Twin polymerization was used to prepare composite materials composed of SnO2 nanoparticles entrapped in a polymer matrix. Novel, well-defined tin-containing molecular precursors, so-called twin monomers, were synthesized by transesterification starting from Sn(OR)4 (R = tBu, tAm) to give Sn(OCH2-CH2OCH3C6H4)4 (1), [Sn(OCH2-CH2OCH3C6H4H3)], (2), [Sn(OCH2-2-OCH3C6H4H3)], (3), [Sn(OCH2-2,4-(OCH3)2C6H3H3)], (4), and [2,2'-spirobi[4H,1,3,2-dioxastannine]] (5), [2,2'-spirobi[6-methylbenzo(4H,1,3,2-dioxastannine]] (6), and [2,2'-spirobi[6-methoxybenzo(4H,1,3,2-dioxastannine]] (7). 13C and 119Sn NMR spectroscopy in the solid state and in solution as well as IR spectroscopy and elemental analysis were used to characterize the tin alkoxides. The molecular structures of compounds 2 and 3 were determined by single-crystal X-ray diffraction analysis. The moisture sensitivity of the tin(IV) alkoxides was demonstrated by the formation of the tin oxocluster [Sn(μ2-O)(μ2-OH)3(OSiH3)(OCH2C6H3)], (2a), a hydrolysis product of compound 2. Polymerization reactions in the melt (for 1 and 5) and in solution (for 2–4) resulted in cross-linked nanocomposites of the type polymer/SnO2. Subsequent oxidation of the composites gave SnO2 with BET surface areas up to 178 m2g−1. Simultaneous twin polymerization of compounds 5–7 with the silicon derivative 2,2'-spirobi[4H,1,3,2-benzodioxasiline] resulted in the formation of polymer/SnO2/SiO2 hybrid materials. Oxidation gave porous materials with SnO2 nanoparticles embedded in a silica network with BET surface areas up to 378 m2g−1. The silica acts as a crystal growth inhibitor, which prevents sintering of the SnO2 nanoparticles 20–32 nm in size.

Introduction

There is an ongoing interest in the development of synthetic strategies for tin oxide, which results from its use in various technical applications. Well known is its utilization in gas sensors,[11–15] solar cells,[16–19] transparent electrodes,[20,21] heat-reflecting filters,[22] catalysts (e.g., CO oxidation),[23] and as anode materials for lithium-ion batteries.[24–27] Therefore, a variety of methods for the preparation of high-surface-area tin oxide have been reported, for example, sol–gel synthesis,[28,29] precipitation methods,[30,31] hydrothermal routes,[32,33] molten salt processes,[34] and methods using ultrasonic spraying.[35] However, the synthesis of SnO2 nanoparticles with high surface area and without contamination, such as chloride, sodium, potassium, or carbon, is still a challenge. Recently, nonaqueous solution routes for the preparation of metal oxide nanoparticles were shown to be valuable methods to control the shape, size, and crystallinity of metal oxides.[36–38] Herein, we report a novel nonaqueous route to synthesize high-surface-area tin oxide nanoparticles using so-called twin polymerization (TP). This novel strategy was developed by Spange et al. for the synthesis of high-surface-area metal oxides, such as SiO2, TiO2, and SnO2, as well as for the preparation of metal oxide nanoparticles.[39] The concept of this synthetic route is the reaction of a well-defined metal-containing monomer to result in interpenetrating networks of, for example, a metal oxide and a polymer. Insight into some characteristic details was provided recently, which demonstrated the balance between the fast formation of a dense organic network that im-

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pedes phase separation and the slower formation of the inorganic network. Most remarkably, the as-prepared organic–inorganic hybrid materials finally consist of two interpenetrating networks with domains in the nanometer range. In a subsequent oxidation step the carbon-containing material is removed and a metal oxide with high surface area is produced. The approach was recently extended to the concept of simultaneous twin polymerization (STP), which is classified as a process in which two well-defined precursors are polymerized simultaneously in a single process step to provide a single organic homopolymer and nanoscaled metal oxide phases. Herein, both concepts, TP and STP, are applied for the first time to tin alkoxides to provide porous SnO$_2$ and SnO$_2$/SiO$_2$ composites.

Results and Discussion

The concept of TP is based on the preparation of well-defined tin-containing twin monomers that readily polymerize after addition of an initiator or upon heat treatment. All the tin compounds reported herein were prepared by transesterification of tetra-tert-butoxystannane or tetra-tert-pent oxystannane with furfuryl alcohol, 2-thiophenemethanol, (2-methoxyphe nyl)methanol, (2,4-dimethoxyphenyl)methanol, 2-(hydroxymethyl)phenol, 2-(hydroxymethyl)-4-methylphenol, and 2-(hydroxymethyl)-4-methoxyphenol to give compounds 1–7, respectively (Scheme 1).

The polymerization of the tin-containing precursors 1–7 results in polymer/SnO$_2$ hybrid materials that were subsequently oxidized to give porous SnO$_2$. Although this is in principle a nonaqueous synthetic route, the polymerization of the organic moiety in compounds 1–4 produces water as a byproduct. With regard to the moisture sensitivity of tin(IV) alkoxides, we additionally synthesized the novel tin-containing precursors 5–7, which are based on “spirocyclic” structures. Such twin monomers do not eliminate water during the polymerization step, as was shown previously in the TP of the spirocyclic silicon compound 2,2’-spirobi[4H-1,3,2-benzodioxasiline] (Scheme 2). The latter is also suitable as a precursor for the STP, in which the silicon derivative reacts simultaneously with a spirocyclic tin derivative of type 5–7 and hence serves as a template for the formation of nanosized SnO$_2$ in a SiO$_2$ matrix (see the section Simultaneous Twin Polymerization).

Synthesis and characterization of the tin monomers 1–7

Tetra(furan-2-ylmethoxy)stannane (1) is a highly moisture sensitive solid of low solubility, but a freshly prepared sample does not show IR bands for OH groups that are typically observed after partial hydrolysis. The analytical data for 1 support the suggested composition and the solid-state $^{13}$C NMR spectrum shows the expected signals assigned to the furan-2-ylmethanolate ligand. Two different chemical environments for the tin atoms are suggested on the basis of two $^{119}$Sn NMR chemical shifts of similar intensity at $\delta = -595$ and $-602$ ppm and the characteristic resonances at $\delta = 154$ and 159 ppm in the solid-state $^{13}$C NMR spectrum (Figure 1).

Scheme 1. Novel tin-containing precursors for twin polymerization.

Scheme 2. Twin polymerization of tin(IV) alkoxides with and without elimination of water.
is enhanced. The molecular structure of compound 2 is shown in Figure 2 and selected bond lengths and angles are given in the caption. Compound 2 crystallizes in the triclinic space group P1 with one formula unit per unit cell (see Table 1). The tin(IV) alkoxide 2 is isostructural with previously reported [Sn(OR)₄·HOBu]₄[HOCH₂-C₆H₄]₂·HOBu] as well as with [Sn(OCH₂-2-OCH₃C₆H₄)₄·HOCH₂-2-OCH₃C₆H₄]·(3), which is also reported here (Figure S1 in the Supporting Information). Compounds of the general type [Sn(OR)₂HOR] are built up by two edge-sharing octahedra with hexacoordinated tin atoms showing comparable tin–oxygen bond lengths. In compound 2 these amount to 1.960(7) Å for Sn(1)–O(1) and 1.967(6) Å for Sn(1)–O(4), which are both assigned to the two monodentate terminal ligands. The Sn–O bond lengths of the μ₂-oxygen ligands amount to 2.089(5) and 2.080(5) Å for Sn(1)–O(2) and Sn(1)–O(2'), respectively, and thus are comparable to the bond lengths Sn(1)–O(3) (2.075(5) Å) and Sn(1)–O(5) (2.167(5) Å) assigned to the two remaining terminal ligands. The latter two ligands form hydrogen bonds (O(3)–O(5) 2.639(3) Å) resulting in Sn–O bond elongation and distortion of the trans O(3)–Sn(1)–O(5) bond angle to 161.8(2)°. Despite the presence of methoxy groups attached to the benzylic ligand, which might coordinate intramurally, in compound 3 no such intramolecular coordination is observed. Thus, the molecular structure of compound 3 matches well that of compound 2.

The ¹¹⁹Sn NMR spectra in C₆D₆ of compounds 2–4 show single

Table 1. Crystallographic data for compounds 2, 2a, and 3.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>2a·0.5 C₆H₄</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C₆H₄O₃Sn₂Sn₁</td>
<td>C₆H₄O₃Sn₂Sn₀·0.5 C₆H₄</td>
<td>C₆H₄O₃Sn₂</td>
</tr>
<tr>
<td>formula weight [g mol⁻¹]</td>
<td>1371.01</td>
<td>1089.51</td>
<td>1610.99</td>
</tr>
<tr>
<td>crystal system</td>
<td>triclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>crystal size [mm³]</td>
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<td>0.4×0.4×0.2</td>
<td>0.3×0.3×0.2</td>
</tr>
<tr>
<td>space group</td>
<td>P1</td>
<td>P1</td>
<td>P1</td>
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<tr>
<td>unit cell dimensions</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>b [Å]</td>
<td>11.624(1)</td>
<td>14.1373(6)</td>
<td>12.4422(9)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>13.0284(13)</td>
<td>17.0598(8)</td>
<td>14.3736(17)</td>
</tr>
<tr>
<td>α [°]</td>
<td>71.263(8)</td>
<td>94.417(4)</td>
<td>67.219(9)</td>
</tr>
<tr>
<td>β [°]</td>
<td>79.299(8)</td>
<td>97.524(4)</td>
<td>68.641(9)</td>
</tr>
<tr>
<td>γ [°]</td>
<td>67.676(8)</td>
<td>115.899(4)</td>
<td>82.435(7)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ρmeas [mg m⁻³]</td>
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<td>1.710</td>
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<tr>
<td>μ [mm³]</td>
<td>11.126</td>
<td>13.578</td>
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<td>F(000)</td>
<td>692</td>
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<td>832</td>
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<td>θ range for data collection [°]</td>
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<td>3.54–62.00</td>
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<td>–16 ≤ h ≤ 15</td>
<td>–13 ≤ h ≤ 14</td>
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<td></td>
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<td>–16 ≤ k ≤ 16</td>
<td>–13 ≤ k ≤ 14</td>
</tr>
<tr>
<td></td>
<td>–14 ≤ l ≤ 14</td>
<td>–19 ≤ l ≤ 19</td>
<td>–16 ≤ l ≤ 16</td>
</tr>
<tr>
<td>reflections collected</td>
<td>9672</td>
<td>21 880</td>
<td>10278</td>
</tr>
<tr>
<td>independent reflections/Rint</td>
<td>4310.0/0.244</td>
<td>9122.0/0.257</td>
<td>5986.0/0.0562</td>
</tr>
<tr>
<td>R1 (Rw) (I &gt; 2σ(I))</td>
<td>0.0671</td>
<td>0.0443</td>
<td>0.0522</td>
</tr>
<tr>
<td>Rw2 (P1) (all data)</td>
<td>0.1918</td>
<td>0.1356</td>
<td>0.1216</td>
</tr>
<tr>
<td>goodness-of-fit on F²</td>
<td>1.082</td>
<td>1.121</td>
<td>0.889</td>
</tr>
<tr>
<td>largest diff. peak and hole [e Å⁻³]</td>
<td>2.890/–1.418</td>
<td>1.733/−0.935</td>
<td>1.338/−0.827</td>
</tr>
</tbody>
</table>
The moisture sensitivity of the tin(IV) alkoxides is demonstrated by the isolation of single crystals from a pentane solution of compound 2 after contact with moisture, which proved to be a hydrolysis product with the formula \([Sn(OBu)_2]_2(OR)_6(HOR)\) (R = C\(_2\)H\(_5\)C\(_6\)H\(_4\)). The molecular structure of the hexanuclear cluster 2\(a\) is shown in Figure 3 and the inner tin–oxygen core structure is given in Figure S2.

The hexanuclear cluster might be regarded as a hydroxy-bridged dimer of \([Sn(OBu)_2]_2(OR)_6(HOR)\). This type of trinuclear structure was first reported by Reuter and Kremser for R = iBu.\(^{50}\) The hydrogen atoms were not located for 2\(a\) but the long distances corresponding to Sn(1)–O(2) and Sn(1)–O(2') (2.089(4) and 2.098(4) Å) in combination with the distance O(2)–O(6') of 2.732(6) Å, which is in the range typically observed for weakly hydrogen bonded systems, confirm the OH assignment. The presence of the coordinated alcohol ROH at O(10) is deduced from the presence of a quite short oxygen–oxygen distance O(10)–O(8) of 2.466(6) Å, which is indicative of a strong hydrogen bond, and the elongated tin–oxygen distance Sn(3)–O(10) of 2.130(4) Å, as compared with Sn(2)–O(8) of 2.053(4) Å.

2,2'-Spirobi[4H-1,3,2-benzodioxastannine] 5 is a moisture-sensitive solid material with low solubility in common organic solvents that decomposes at 250°C. The suggested composition is supported by elemental analysis and IR and NMR spectroscopy. The solid-state \(^{13}\)C NMR spectrum of compound 5 shows the expected signals assigned to the 2-(oxidoethyl)-phenolate ligand (Figure 4). The signal assigned to the methyl group is shifted downfield from \(\delta = -64\) ppm (salicyl alcohol) to \(\delta = 71\) ppm in compound 5. The \(^{119}\)Sn NMR chemical shift in the solid state at \(\delta = -697\) ppm confirms hexacoordination of the tin atom and excludes the formation of mononuclear species.\(^{51–53}\)

This assumption is also reinforced by comparison of the solid-state \(^{119}\)Sn NMR data of the tetracoordinated tin atom in Sn(OtBu)\(_4\) (\(\delta = -371\) ppm) with the hexacoordinated tin atom in [Sn(OPr)\(_2\)]\(_2\)(HOPr)\(_2\) (\(\delta = -648\) ppm).\(^{49}\) The significant high-field shift is thus a result of the increase of the coordination sphere of the tin atom from four in mononuclear Sn(OtBu)\(_4\) to six in the coordination polymer 2,2'-spirobi[4H-1,3,2-benzodioxastannine] 5. Introduction of a CH\(_3\) or OCH\(_3\) substituent at the 6-position to give 2,2'-spirobi[4H-1,3,2-dioxastannine] 6 and 2,2'-spirobi[4H-1,3,2-dioxastannine] 7 significantly enhances the solubility of the precursors in common organic solvents compared with compound 5. Similar to the tin alkoxide 5, the IR spectra of compounds 6 and 7 do not show OH absorption bands and the CHN analyses confirm the suggested compositions. The solid-state \(^{119}\)Sn NMR spectra reveal signals at \(\delta = -705\) and \(-683\) ppm for compounds 6 and 7, respectively, which indicates hexacoordination of the tin atom and formation of coordination polymers in the solid state similar to compound 5.\(^{51–53}\) The solid-state \(^{13}\)C NMR spectra of the tin precursors 6 and 7 (Figure S3) are quite similar to that of compound 5, besides additional signals at \(\delta = 20\) and \(55\) ppm for the CH\(_3\) and OCH\(_3\) groups, respectively.

Figure 3. Molecular structure of \([Sn(OBu)_2]_2(OR)_6(HOR)\) as determined by single-crystal X-ray diffraction analysis. Thermal ellipsoid representation is at 50 % probability level. Hydrogen atoms and disordered toluene molecules have been removed for clarity. Selected bond lengths and angles are given in the caption of Figure S2, which shows the tin–oxygen core structure.

Figure 4. Solid-state \(^{13}\)C-{\(^1\)H}-CP-MAS NMR and \(^{119}\)Sn-{\(^1\)H}-MAS NMR spectra (inset of compound 5 and comparison with \(^{13}\)C NMR data of 2-(hydroxymethyl)phenol in CDCl\(_3\). Asterisks (*) indicate spinning side bands.
Twin polymerization

To explore whether the novel tin monomers are suitable precursors for the so-called twin polymerization (TP), compounds 1 and 5 were converted in the melt and compounds 2–4 in CHCl₃ solution into organic–inorganic hybrid materials of the type A–E (Scheme 3).

In solution, addition of an initiator such as CF₃SO₃H to CHCl₃ solutions of compounds 2–4 is necessary to give a spontaneous reaction, whereas polymerization of the tin precursor 1 in the melt is self-initiated by its Lewis acidic nature to give hybrid material A. The thermally induced polymerization of compound 5 requires the use of acids, such as 4-methylbenzenesulfonic acid, as initiator to produce hybrid material E, otherwise decomposition to give undefined components is observed. CF₃CO₂H-induced polymerization of compounds 2 and 3 proceeds sluggishly and low conversion to give the hybrid materials B and C is observed (Table 2).

The hybrid materials were analyzed by CHN analyses and solid-state (¹³C, ¹¹⁹Sn) NMR spectroscopy. For example, the final black hybrid material A, obtained by thermally induced polymerization of compound 1, contains a low carbon content of 20.5%, which is significantly lower than expected for quantitative conversion (calc 51%). However, the absence of a signal for the SnOCH₂ group and the presence of a typical signal for a methylene group of poly(furfuryl alcohol) (PFA) in the solid-state ¹³C NMR spectrum indicate polymerization of the tin precursor (Figure 5). The broad ¹¹⁹Sn NMR signal, relative to crystalline SnO₂, results from the embedding of amorphous or nanocrystalline SnO₂ [54] and most likely some incompletely condensed tin oxide precursors within the polymer matrix (Figure 6).

The low carbon content of the hybrid material A is explained by the formation of soluble oligomers that are removed by the workup procedure, which is confirmed by the ¹³C-¹H) CP-MAS NMR spectrum of PFA/SnO₂ (A) that shows several signals of high intensity assigned to end groups of incompletely polymerized PFA (Figure 5). In contrast to compound 1, TP of compound 2 gave almost complete conversion into the poly(thiophene-2-methanol)/SnO₂ hybrid material B (Table 2). The solid-state ¹³C NMR spectrum is indicative of a high degree of polymerization and the solid-state ¹¹⁹Sn NMR spectrum as well as electron diffraction are in accordance with the formation of SnO₂, entrapped in the polymer matrix (Figures 7 and S3). TEM analysis of B is indicative of the formation of crystalline SnO₂ primary particles 2–3 nm in size, consistent with powder X-ray diffraction (PXRD) studies (Table 3), which tend to some agglomeration in the polymer matrix.

Compounds 3 and 4 both react spontaneously in CHCl₃ upon addition of CF₃SO₃H to give a hybrid material, in the case of 3 (hybrid material C) with a low (C found = 23.5%; C calcld = 63.9%) and in the case of 4 (hybrid material D) with a high extent (C found = 50.8%; C calcld = 59.9%) of conversion. The ¹³C and ¹¹⁹Sn NMR spectra of hybrid material C are indicative of the formation of SnO₂ within the polymer matrix, similar to

### Table 2. Conditions for polymerization reactions of the tin precursors 1–5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Initiator</th>
<th>M/I[^a]</th>
<th>Hybrid material, reaction time</th>
<th>Carbon content [%] found[^c]/calcld[^c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>melt</td>
<td>–</td>
<td>–</td>
<td>A, 3 h</td>
<td>20.5/51.0</td>
</tr>
<tr>
<td>2</td>
<td>CHCl₃</td>
<td>CF₃SO₃H</td>
<td>1:0.02</td>
<td>B, spontaneous reaction</td>
<td>41.5/47.6</td>
</tr>
<tr>
<td>3</td>
<td>CHCl₃</td>
<td>CF₃CO₂H</td>
<td>1:0.05</td>
<td>B, 3 months</td>
<td>33.1/47.6</td>
</tr>
<tr>
<td>4</td>
<td>CHCl₃</td>
<td>CF₃SO₃H</td>
<td>1:0.05</td>
<td>C, spontaneous reaction</td>
<td>23.3/63.9</td>
</tr>
<tr>
<td>5</td>
<td>solid</td>
<td>4-CH₃C₆H₄SO₃H</td>
<td>1:0.1</td>
<td>C, 36 h</td>
<td>19.2/63.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D, spontaneous reaction</td>
<td>50.8/59.9</td>
</tr>
</tbody>
</table>

[^a]: Based on number of ligands per tin atom. M = monomer, I = initiator. [^b]: Carbon content of the nanocomposite material after workup. [^c]: Carbon content expected for quantitative conversion into polymer/SnO₂.


![Scheme 3](image)

<table>
<thead>
<tr>
<th>Table 3. Parameters for the oxidation of hybrid materials A–E and BET surface area, crystallite size, and carbon content of the as-prepared SnO₂.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid material</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>A</td>
</tr>
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<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
</tbody>
</table>

[^h]: Heating rate 2 K min⁻¹. [^i]: Heating rate 5 K min⁻¹. [^c]: Calculated using the Scherrer equation. [^d]: Not measured.
compound 1 (Figure S4). However, the degree of polymerization is low and oligomers are removed upon workup.

In the case of compound 4, almost complete conversion to give calix[4]resorcinarene octamethyl ether/SnO₂ as a result of cyclooligomerization instead of polymerization is observed. The half-height width of the ¹¹⁹Sn NMR signal is reduced to \( n \approx 2 = 2685 \text{ Hz} \) for the hybrid material D as compared to \( n \approx 3 = 8344 \text{ Hz} \) in the hybrid material C (Figure S5). We were able to separate and crystallize the calix[4]resorcinarene octamethyl ether by sublimation. Information about its single-crystal X-ray structure analysis, including its molecular structure, is given in Table S1 and Figure S6.

HAADF-STEM analysis of the hybrid material D indicates that tin(IV)oxide nanoparticles (≈ 2–4 nm) are formed, which build agglomerates (Figure S7). Similarly, hybrid material D consists of SnO₂ agglomerates on the micrometer scale with primary particle size of 2–4 nm and shows an inhomogeneous distribution of SnO₂ particles in the polymer matrix.

The thermally induced polymerization of 5 results in almost quantitative conversion indicated by a carbon content of 42.6% (calcld 46.3%) for the hybrid material E. The broad signal at \( \delta = 33 \text{ ppm} \) in the \(^{13}C\) NMR spectrum is characteristic for the formation of methylene groups in a phenolic resin. In addition to ortho–ortho' linkage between the monomeric units in the polymer, as indicated by a signal at \( \delta = 116 \text{ ppm} \) (the ortho and para assignments are relative to the hydroxy-substituted carbon),\(^{56–58}\) As observed for the hybrid material A, the broad signal at \( \delta = -607 \text{ ppm} \) \( (\nu_s = 9996 \text{ Hz}) \) in the solid-state \(^{119}Sn\) NMR spectrum indicates the formation of nanocrystalline SnO₂ and/or an incompletely condensed tin oxide-based material (Figure S8).\(^{54}\)

**Oxidation of the hybrid materials**

Thermogravimetric analyses of the hybrid materials A–E were performed to compare the thermal behavior with that of the pure polymers and calix[4]resorcinarene octamethyl ether, respectively, and to identify the ideal decomposition temperature to remove carbon (Figure S9). For all hybrid materials decomposition under air to give crystalline SnO₂ is completed below 600 °C. Thus, in the case of the hybrid materials A–C and E, the full decomposition is observed at a lower temperature than for the oxidation of the pure polymers. In the case of hybrid material D, decomposition of calix[4]resorcinarene octamethyl ether is not altered significantly by the presence of SnO₂.

Additionally, the thermal behavior of reference samples was studied to analyze whether the addition of SnO₂ nanoparticles to a separately prepared polymer matrix significantly influences the decomposition temperature (Figure S10). For example, the thermal behavior of a sample prepared by mechanically mixing SnO₂ nanoparticles (29 nm) with poly(2-methoxybenzyl alcohol) is comparable to that of the pure polymer and the decomposition is completed at 720 °C. In contrast, the thermal
behavior of a hybrid material prepared by polymerization of (2-methoxyphenyl)methanol in the presence of SnO$_2$ nanoparticles (29 nm) is different. Complete decomposition of the polymeric resin is observed at 600 °C, only slightly above the temperature for the complete decomposition of the organic parts in the corresponding hybrid material C.

Based on these results we have chosen oxidation temperatures for the bulk materials B–E of 450 to 600 °C. For comparison, oxidation of the hybrid material PFA/SnO$_2$ (A) was performed between 500 and 900 °C in steps of 100 °C. Notably, SnO$_2$ prepared from A did not show the presence of residual carbon. As expected the primary particle size, as calculated from PXRD patterns, is increased from 8 to 45 nm by increasing the oxidation temperature stepwise to 900 °C and the BET surface area is reduced (Table 3, Figure 8).

The highest BET surface area of 178 m$^2$ g$^{-1}$ was observed for the final material obtained upon oxidation of the hybrid material B. The residual carbon content of 0.50% is quite low. Starting from hybrid material C, BET surface areas of 133 m$^2$ g$^{-1}$ (residual carbon content: 0.28%) and 137 m$^2$ g$^{-1}$ (no residual carbon detected) were observed, which is in the same range as that observed for the final material obtained by oxidation of hybrid material E (143 m$^2$ g$^{-1}$, no residual carbon content). The oxidized hybrid material D (78 m$^2$ g$^{-1}$, residual carbon content: 0.38%) shows a smaller BET surface area than the final materials obtained from B, C, and E and is in the same range as for the oxidized materials starting from hybrid material A. TEM images of the calcined materials A$_{ox}$ (500 °C), B$_{ox}$ (600 °C), and C$_{ox}$ (450 °C) (Figure 9) show that the particle size is consistent with PXRD in the range 5–15 nm and that the materials A$_{ox}$ and C$_{ox}$ do not differ significantly. Somewhat smaller particles 5–10 nm in size are obtained for material B$_{ox}$.

Simultaneous twin polymerization

To prepare SnO$_2$/SiO$_2$ composites we chose the concept of simultaneous twin polymerization (STP). Thus, starting from mixtures of the silicon monomer 2,2’-spirobi[4H,1,3,2-benzodioxasiline] (Si-spiro, m.p. 82–84 °C) and the tin alkoxides 5–7 in a 2:1 ratio, organic–inorganic hybrid materials are observed, which are transformed into SnO$_2$/SiO$_2$ composites by subsequent oxidation (Scheme 4). In the first step homogeneous melts were observed and heated at temperatures of 80–100 °C for 30 min to give a solid material. After the workup procedure to remove soluble components, high carbon contents of the organic–inorganic hybrid materials are indicative of effective cross-linking of the polymer (Table 4). Notably, addition of an

Figure 7. Left: Solid-state $^{13}$C-$^1$H)-CP-MAS NMR spectrum of poly(thiophene-2-methanol)/SnO$_2$ hybrid material B (CF$_3$SO$_3$H-initiated). The asterisk (*) indicates a spinning side band. Right: High-angle annular dark-field (HAADF)–scanning electron transmission microscopy (STEM) image of poly(thiophene-2-methanol)/SnO$_2$ hybrid material B (CF$_3$SO$_3$H-initiated). Inset: Selected-area electron diffraction of hybrid material B.
A characteristic for methylene bridges in polymeric structures. In contrast to 

d signals of weak intensity in the range 60–72 ppm and at 

60 ppm (for F), and 78 to 91 ppm. The solid-state NMR data indicate 

that the less reactive compounds 5 and 6 are not fully converted 

into SnO2 as is observed for the more reactive compound 7. The amorphous character of the hybrid materials F–H was shown by PXRD. Electron microscopy of the hybrid materials F–H shows the typical morphology of twin polymers with organic and inorganic domains in the range of 20–40 nm and primary particles with a size of about 3 nm (Figure S12).

Oxidation reactions

The as-prepared polymer/SnO2/SiO2 materials were oxidized in synthetic air to give porous SnO2/SiO2 hybrid materials. The optimum for the oxidation temperatures to remove the carbon was determined by thermogravimetric analyses (Table 5).

X-ray photoelectron spectroscopy measurements demonstrate that tin exclusively in the oxidation state IV is present. The Sn 3d element spectra show typical peak maxima of the Sn3d5/2 peaks for SnO2. In addition, the calculated tin/silicon ratio was determined from the high-resolution Sn 3d and Si 2p signals at 119 ppm. The solid-state NMR data indicate that the less reactive compounds 5 and 6 are not fully converted into SnO2 as is observed for the more reactive compound 7. The amorphous character of the hybrid materials F–H was shown by PXRD. Electron microscopy of the hybrid materials F–H shows the typical morphology of twin polymers with organic and inorganic domains in the range of 20–40 nm and primary particles with a size of about 3 nm (Figure S12).

Table 4. Simultaneous twin polymerization of 2,2′-spirobi[4H-1,3,2-benzo-

dioxasilin] with the tin alkoxides 5–7.

<table>
<thead>
<tr>
<th>Tin precursor</th>
<th>Polymerization in melt</th>
<th>Carbon content [%] found/calculated</th>
<th>Hybrid material</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>100/0.5</td>
<td>48.5/55.6</td>
<td>F</td>
</tr>
<tr>
<td>6</td>
<td>100/0.5</td>
<td>51.5/56.5</td>
<td>G</td>
</tr>
<tr>
<td>7</td>
<td>80/0.5</td>
<td>48.7/54.6</td>
<td>H</td>
</tr>
</tbody>
</table>

(a) Si/Sn ratio 2:1. (b) Carbon content of the nanocomposite material after workup. (c) Carbon content expected for quantitative conversion into polymer/SnO2/SiO2 hybrid materials.

initiator is not necessary, because the reaction is self-initiated by the Lewis acidic nature of the tin alkoxides.

Solid-state 13C NMR spectra of the hybrid materials F–H (Figure 10) show a high-field shift for the SiOCH2 and SnOCH2 groups to 31 ppm compared with the parent alcohol, which is characteristic for methylene bridges in polymeric structures. Ortho–ortho’ and ortho–para’ linkage in the polymer domains is deduced from signals at δ = 121 and 116 ppm, respectively. In contrast to H, the hybrid materials F and G show 13C NMR signals of weak intensity in the range δ = 60–72 ppm and at δ = 158 ppm that are indicative of unreacted Sn/Si—O—CH2Ar moieties. This observation is in accordance with the expected high reactivity of the methoxy-substituted tin alkoxide 7. Hybrid materials F and G show quite sharp signals in the solid-state 119Sn NMR spectra at δ = −696 and −706 ppm, respectively, whereas the hybrid material H shows a rather broad signal in the range δ = −600 to −700 ppm. In the solid-state 29Si NMR spectra signals at δ = −94 and −101 ppm (for F), δ = −94 ppm (for G), and δ = −98 ppm (for H) are observed (Figure S11). The formation of stannosilicates is thus ruled out, as they typically show 29Si NMR chemical shifts in the range of δ = −78 to −91 ppm. The solid-state NMR data indicate that the less reactive compounds 5 and 6 are not fully converted into SnO2 as is observed for the more reactive compound 7. The amorphous character of the hybrid materials F–H was shown by PXRD. Electron microscopy of the hybrid materials F–H shows the typical morphology of twin polymers with organic and inorganic domains in the range of 20–40 nm and primary particles with a size of about 3 nm (Figure S12).

Figure 9. TEM images of the oxidized hybrid materials Aox (500 °C), B′ox (600 °C), and C′ox (450 °C).

Scheme 4. Simultaneous twin polymerization of 2,2′-spirobi[4H-1,3,2-benzo-
dioxasilin] and compounds 5–7 to give a hybrid material consisting of phenolic resins (e.g., o/o’ substitution), SnO2, and SiO2.
ties as result of hydrogen bonding, the presence of Si–OH groups, or the partial incorporation of tin. The solid-state 
$^{29}\text{Si}$ NMR spectrum of the hybrid materials such as $\text{F}$ shows signals at $\delta = -94$ ppm (Q$_2$), $\delta = -100$ ppm (Q$_3$), and $\delta = -109$ ppm (Q$_4$) (Figure 11). The signals for Q$_{2/3}$ are indicative of an incompletely condensed silicon oxide phase (Si–OH or Si(OH)$_2$ moieties) and the Q$_4$ signal is typical for fully condensed SiO$_2$. The degree of condensation was increased by oxidation as is demonstrated by a shift of the $^{29}\text{Si}$ NMR signal to $\delta = -109$ ppm for the oxidized hybrid material $\text{F}_{\text{ox}}$. In the corresponding $^{119}\text{Sn}$ NMR spectrum the signal is shifted from $\delta = 696$ ppm, as observed in the polymer-based hybrid $\text{F}$, to $\delta = 603$ ppm ($\nu_{\text{as}} = 2533$ Hz) for the oxidized silica/SnO$_2$ ($\text{F}_{\text{ox}}$), which is indicative of amorphous or nanocrystalline SnO$_2$.[54]

The PXRD patterns of the SiO$_2$/SnO$_2$ hybrid materials are indicative of the formation of SnO$_2$ primary particles approximately 20 to 32 nm in size embedded in an amorphous SiO$_2$ matrix (Figure S14). The corresponding TEM images confirm that small particles are present with sizes in the range from 5 to 25 nm for $\text{F}_{\text{ox}}$ and 5 to 32 nm for $\text{G}_{\text{ox}}$ (Figure 12). Notably, a smaller crystallite size of the SnO$_2$ particles is obtained by STP of 2,2’-spirobi[4H-1,3,2-benzodioxasiline] with compounds 5–7 compared with TP of compounds 1–5. Hence, the silica acts as a crystal growth inhibitor for SnO$_2$ during the oxidation process.

The BET surface areas of the SnO$_2$/SiO$_2$ materials range from 165 m$^2$ g$^{-1}$ for $\text{F}$ to 378 m$^2$ g$^{-1}$ for $\text{H}$ (Table 5). Nitrogen adsorption–desorption isotherms (Figure S15) of the as-prepared SnO$_2$/SiO$_2$ materials exhibit isotherm curves between type I and type IV. The isotherms of the oxidized hybrid materials $\text{F}_{\text{ox}}$ and $\text{G}_{\text{ox}}$ show hysteresis loops in the oxidized material (%) for the oxidized material $\text{F}_{\text{ox}}$ and $\text{G}_{\text{ox}}$.

Table 5. Analytical data for SnO$_2$/SiO$_2$ composites ($\text{F}_{\text{ox}}$, $\text{G}_{\text{ox}}$, and $\text{H}_{\text{ox}}$) obtained by oxidation of the organic–inorganic hybrid materials $\text{F}$–$\text{H}$.

<table>
<thead>
<tr>
<th>SnO$_2$/SiO$_2$ hybrid material</th>
<th>Oxidation[a]</th>
<th>BET surface area [m$^2$ g$^{-1}$]</th>
<th>Crystallite size of SnO$_2$[b] [nm]</th>
<th>Carbon content in the oxidized material [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_{\text{ox}}$</td>
<td>800/5</td>
<td>227</td>
<td>25</td>
<td>0.02</td>
</tr>
<tr>
<td>$\text{G}_{\text{ox}}$</td>
<td>700/5</td>
<td>165</td>
<td>32</td>
<td>0.03</td>
</tr>
<tr>
<td>$\text{H}_{\text{ox}}$</td>
<td>700/5</td>
<td>378</td>
<td>20</td>
<td>0.09</td>
</tr>
</tbody>
</table>

[a] Heating rate 10 K min$^{-1}$. [b] Calculated using the Scherrer equation.

Figure 10. Solid-state $^{13}\text{C}$-{H}-CP-MAS NMR spectra of hybrid materials $\text{F}$–$\text{H}$. Asterisks (*) indicate spinning side bands. The x indicates signals that are assigned to the unreacted tin compounds and/or incompletely condensed precursors.

Figure 11. Solid-state $^{29}\text{Si}$-{H}-CP-MAS NMR and $^{119}\text{Sn}$-{H}-MAS NMR spectra (inset) of hybrid materials $\text{F}$ and $\text{F}_{\text{ox}}$.

Figure 12. TEM images of the SnO$_2$/SiO$_2$ hybrid materials $\text{F}_{\text{ox}}$ and $\text{G}_{\text{ox}}$. STP of 2,2’-spirobi[4H-1,3,2-benzodioxasiline] with compounds 5–7 compared with TP of compounds 1–5. Hence, the silica acts as a crystal growth inhibitor for SnO$_2$ during the oxidation process. The BET surface areas of the SnO$_2$/SiO$_2$ materials range from 165 m$^2$ g$^{-1}$ for $\text{F}$ to 378 m$^2$ g$^{-1}$ for $\text{H}$ (Table 5). Nitrogen adsorption–desorption isotherms (Figure S15) of the as-prepared SnO$_2$/SiO$_2$ materials exhibit isotherm curves between type I and type IV. The isotherms of the oxidized hybrid materials $\text{F}_{\text{ox}}$ and $\text{G}_{\text{ox}}$ show hysteresis loops in the oxidized material (%) for the oxidized material $\text{F}_{\text{ox}}$ and $\text{G}_{\text{ox}}$. The degree of condensation was increased by oxidation as is demonstrated by a shift of the $^{29}\text{Si}$ NMR signal to $\delta = -109$ ppm for the oxidized hybrid material $\text{F}_{\text{ox}}$. In the corresponding $^{119}\text{Sn}$ NMR spectrum the signal is shifted from $\delta = -696$ ppm, as observed in the polymer-based hybrid $\text{F}$, to $\delta = -603$ ppm ($\nu_{\text{as}} = 2533$ Hz) for the oxidized silica/SnO$_2$ ($\text{F}_{\text{ox}}$), which is indicative of amorphous or nanocrystalline SnO$_2$.[54]

The PXRD patterns of the SiO$_2$/SnO$_2$ hybrid materials are indicative of the formation of SnO$_2$ primary particles approximately 20 to 32 nm in size embedded in an amorphous SiO$_2$ matrix (Figure S14). The corresponding TEM images confirm that small particles are present with sizes in the range from 5 to 25 nm for $\text{F}_{\text{ox}}$ and 5 to 32 nm for $\text{G}_{\text{ox}}$ (Figure 12). Notably, a smaller crystallite size of the SnO$_2$ particles is obtained by
whereas in H_{mic} smaller pore sizes between 1 and 5 nm dominate.

As expected, the BET surface areas are significantly lower than that observed for mesoporous SiO\(_2\) prepared by TP of 2,2′-spiropyli[4H-1,3,2-benzodioxasilin] (904 m\(^2\) g\(^{-1}\)),\(^{[44]}\) but comparable with the highest values reported for SnO\(_2\)/SiO\(_2\) hybrid materials prepared by the sol–gel process.\(^{[66]}\) SiO\(_2\)/SnO\(_2\) materials with tin oxide content of 22 and 29 wt\% show surface areas in the range 269–343 m\(^2\) g\(^{-1}\) (heat treatment 700–400 °C\(^{[22]}\) and 375–494 m\(^2\) g\(^{-1}\) (heat treatment 800–400 °C\(^{[67]}\) whereas with increasing tin oxide content of 90 and 75 wt\% surface areas of 211–340 m\(^2\) g\(^{-1}\) (heat treatment 600–400 °C\(^{[31]}\) and 133–209 m\(^2\) g\(^{-1}\) (heat treatment 800–400 °C\(^{[20]}\) have been reported. The SiO\(_2\)/SnO\(_2\) materials obtained from the TP show comparatively high surface areas up to 378 m\(^2\) g\(^{-1}\) (700 °C heat treatment) with a tin oxide content of 54 wt\%. Notably, long aging times for the preparation of xerogels, which in some cases are several days or even weeks, are not necessary in the TP process.\(^{[67,68]}\)

**Conclusion**

Seven novel tin(IV) alkoxides 1–7 with potential for so-called twin polymerization were obtained by transesterification starting from Sn(OR)\(_2\) (R = iBu, tAm: 2-methyl-2-butyl) and furfuryl alcohol, 2-thiophenemethanol, (2-methoxyphenyl)methanol, (2,4-dimethoxyphenyl)methanol, 2-(hydroxymethyl)-4-methylphenol, and 2-(hydroxymethyl)-4-methoxyphenol, respectively. Compounds 2–4, 6, and 7 are soluble in organic solvents, whereas compounds 1 and 5 are not. Hence, polymerization reactions of 1 and 5 were performed without the use of a solvent, whereas the other precursors were reacted in solution to give polymer/SnO\(_2\) hybrid materials. In the case of 4, cycloligomerization to give calix[4]resorcinarene octamethyl ether instead of a polymer is observed. Thus, it is concluded that the (2,4-dimethoxybenzyl)oxo substituent is not well suited as a ligand for twin polymerization, despite its high reactivity. In the case of polymerization of the tin precursors 2–5 in solution, CF\(_3\)SO\(_2\)H is the most effective initiator for the cationic polymerization. The use of CF\(_3\)COOH results in lower yields and longer reaction times. Starting from the hybrid materials obtained from compounds 1–5, high-surface-area tin(IV)oxide with BET surface area up to 178 m\(^2\) g\(^{-1}\) is accessible by treatment of the hybrid materials with air at approximately 600 °C. Materials with higher surface area of up to 378 m\(^2\) g\(^{-1}\) composed of SnO\(_2\)/SiO\(_2\) are accessible by using the concept of simultaneous twin polymerization in which 2,2′-spiropyli[4H-1,3,2-benzodioxasilin] is reacted with tin precursors such as compounds 5–7 resulting in polymer/SnO\(_2\)/SiO\(_2\) nanocomposites, which are finally oxidized to remove the organics. Notably, the polymerization is self-initiated as a result of the high Lewis acidity of the tin compounds and addition of any additional initiator even at temperatures below 100 °C is not necessary. In the as-prepared SnO\(_2\)/SiO\(_2\) materials, the SiO\(_2\) network inhibits the crystal growth of the simultaneously formed SnO\(_2\) particles that exhibit crystallite sizes of approximately 20 nm. The extension of this concept to other metal oxide/SiO\(_2\) composites is currently being investigated in our laboratories.

**Experimental Section**

**General procedures and starting materials**

All reactions were performed under inert argon atmosphere. Diethyloxyl ether, n-pentane, and toluene were distilled over sodium before use. Tetra-tet-butoxystannane and tetra-tet-pentyloxystannane were prepared from SnCl\(_4\) according to literature procedures.\(^{[49]}\) Furfuryl alcohol was purchased from Merck KGaA and distilled over sodium hydride before use. 2-Thiophenemethanol and 2-methoxybenzyl alcohol were purchased from Aldaer and used without further purification. 2,4-Dimethoxybenzyl alcohol was prepared from 2,4-dimethoxybenzaldehyde.\(^{[66]}\) SnO\(_2\) nanoparticles were purchased from Sigma-Aldrich, with primary particle sizes of 29 nm (calculated by the Scherrer equation) and BET surface areas around 46 m\(^2\) g\(^{-1}\). \(1,1\)-Cyclohexylketene was synthesized with a PerkinElmer TGA 7 instrument. Specific surface area analysis was performed by a Thermo Type Flash A112 analyzer. Thermogravimetric measurements were performed at 9.4 T on a Bruker Avance III 500 spectrometer at 500.3, 125.8, and 186.4 MHz, respectively. The spectra were referenced to SiMe\(_4\) (\(\delta = 0\) ppm for \(1^H\), \(1^C\)) and SnMe\(_4\) (\(\delta = 0\) ppm for \(119^Sn\)). Solid-state NMR measurements were performed at 9.4 T on a Bruker Avance 400 spectrometer equipped with double-tuned probes capable of magic angle spinning (MAS). \(13^C\)-(\(1^H\))-CP-MAS NMR spectroscopy was accomplished in 4 mm rotors made of zirconium oxide spinning at 12.5 kHz. Cross-polarization with contact times of 3 ms was used to enhance sensitivity. The recycle delay was 5 s. \(119^Sn\)-(\(1^H\))-CP-MAS NMR spectroscopy was performed in 4 mm rotors spinning at 12.5 kHz. The recycle delay was 10 s. All spectra were obtained under \(^1H\) decoupling using a two-pulse phase modulation sequence. The spectra were referenced with respect to tetramethylsilane (TMS) with tetrayclohexylstannane as a secondary standard (\(\delta = 3.6\) ppm for \(13^C\), \(\delta = 97.3\) ppm for \(119^Sn\)). If not stated otherwise, all spectra were acquired at room temperature. Single-crystal X-ray diffraction analyses for compounds 2, 2a, and 3 were performed by using an Oxford Gemini S diffractometer with graphite-monochromated CuK\(_\alpha\) radiation at 293 (2), 160 (2a), and 120 K (3). The structures were solved by direct methods with SHELXS-97 and refined with SHELXL-97. The figures were created by DIAMOND (version 3.1, 2006). CCDC 854547 (2), 854689 (2a), 854548 (3), and 854549 (calix[4]resorcinarene octamethyl ether) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction (PXRD) patterns were measured with a STOE-STADI-P diffractometer using CuK\(_\alpha\) radiation (40 kV, 40 mA). The crystallite size was estimated by using the formula determined by the Scherrer equation: \(t = \frac{K\lambda}{\beta\cos\theta}\) in which \(t\) is the volume-weighted crystallite size in nm, \(K\) is the Scherrer constant here taken as 1.0, \(\lambda\) is the X-ray wavelength, \(\theta\) is the Bragg angle in rad, and \(\beta\) is the full width of the diffraction line at half of the maximum intensity.

Attenuated total reflection–IR spectra were recorded on a Biorad FTS-165 spectrometer with a Spectromat Golden-Gate attachment. Elemental analysis was performed by a Thermo Type Flash AE 1112 elemental analyzer. Thermogravimetric measurements were performed with a PerkinElmer TGA 7 instrument. Specific surface analyses were performed with \(N_2\) adsorption–desorption isotherms at liquid nitrogen temperature (77 K) using a Quantachrome Autosorb IQ2 apparatus, and were evaluated by the Brunauer–Emmett–Teller (BET) method at the \(p/p_0\) ratio of 0.150.
Synthesis of the tin monomers

Synthesis of tetra(furan-2-ylmethoxy)stannane (1): Furfuryl alcohol (2.67 g, 27.23 mmol) was dropped into an ice-cold solution of tetra-tert-butoxystannane (2.78 g, 6.76 mmol) in n-pentane (40 mL). After 1 h the precipitate was isolated by filtration and washed with diethyl ether (30 mL). The beige solid was dried in vacuo (10⁻³ mbar, 50 °C) to afford compound 1 (2.68 g, 78 %, m.p. 107–109 °C). ¹³C{¹H}-CP-MAS NMR (100.6 MHz): δ = 159.2, 154.1, 142.7, 111.6, 107.8, 58.5 ppm; ¹¹⁹Sn-{¹H}-CP-MAS NMR (149.2 MHz): δ = 595, –602 ppm; IR: ν = 3145/3121 (w), 2929/2865 (w), 1500/1599 (m), 1475 (s), 1434 (m), 1366 (w), 1280 (w), 1198 (s), 1010 (m), 929 (m), 783 (m), 621 (s), 550 cm⁻¹ (m); elemental analysis calcd (%) for C₂₀H₂₀O₈Sn₂: C 56.56, H 5.91; found: C 55.46, H 6.00.

Synthesis of bis(µ-thiophen-2-ylmethoxy)-hexakis(thiophen-2-ylmethoxy)bis(thiophen-2-ol)-tristannane (2): 2-Thiophenemethanol (2.31 g, 20.20 mmol) was dropped into a solution of tetra-tert-butoxystannane (1.67 g, 4.05 mmol) in toluene (10 mL). The mixture was stirred for 1 h and the orange solution was covered with n-pentane (10 mL) to give large orange crystals of 2 (1.48 g, 53 %, m.p. 109–109 °C). Slow diffusion of moisture into a reaction vessel of 2 in n-pentane resulted in the formation of a crop of single crystals of di[(µ-hydroxy)-(µ-oxido)-tris(µ-thiophen-2-ylmethoxy)-hexakis(2-thiophen-2-ol)-2-tristannane] (2 a) used for single-crystal X-ray diffraction analysis.

2: ¹¹⁹Sn NMR (500.3 MHz, CDCl₃): δ = 692 (s), 547/513 (m), 464 (m), 416 cm⁻¹ (m); IR: ν = 3066/3005 (w), 2936/2898 (w), 2833 (w), 1588 (m), 1488/1460/1436 (s), 1372 (m), 1282 (m), 1233 (s), 1114 (m), 1021 (s), 928 (m), 813 (w), 744 (s), 712 (m), 660 (m), 610 (m), 580 (w), 521 (m), 482 (s), 435 cm⁻¹ (m); elemental analysis calcd (%) for C₂₀H₂₀O₈Sn₂: C 59.64, H 5.76; found: C 59.46, H 6.13.

Synthesis of bis[µ-(2,4-dimethoxybenzyl)oxy]-hexakis[2,4-dimethoxybenzyl]oxy]-bis[2,4-dimethoxyphenyl](methanol)-distannane (4): Tetra-tert-pentyltinoxystannane (0.5 mL, 1.31 mmol) was dissolved in diethyl ether (15 mL) and cooled to 0 °C. A solution of 2,4-dimethoxybenzyl alcohol (1.77 g, 10.51 mmol) in diethyl ether (15 mL) was dropped into the reaction mixture. The viscous precipitate was washed with diethyl ether until a colorless amorphous solid was formed. The product was dried in vacuo (10⁻³ mbar, 50 °C) to give 4 as a colorless solid (0.44 g, 42 %, m.p. 85–120 °C). ¹¹⁹Sn NMR (500.3 MHz, CDCl₃): δ = 7–9.96–6.24 (30H; aryl groups), 5.44–4.68 (br, 20H; CH₃), 3.82–3.51 ppm (br, 60H; OCH₃); ¹³C{¹H}-CP-MAS NMR (100.6 MHz): δ = 174, 120.9, 127.6, 157.9 ppm; ¹¹⁹Sn-{¹H}-CP-MAS NMR (149.2 MHz, C₆D₆): δ = –697 ppm; IR: ν = 3066, 3005 (w), 2936, 2898 (w), 3066, 3005 (w), 2936, 2898 (w), 2833 (w), 3066, 3005 (w), 2936, 2898 (w), 2833 (m), 1610/1587 (m), 1504 (s), 1456 (s), 1282 (s), 1203 (s), 1153 (s), 1020 (m), 1032 (s), 929 (s), 819 (s), 783 (m), 627 (m), 571 (w), 521 (m), 509 (m), 451 cm⁻¹ (m); elemental analysis calcd (%) for C₁₄H₂₀O₈Sn₂: C 56.56, H 5.91; found: C 55.46, H 6.00.
Synthesis of 2,2'-spirobi[6-methoxybenzo(4H-1,3,2)dioxastannine] (7): A solution of tetra-tert-butoxyxannane (1.23 g, 2.99 mmol) in tetrahydrofuran (20 mL) was dropped into a solution of 2-(hydroxy-methyl)-4-methoxyphenol (1.15 g, 7.47 mmol) in tetrahydrofuran (20 mL) at −60°C. The colorless mixture was stirred for 30 min at −60°C and 30 min at room temperature. Tetrahydrofuran was removed and the viscous yellow crude product was washed with n-pentane (50 mL) and diethyl ether (50 mL). The pale yellow solid was dried in vacuo (∼20 mbar, 50°C) to afford compound 7 (1.13 g, 90%, decomposed at 240°C). 1H NMR (500.3 MHz, CDCl3): δ = 6.79 (br, 6H; aryl groups), 4.67 (br, 4H; CH2), 3.74 ppm (br, 6H; OCH3); 11C-{1H}-CP-MAS NMR (100.9 MHz): δ = 54.9, 72.3, 110.9, 118.2, 126.5, 153.6 ppm; 119Sn-{1H}-CP-MAS NMR (149.2 MHz): δ = −683 ppm; IR: ν = 2938 (w), 2832 (w), 1599 (w), 1485 (s), 1423 (m), 1248 (m), 1203 (s), 1153 (m), 1037 (m), 918 (m), 852 (m), 794 (s), 785 (s), 719 (m), 669 (m), 571 (s), 503 cm⁻¹ (s); elemental analysis calc (%) for C23H₂0Sn: C 45.43, H 3.81; found: C 45.13, H 4.10.

Cationic polymerization
Polymerization in melt: Compound 1 was heated to 120°C for 3 h under inert conditions. The resulting dark brown composite was extracted with dichloromethane until the extracts were colorless and dried in vacuo to constant weight.

Heat treatment: Compound 5 and 4-methylbenzenesulfonylic acid were suspended in toluene. After stirring for a few minutes, the solvent was removed and the reaction mixture was heated to 280°C for 15 min under argon. The dark red composite material was washed with chloroform and acetone and dried at 70°C.

Polymerization in solution: The tin monomers were dissolved at room temperature in dry chloroform (0.1 mol L⁻¹) under inert conditions. The resulting dark brown composite material was washed with chloroform and acetone and dried at 70°C.

Simultaneous twin polymerization
Compound 5 (1.02 g, 3.74 mmol) was suspended in a solution of 2,2'-spirobi[4H-1,3,2-benzodioxasiline] (0.68 g, 1.87 mmol) in dry chloroform (10 mL) at a Si/Sn ratio of 2:1. After stirring for a few minutes, the solvent was removed and the reaction mixture was heated slowly to 80°C for half an hour. The brown composite material was washed with acetone and dried at 70°C.

Oxidation reactions
The removal of the organic polymeric material by oxidation was performed in a tube furnace. The composite was treated with a constant airstream (200 L h⁻¹) to give a light beige solid of SnO2. The oxidation conditions are given in Tables 3 and 5.

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Keywords: nanoparticles · NMR spectroscopy · organic–inorganic hybrid materials · tin alkoxides · twin polymerization

Double act: Well-defined tin alkoxide precursors have been prepared for application in the twin polymerization process, which provides composite materials composed of SnO$_2$ nanoparticles entrapped in a polymer matrix (see scheme). Subsequent oxidation of the composite materials gives high-surface-area tin oxide and composites composed of SnO$_2$/SiO$_2$. 

Tin Oxide Nanoparticles and SnO$_2$/SiO$_2$ Hybrid Materials by Twin Polymerization Using Tin(IV) Alkoxides


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