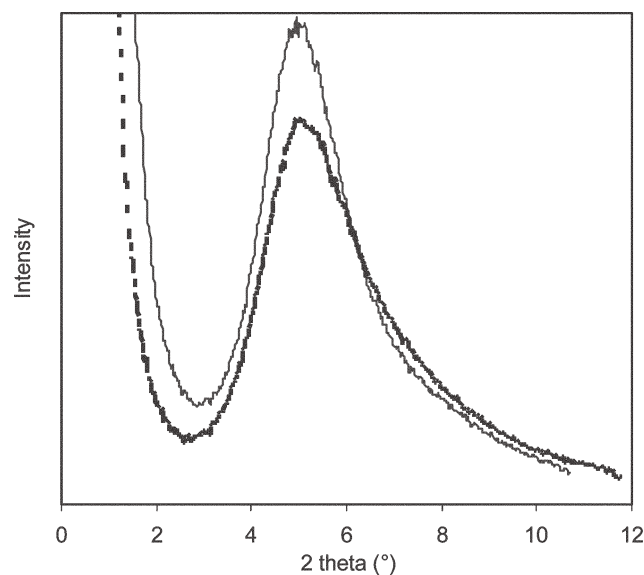
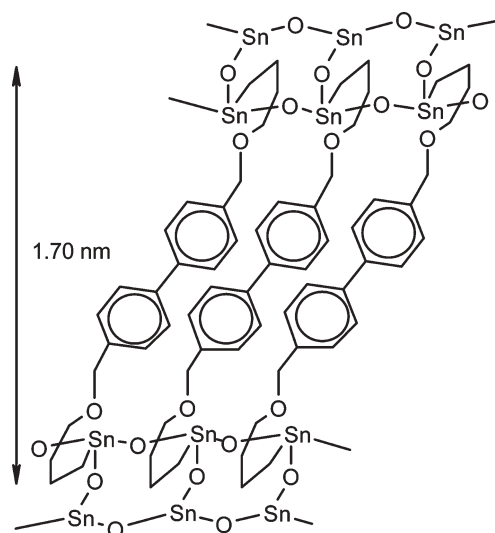


Fig. 2 X-Ray powder diffraction patterns of **3** prepared in THF (thick line) or in toluene (thin line).

The distance found between the polystannoxane walls is far lower than that expected from a fully extended organic chain ($d_{\text{calc}} = 2.9$ nm), the conformation adopted in tin-based hybrids where the tin atoms are separated by polymethylene spacers.⁸ In the present case, the distance lies in the same range as the distance ($d_{\text{calc}} = 1.85$ nm) calculated from the measured tin–tin separation found in **1** (1.60 nm), assuming a fully condensed network of tin oxide without coordinated water. This result suggests the existence of tilted organic chains with a tilt angle of about 23° , in the same range as reported for a tin-based hybrid with a 4,4'-dimethylene-biphenyl spacer (19°) but smaller than the value of 30° reported for ordered silicon-based hybrid materials.⁶

Our interpretation of these data is as follows. During the hydrolysis of uncoordinated **2**, substituting the carbon with the oxygen atoms sufficiently enhances the electrophilicity of the tin atoms such that a stabilizing coordination expansion at tin by the oxygen atom of the chains, which are in a suitable position, becomes possible. This intramolecular coordination leads to the formation of two additional [1,2]oxastanninane-like six-membered rings, as demonstrated for **1** in the solid state and even in solution. Thus, the distance between the tin atoms is reduced by the formation of these two rings, which leads to the short distance between the tin oxide walls measured by PXRD. This explanation is reinforced by the results obtained in the study of the hybrid material **4** obtained after hydrolysis of 4,4'-bis(1-(triprop-1-ynylstannyl)butyl)biphenyl **5**. Its PXRD spectrum showed a peak at 4.3° corresponding to a distance of 2.01 nm between refractive planes, while a distance of 2.05 nm was calculated from the crystal structure of the corresponding hexachloride **6**, which lies about inversion centers in the crystal lattice. Thus, in the case of a non-coordinating spacer of similar length, the alkylene chains of the corresponding hybrid are extended, which confirms that the low distance between the polystannoxane walls in **3** is due to the specific folding of the side-chains of the spacer (see Scheme 1).

In conclusion, hydrolysis of distannylated alkynides, where the tin atoms bear labile alkynyl groups and are separated by an organic chain containing oxygen atoms, leads to a hybrid material where the spacer is doubly folded by intramolecular coordination. This remarkable organization appears to be unique in the



Scheme 1 Structural model for hybrid **3**.

chemistry of hybrid materials where linear arrangements of the spacers have been found in the few cases where the organization could be determined. This work opens the way to studies on the modulation of the geometrical properties of hybrid materials by weak interactions in their organic component.

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Notes and references

‡ Crystal data for **1**: $C_{22}H_{28}Cl_6O_2Sn_2$, $M_r = 774.57$, triclinic, $P\bar{1}$, $a = 7.0738(2)$, $b = 7.4590(2)$, $c = 14.2470(6)$ Å, $\alpha = 101.473(1)$, $\beta = 91.444(1)$, $\gamma = 105.224(1)^\circ$, $V = 708.46(4)$, $Z = 1$, $\rho_{\text{calc}} = 1.815 \text{ g cm}^{-3}$. Data collection: Kappa-CCD area detector, Mo- K_α radiation, $T = 150 \text{ K}$, 3192 unique reflections, 2901 observed ($I > 2\sigma(I)$), $R_{\text{int}} = 0.0166$, $\theta_{\text{max}} = 27.5^\circ$. Structure solved by direct methods and refined by full-matrix least-squares on F^2 (SHELX-97), 146 parameters, $R_1 = 0.0247$, $wR_2 = 0.0557$. CCDC 288987.

Crystal data for **6**: $C_{20}H_{24}Cl_6Sn_2$, $M_r = 714.51$, triclinic, $P\bar{1}$, $a = 6.616(3)$, $b = 8.932(11)$, $c = 10.654(8)$ Å, $\alpha = 90.03(7)$, $\beta = 90.44(5)$, $\gamma = 99.49(5)^\circ$, $V = 621.0(9)$, $Z = 1$, $\rho_{\text{calc}} = 1.911 \text{ g cm}^{-3}$. Data collection: Kappa-CCD area detector, Mo- K_α radiation, $T = 170 \text{ K}$, 1744 unique reflections, 1571 observed ($I > 2\sigma(I)$), $R_{\text{int}} = 0.0871$, $\theta_{\text{max}} = 26.37^\circ$. Structure solved by direct methods and refined by full-matrix least-squares on F^2 (SHELX-97), 126 parameters, $R_1 = 0.0468$, $wR_2 = 0.1185$. Seven aromatic bonds, the Sn–O bond and a C–C aliphatic bond were restrained during the refinement. CCDC 288988. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515260g

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