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Functionalization of Silica Gel with Organotrialkynyltins: New Method of Covalent Attachment of Organic Groups on Silica Gel

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A new precursor molecule for chemical modification of oxide surfaces, the trialkynyl(fluoroorgano)-tin(IV) $(C_4H_9-C{\equiv}C)_3Sn(CH_2)_2(CF_2)_7CF_3$, **1**, was synthesized in three steps from tricyclohexyltin hydride. Compound **1** reacted with Biosepra 100 silica to give chain loadings as high as 0.28 mmol·g^{-1} to be compared to 0.44 mmol·g^{-1} reached with the trichlorosilane analogue $Cl_3Si(CH_2)_2(CF_2)_7CF_3$, **2**. The modified powders have been thoroughly characterized using elemental analysis, FTIR spectroscopy, solid-state ^{29}Si, ^{13}C, and ^{29}Si CP-MAS NMR, XPS, and TGA-MS. Irreversible chemisorption took place in solution at room temperature to give a fluorinated chain thin layer, likely a monolayer, via removal of three hex-1-yne molecules and formation of $Si_{bulk}-O-Sn-C$ linkages. The chemisorption process involves hydrolysis of the precursor in solution before reaction with the silica surface and led to surface-modified silica thermally stable up to 350 °C. Trialkynylorganotins in solution might be therefore advantageously exploited to modify chemically SnO_2 or TiO_2 surfaces to get dye-sensitized oxide materials able to achieve light-to-electricity conversion.

Introduction

Surface functionalization and modification with organosilicon compounds bearing organic functional groups confer new properties on silica layers, for instance, water or/and fat repulsion,[1] ion[2] or DNA[3] detection, catalyst immobilization,[4] and light absorption in the visible range.[5] Alkoxy-,[6] chloro-,[7] and hydridosilanes[8] are the most commonly used to obtain self-assembled monolayers (SAMs) at room temperature, but they suffer some limitations arising from handling and purification problems related to their sensitivity to hydrolysis. More recently, similar graftings have been achieved with (allyl)organosilanes at 120 °C.[9] Furthermore, the reactivity of organo- or hydridotins in a vacuum toward activated silica or alumina is rather well-documented by Basset et al.[10] Surface modification of oxides with highly air- and moisture-sensitive tetraalkoxy-[11] and aminotins[12] was also reported to prepare self-assembled mono- and multilayered thin films of chromophores.[12c,d] Nonetheless, little attention has been paid to solution preparations of surface-modified oxides from organostannanes. Since their first report at the beginning of the 1960s[13] it has been shown that alkynylorganotins, which can be conveniently purified by column chromatography over Florisil, are versatile sol−gel precursors thanks to easy cleavage of the tin−alkynyl bond in the presence of water. For instance, tin dioxide-based

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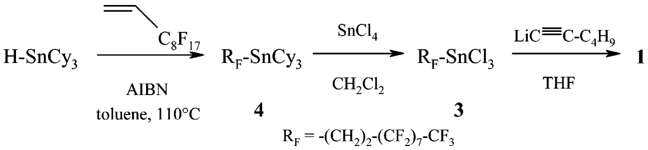
Scheme 1

$F_3C(CF_2)_7(CH_2)_2Sn(C{\equiv}C\text{-}C_4H_9)_3$ **1** $F_3C(CF_2)_7(CH_2)_2SiCl_3$ **2**

Scheme 2



clusters[14] or hybrid materials[15] and conductive F-doped tin dioxide powders[16] have been prepared by controlled hydrolysis of trialkynylorganotins and hexaalkynylorganoditins. Owing to the stability of the $Sn{-}C_{sp2\ or\ sp3}$ bond under neutral hydrolytic conditions and the reactivity of the $Sn{-}C_{sp}$ bonds toward hydroxyl functions, they should be good candidates to modify metal oxide surfaces. On the other hand, oxide surfaces modified with perfluoroalkyl chains are of great interest for both their hydrophobic/lipophobic characteristics and their low surface energy.[17]

With the aim to develop a new method of covalent attachment of organic functions onto oxide surfaces, we assessed the reactivity of trialkynylorganotins toward different oxides. The present paper deals with the reactivity of a trialkynylorganotin **1** (Scheme 1) bearing a 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl chain toward the surface of a nonporous Biosepra 100 silica, a support exhibiting reactivity very similar to that of glass surfaces.[18] Emphasis has been put on the study, on one hand, of the parameters (concentration, temperature, reaction time) governing the reactivity of the trialkynylorganotins and, on the other hand, of the thermal stability of the resulting surface-modified silica. These new materials have been compared with those prepared from the corresponding trichloroorganosilane **2** in the same experimental conditions.

Results

Synthesis. The new precursor molecule **1** was straightforwardly synthesized in three steps from tricyclohexyltin hydride in an overall yield of 25% (Scheme 2). The synthesis of the tricyclohexylfluoroorganotin **4** was successfully achieved in high yield (70%) by hydrostannation of 1*H*,1*H*,2*H*-heptadecafluorodec-1-ene with tricyclohexyltin hydride in the presence of AIBN as a radical initiator. The electrophilic cleavage of the $Sn{-}R_F$ bond in **4** by tin tetrachloride led to pure fluoroorganotrichlorotin **3** in fair yield (50%) after purification by distillation. This method appeared to be more efficient for preparation of **3** than the usual synthetic route toward trichloroorganotins involving electrophilic cleavage of the tin−phenyl bond with hydrochloric acid.[19] It is also worth mentioning that **3** decomposed above 100 °C, likely due to a disproportionation reaction yielding $Cl_2Sn(R_F)_2$ and $SnCl_4$ as suggested by mass spectrometry data. Treatment of **3** with 3 equiv of hex-1-ynyllithium[14] produced analytically pure **1** in high yield (71%) after purification by column chromatography on Florisil. Compound **1** was fully characterized by multinuclear NMR and IR spectroscopies, mass spectrometry, and elemental analysis. The $\{^1H\}-^{119}Sn$ NMR solution spectrum of **1** exhibits a well-defined multiplet at −242.4 ppm characteristic of a trialkynylorganotin with a four-coordinate tin center.[20] The hyperfine structure (triplet of triplet, $J = 6$ and 9 Hz) can be assigned to unusual long-range $^{4,5}J(^{119}Sn-^{19}F)$ couplings having values close to the one we recently reported for the 3,3,3-trifluoropropyl analogue.[16]

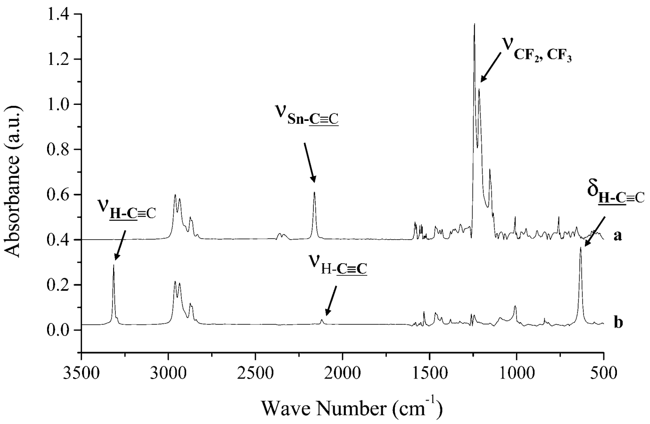


Figure 1. Solution FTIR spectra of the grafting solution used for $G_1^{0.18}$ after subtraction of the CCl_4 spectrum: (a) before reaction with silica and (b) after reaction with silica for 17 h.

Reactivity of 1 with Silica. *Qualitative Aspects.* The reactivity of **1** toward silica powder was subsequently investigated. Surface modification of silica was achieved by putting 0.5 g of Biosepra 100 silica into contact with 0.095 mmol of **1** in 25 mL of carbon tetrachloride. After 17 h at room temperature, the disappearance, in the IR spectrum of the supernatant, of the stretching bands of Sn−alkynyl (2160 cm^{-1}) and C−F (1243, 1215, and 1153 cm^{-1}) bonds clearly demonstrated that **1** had almost completely reacted with the silica support (Figure 1), i.e., 0.18 mmol of precursor molecule per gram of silica support. In addition, new bands at 3314, 2119, and 633 cm^{-1} assigned to the stretching or bending vibration of H−C≡ and C≡C bonds indicated the formation of free hex-1-yne, the amount of which was estimated to be 0.27 mmol by careful integration of the band at 3314 cm^{-1}.[21] These results were consistent with the release of 3 mol of hex-1-yne per mole of deposited **1**, revealing that all the functionalities of **1** had reacted. Decantation, removal of the supernatant, and washing four times with

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(21) The ^1H NMR spectrum of the supernatant recorded in $CDCl_3/CCl_4$ mixture showed new resonances after reaction characteristic of free hex-1-yne, in particular a well-defined triplet at 1.8 ppm assigned to *H*−C≡.

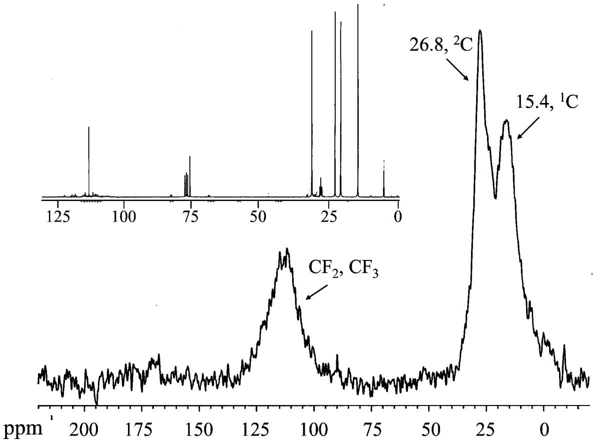

Figure 2. ^{13}C CP-MAS NMR spectrum of silica treated with **1** in CCl_4 then washed and dried. Spin rate 4 kHz. For comparison, the solution ^{13}C NMR spectrum of **1** recorded in $CDCl_3$ has been represented in the inset.

carbon tetrachloride followed by drying at 50 °C overnight under 0.2 mmHg gave 0.55 g of the modified Biosepra 100 powder. Elemental analysis of the solid revealed that it contained 2.0 wt % Sn, corresponding to 0.19 mmol per gram of the starting Biosepra 100 powder, which is in good agreement with the IR measurements. The material also contained 2.5 wt % C and 6.2 wt % F, i.e., C/F/Sn = 12/19/1, ratios in fair agreement with those of the coupling agent **1** (10/17/1). This was therefore consistent with the introduction of 0.18 $mmol{\cdot}g^{-1}$ fluoroalkyl chain onto the silica powder and complete removal of the hex-1-ynyl groups.

To gain a better insight into the chemically modified silica surface and probe the chemical environment of the tin center after reaction, ^{13}C, ^{117}Sn, and ^{29}Si solid-state NMR investigations were carried out. Since the above-mentioned material has low carbon and tin contents (2.5% and 2%, respectively) and since these nuclei are rather insensitive NMR nuclei, sample preparations were repeated using a silica support with higher specific area in order to achieve amounts of deposited stannane compatible with the sensitivity of solid-state NMR techniques. The ^{13}C CP-MAS NMR spectrum of a modified silica containing 0.42 $mmol{\cdot}g^{-1}$ of fluorinated chain is shown Figure 2. Three main detected features reveal the presence of the fluorinated chain: (i) a very broad signal at 111.2 ppm ascribed to both $^{13}CF_2$ and $^{13}CF_3$ resonances; (ii) a strong signal at 26.7 ppm assigned to the $^{13}CH_2$ bound to CF_2 groups; (iii) a broad signal at 15.4 ppm assigned to the $^{13}CH_2$ group directly linked to the tin atom. As evidenced by the disappearance of the resonance at 75.7 ppm, characteristic of the $^{13}C_{sp}{-}Sn$ carbon according to the solution ^{13}C NMR spectrum of **1**, each alkynyl functionality of the coupling agent **1** has actually reacted, which is fully consistent with the IR data reported above. Furthermore, after reaction the resonance of the CH_2 group directly linked to the tin atom was deshielded by 12 ppm,[22] which is in agreement with introduction of oxygenated groups on the tin atom.

The corresponding ^{117}Sn CP-MAS spectrum exhibited an isotropic chemical shift located at −390 ppm associated with its pattern of spinning sidebands. This value appears in the ^{117}Sn chemical shift range characteristic of five- or six-coordinate monoalkyltin sites endowed with oxygenated ligands. Indeed, the oxo−hydroxobutyltin $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ cluster displays two resonances in the solid-state ^{119}Sn NMR spectrum located at −280 and −450 ppm, assigned unambiguously to five- and six-coordinate tin centers, respectively.[23]

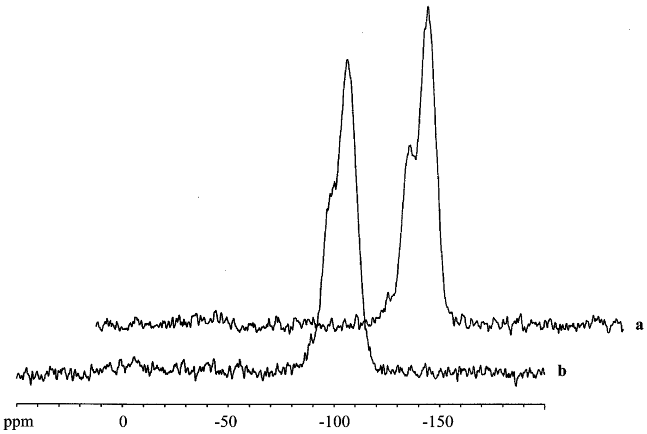

Figure 3. ^{29}Si MAS NMR spectra of silica treated (a) with CCl_4 then dried and (b) with **1** in CCl_4 then washed and dried. Spin rate 5 kHz.

The ^{29}Si MAS NMR spectra of silica before and after surface modification are displayed in Figure 3 and characteristic of a highly condensed silica network.[24] The spectrum of the modified silica had a main peak at −107 ppm with a shoulder around −100 ppm, whereas that of the starting silica showed two resonances at −107 and −99 ppm assigned to Q^4 and Q^3 species. The normalized integrated intensities deduced from deconvolution[25] of the modified silica (starting silica) were 85% (70%) for Q^4 and 15% (30%) for Q^3. On the other hand, the ^{29}Si CP-MAS NMR spectrum of the modified silica exhibits two main peaks at −107 and −98 ppm with a shoulder at −88 ppm assigned to Q^4, Q^3, and Q^2 species, respectively (Figure 4b), while the spectrum of the nonmodified silica, recorded with the same contact time, exhibited a main peak at −98 ppm and two minor ones at −107 and −88 ppm (Figure 4a). To ensure that comparison of these spectra is relevant, it was checked, by varying the contact time, that the built up of the signals in modified and nonmodified silica took place with identical amplitude profiles.[26] As a result, both solid-state ^{29}Si NMR experiments clearly indicated the presence of more condensed species, i.e., the decrease of the number of surface hydroxyl groups, in the surface-modified silica, in agreement with grafting of the precursor molecule **1**.

Quantitative Aspects. Similar experiments were conducted by varying the nature of the coupling agent and the concentration of the starting solution (Table 1). In the following the samples are labeled G_x^y where x and y stand

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(22) The ^{13}C chemical shift of the $CH_2{-}Sn$ was found at 3.8 ppm in the solution ^{13}C NMR spectrum of **1**.

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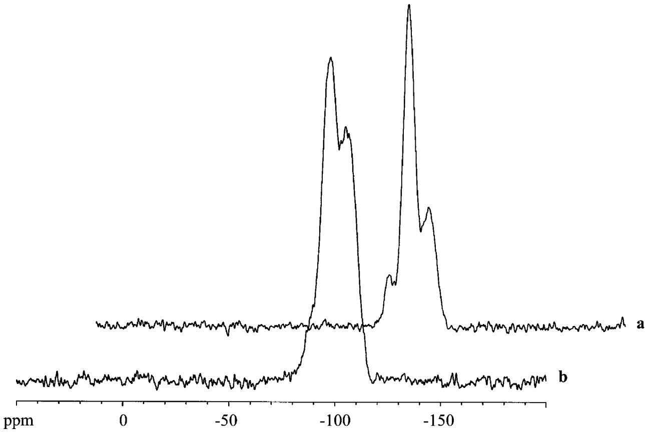

Figure 4. ^{29}Si CP-MAS NMR spectra of silica treated (a) with CCl_4 then dried and (b) with **1** in CCl_4 then washed and dried. Spin rate 5 kHz. Contact time 8 ms.

Table 1. Loadings of 1 and 2 and Chain Densities on Nonporous Biosepra 100 Silica after Reaction at Room Temperature for 17 h

sample	coupling agent	mole number introduced (mmol·g^{-1})	loading (mmol·g^{-1})	chain density (chain·nm^{-2})	number of hex-1-yne released (per chain deposited)
$G_1^{0.18}$	**1**	0.20	0.18	1.05	3
$G_1^{0.19}$	**1**	0.25	0.19	1.15	
$G_1^{0.22}$	**1**	0.40	0.22	1.30	3
$G_1^{0.27}$	**1**	0.68	0.27	1.60	
$G_1^{0.28}$	**1**	1.23	0.28	1.70	3
$G_2^{0.19}$	**2**	0.20	0.19	1.15	
$G_2^{0.44}$	**2**	0.68	0.44	2.65	
$G_2^{0.44}$	**2**	1.23	0.44	2.65	
$G_3^{0.05}$	**3**	0.20	0.05	0.28	
$G_3^{0.06}$	**3**	1.23	0.06	0.40	

Table 2. XPS Binding Energies and Atomic Ratios for $G_1^{0.19}$ and $G_2^{0.19}$

sample	atomic species	XPS binding energy (eV)	atomic ratios
$G_1^{0.19}$	Sn3d$_{5/2}$	486.5	C/Sn = 13
	Si2p	103.6	F/Sn = 17.2
	F1s	687.0	
	O1s	531.4	
	C1s	284.7, 286.4, 290.2, 291.5, 292.6	
$G_2^{0.19}$	Si2p	103.5	F/C = 1.7
	F1s	687.1	
	O1s	531.5	
	C1s	284.6, 286.2, 289.9, 291.4, 292.6	

for the nature of the coupling agent and the chain loading, respectively. No significant amount of fluorinated chain could be detected after reaction of the silica gel with the trichloride **3**. By contrast, the amount of chemisorbed stannane **1** progressively increased with the concentration of the mother solution until a plateau value of about 0.27−0.28 mmol·g^{-1}. This amount corresponded to a bonding density of 1.7 chain·nm^{-2}. In addition, 3 mol of hex-1-yne per molecule of chemisorbed **1** was released whatever the concentration used. For comparison, grafting performed in the same experimental conditions with **2** led to a bonding density of 2.8 chains·nm^{-2} (0.44 mmol·g^{-1}).

The surface species present in these samples were also studied by XPS measurements. For $G_1^{0.19}$ and $G_1^{0.28}$, each atomic species expected (Si, O, Sn, C, F) was observed (Table 2)[27] with no trace amount of remaining chlorine that could possibly have arisen from incomplete removal of the solvent. The binding energy found for Sn 3d$_{5/2}$ (486.5 eV) was consistent with formation of a tin center endowed with oxygenated groups.[28] In addition, the thickness of the organic layer probed is rather low, as evidenced by the large amounts of silicon and oxygen detected, atomic species belonging to the silica substrate. Quantitative analyses gave C/F/Sn atomic ratios of 13/17/1 and 11/14/1 for $G_1^{0.19}$ and $G_1^{0.28}$, respectively, in fair agreement with the theoretical ratio, i.e., C/F/Sn of 10/17/1, calculated by postulating the chemisorption of a $\equiv Sn-(CH_2)_2(CF_2)_7CF_3$ chain. Furthermore, XPS analyses showed that the relative surface concentration ratios Si/Sn found in samples $G_1^{0.19}$ and $G_1^{0.28}$ decreased from 14.9 to 10.3, in close agreement with the number of deposited chain determined, in each case, by microanalysis and FTIR spectroscopy. Finally, a fit of the C1s XPS spectra gave an idea of the different groups included in the organic chain. Deconvolution of the XP spectra recorded for $G_1^{0.19}$ and $G_2^{0.19}$ (Figure 5) was therefore performed with the assumption that the intensities for each kind of carbon were equal. In both cases we could clearly identify the contributions of $-CF_3$ (292.6 eV), $-(CF_2)_6-CF_3$ (291.5 eV), $-CF_2-(CF_2)_6-$ (290.2 eV), $-CH_2-CF_2-$ (286.4 eV), and $-CH_2-CH_2-$ (284.7 eV) groups.

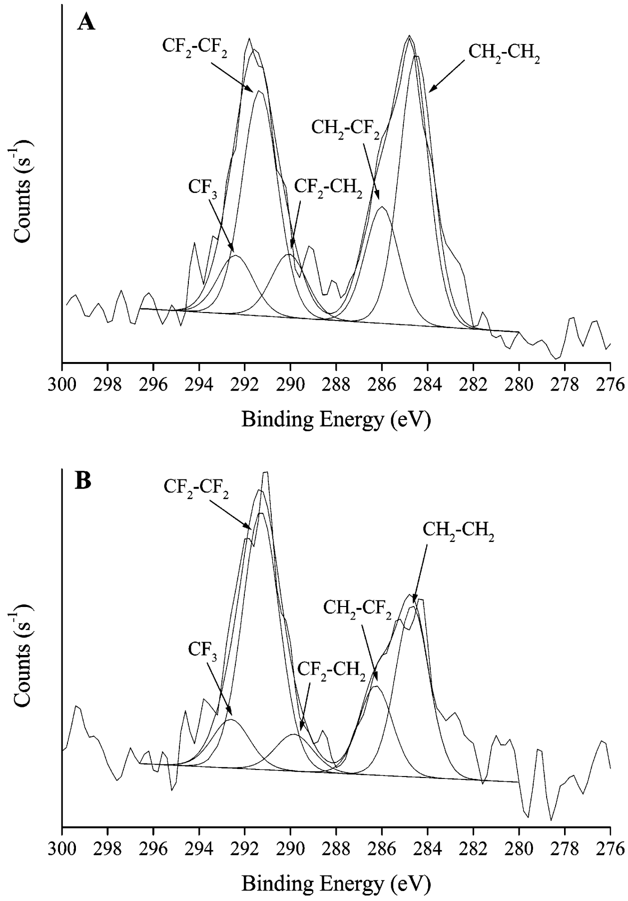

Figure 5. XPS C1s fit for (A) $G_1^{0.19}$ and (B) $G_2^{0.19}$.

Thus far we have described experiments carried out at room temperature overnight (17 h). We also wanted to evaluate the relative reactivity of **1** in comparison with **2**. For this purpose the reaction time was varied from 2 to 48 h using an initial coupling agent amount giving the highest

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(27) See Supporting Information.

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Table 3. Loadings of 1 and 2 and Chain Densities on Non-porous Biosepra 100 Silica at Room Temperature as a Function of the Reaction Time

sample	coupling agent[a]	reaction time (h)	loading (mmol·g^{-1})	chain density (chain/nm^{-2})
$G'_1{}^{0.08}$	**1**	2	0.08	0.50
$G'_1{}^{0.20}$	**1**	7	0.20	1.20
$G'_1{}^{0.27}$	**1**	17	0.27	1.60
$G'_1{}^{0.27}$	**1**	48	0.27	1.60
$G'_2{}^{0.19}$	**2**	2	0.39	2.35
$G'_2{}^{0.44}$	**2**	17	0.44	2.65

[a] Mole number of coupling agent introduced: 0.68 mmol·g^{-1}.

Table 4. Loadings of 1 and 2 and Chain Densities on Nonporous Biosepra 100 Silica after Reaction for 2 h

sample	coupling agent[a]	temp (°C)	loading (mmol·g^{-1})	chain density (chain·nm^{-2})
$G''_1{}^{0.03}$	**1**	5	0.03	0.20
$G''_1{}^{0.06}$	**1**	20	0.06	0.35
$G''_1{}^{0.13}$	**1**	60	0.13	0.80
$G''_2{}^{0.15}$	**2**	5	0.15	0.90
$G''_2{}^{0.16}$	**2**	20	0.16	0.95
$G''_2{}^{0.16}$	**2**	60	0.16	0.95

[a] Mole number of coupling agent introduced: 0.16 mmol·g^{-1}.

loading possible (Table 3). In the case of **1** the amount of fluoroalkyl chain grafted gradually increased with reaction time to reach 0.28 mmol·g^{-1} after 17 h, without any further change. By contrast, the reaction of **2** with the silica support was almost complete after 2 h. The same trend was observed as the temperature was varied (Table 4). Thus, the reactivity of **2** was complete after 2 h whatever the temperature in the range studied (5−60 °C). On the contrary, loading of **1** after 2 h increased progressively as the temperature increased from 5 to 60 °C. Thus, we can conclude that **1** reacted much more slowly with silica than the trichloroorganosilane **2**. To highlight the influence of water, small amounts of water (0.03 and 0.06 mmol·g^{-1}) were added to the reaction mixture when **1** was used as a precursor. In both cases samples containing 2.2 chains·nm^{-2} were obtained after 17 h, which is in favor of the formation of a denser $\equiv Sn-(CH_2)_2(CF_2)_7CF_3$ layer.

Thermal Behavior of the Modified Silica. The thermolytic behavior of the modified powders was studied by thermogravimetry coupled to mass spectrometry to highlight the thermal stability and nature of the species grafted onto silica.

First, Biosepra 100 silica treated with carbon tetrachloride for 17 h and dried afterward at 50 °C under vacuum was studied as a reference sample. The corresponding TG-DTG plots recorded under air showed two weight losses of 1% and 2.4% centered at 90 and 527 °C, respectively.[27] As previously mentioned in the case of Degussa OX50 and A380 silicas,[29] the first weight loss can be attributed to removal of physically adsorbed water, and dehydroxylation on the surface and inside of the silica likely contribute to the remaining weight loss at higher temperature.

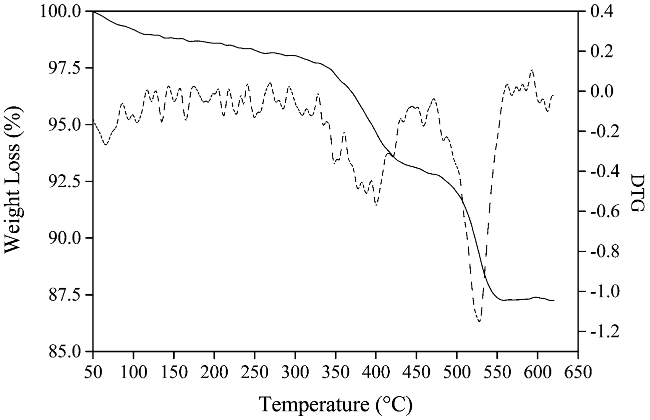

Figure 6. TG-DTG plot of sample $G_1{}^{0.19}$ between 50 and 650 °C recorded at 10 °C·min^{-1} under an air flow.

Pyrolysis of the modified silicas was subsequently investigated. TG analysis under air of $G_1{}^{0.19}$ exhibits a continuous mass loss from 50 to 650 °C including three main stages, 1.5%, 5.5%, and 6.0% weight loss at 90, 396, and 526 °C respectively (Figure 6). The total weight loss of 13% is in fair accordance with the calculated value of 11.1% expected for release of the $-(CH_2)_2C_8F_{17}$ fragment (7.7%) and taking into account the mass loss of the reference silica (3.4%). As the loading was increased to 0.28 mmol·g^{-1} ($G_1{}^{0.28}$), the decomposition process still occurred into three main steps but at significantly lower temperatures, i.e., 80 (1.6%), 358 (7.5%), and 506 °C (6.8%).[27] The same experiment was repeated under a helium flow to analyze the species evolved during pyrolysis by mass spectrometry. The main chemical fragments released during the three steps of the pyrolysis of $G_1{}^{0.19}$ and $G_1{}^{0.28}$ are given in Table 5 and correspond to the species arising from thermal decomposition of the fluoroalkyl chain. As evidenced by the nature of the fragments detected during the second and third mass losses (Figure 7), the different pyrolysis stages can be rationalized as follows: (i) removal of physisorbed water or organic species; (ii) release of a first kind of deposited species; (iii) decomposition of a second sort of chemisorbed fluorinated chain. To determine whether the two last stages were actually a result of the presence of two populations of grafted species, the modified silica $G_1{}^{0.19}$ was calcined in air at 400 and 550 °C for 1 h and the resulting material studied by TGA-MS. After thermal treatment at 400 °C, a single weight loss of 5−6% located around 514 °C was observed with detection of $CO_2{}^+$ ($m/z = 44$), $CF_2{}^+$ ($m/z = 50$), $CF_3{}^+$ ($m/z = 69$), and $CF_2CF_2{}^+$ ($m/z = 100$) as the main fragments. By contrast, a very weak mass loss (<0.5%) was detected between 50 and 650 °C after annealing at 550 °C. As a consequence, the third mass loss obtained for the modified silica actually arose from removal of the fluoroalkyl chain, which is in favor of the presence of different kinds of chemisorbed species which differ in the strength of their anchorage to the oxide surface (see below).

Similar experiments were carried out with samples $G_2{}^{0.19}$ and $G_2{}^{0.44}$. The TG-DTG analysis under air of $G_2{}^{0.19}$ ($G_2{}^{0.44}$) showed a continuous mass loss from 50 to 650 °C occurring in three main steps, 1.5%, 4%, and 5.5% (1%, 10%, and 10.5%) weight loss at 85, 460, and 517 °C (90, 457, and 507 °C).[27] In both cases the total weight loss was in rather good agreement with the release of $\equiv Si(CH_2)_2C_8F_{17}$ chains (7.8% or 16.3%) including the mass loss of the reference silica (3.4%). In addition, the chemical fragments arising from thermal decomposition of the fluorinated chain, detected

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(29) Wang, R.; Baran, G.; Wunder, S. L. *Langmuir* **2000**, *16*, 6298.

Table 5. TGA under He Coupled with MS Data for the Reference Silica and Modified Silica $G_1^{0.19}$ and $G_1^{0.28}$

sample	sampling temp (°C)	mass loss intensity (%)	*m*/*z* (detected fragments)
reference silica	88	1	17 (OH^+), 18 (H_2O^+)
	527	2.4	17 (OH^+), 18 (H_2O^+), 44 (CO_2^+)
$G_1^{0.19}$	75	0.7	44 (CO_2^+)
	398	6.9	12 (C^+), 19 (F^+), 44 (CO_2^+), 50 (CF_2^+), 69 (CF_3^+), 78 ($CH_2CH_2CF_2^+$), 113 ($CHCF_2CF_2^+$), 119 ($CF_3CF_2^+$)
	540	8.2	12 (C^+), 19 (F^+), 44 (CO_2^+), 50 (CF_2^+), 69 (CF_3^+), 100 ($CF_2CF_2^+$)
$G_1^{0.28}$	389	8.4	12 (C^+), 44 (CO_2^+), 50 (CF_2^+), 69 (CF_3^+), 78 ($CH_2CH_2CF_2^+$), 113 ($CHCF_2CF_2^+$), 119 ($CF_3CF_2^+$)
	550	10.7	12 (C^+), 44 (CO_2^+), 50 (CF_2^+), 69 (CF_3^+), 78 ($CH_2CH_2CF_2^+$), 113 ($CHCF_2CF_2^+$), 119 ($CF_3CF_2^+$)

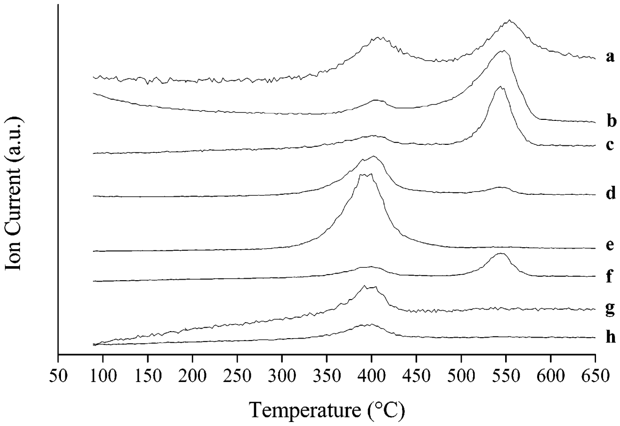


Figure 7. Sample $G_1^{0.19}$ *m*/*z* curves as a function of temperature: (a) $m/z = 19$ (F^+), (b) $m/z = 44$ (CO_2^+), (c) $m/z = 50$ (CF_2^+), (d) $m/z = 69$ (CF_3^+), (e) $m/z = 78$ ($C_2H_4CF_2^+$), (f) $m/z = 100$ ($CF_2CF_2^+$), (g) $m/z = 113$ ($CHCF_2$-CF_2^+), (h) $m/z = 119$ ($CF_2CF_3^+$).

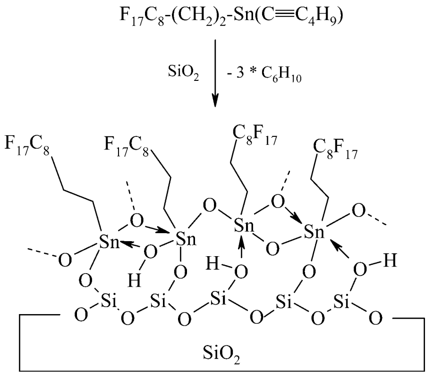
by TGA-MS measurements, were very close to those evidenced during pyrolysis of $G_1^{0.19}$ and $G_1^{0.28}$.

Discussion

Different mechanisms have been proposed in the literature to rationalize the reaction of organotrialkoxy- and organotrichlorosilanes or metal complexes with silica depending on the experimental conditions used. For instance, in the gas phase, irreversible adsorption of metal fragments is believed to occur by displacement of one or more protonated ligands, leading to the formation of covalent Si−O−M linkages at the surface.[30] Furthermore, in solution, it is now generally accepted that trace amounts of water, physisorbed onto the support or remaining in the solvent used, play a key role in the grafting process of trichloro- or trialkoxysilanes.[31] Thus, in situ AFM studies performed during reaction of octadecyltriethoxysilane with silica clearly showed that polycondensation of the coupling agent in solution first takes place yielding aggregates which reacted with silica.[31d,e] These grafted condensed species then grow by reaction with free precursor molecules or smaller aggregates to give dense monolayers.

For the trialkynylorganostannane reactions described here the experimental conditions are close to the latter case. Although the surface hydroxyl groups have not completely disappeared in the modified silica powders, irreversible chemisorption or grafting of **1** onto silica has actually occurred, as evidenced by the decrease of the Si−OH contribution in the solid-state ^{29}Si NMR spectra and release of three hex-1-ynyl groups per deposited precursor molecule according to IR and microanalysis data. At maximum loading the Sn content of the modified Biosepra 100 is 0.28 mmol·g^{-1}, corresponding to 1.7 chain·nm^{-2}, a chain density which has remained unchanged as the concentration of **1** was increased to 1.23 mmol·g^{-1}. This latter result combined with the presence of a large silicon amount detected by XP spectroscopy rules out the continuous polycondensation of **1** yielding a thick layer of organotin oxopolymers adsorbed onto the silica beads. The data are rather consistent with formation of a 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl thin layer, likely a monolayer, covalently anchored to the silica surface via Si_{bulk}−O−Sn−C linkages, including five- or six-coordinate tin atoms according to the ^{117}Sn NMR chemical shift. The coordination observed likely stems from the existence of dative bonds between the tin atoms and either unreacted silanol and stannol groups or neighboring Sn−O−Sn bridges (Scheme 3) as previously reported in the crystal structures of some organotin clusters.[23,32]

Scheme 3



Furthermore, the trialkynylorganostannane **1** is a much better coupling agent than the organotrichlorotin **3**. This result may be related to the hydrolysis rates of the precursors in neutral conditions which are known to decrease in the order $Sn(OR)_3 > Sn(C{\equiv}C{-}R)_3 \gg SnCl_3$. It is also worthwhile to mention that this order significantly differs from that found in silicon chemistry, which has been reported to be $SiCl_3 > Si(OR)_3 \gg Si(C{\equiv}C{-}R)_3$.[33]

However, the maximum loading of the materials prepared from **1** only represents 66% of that obtained under the same

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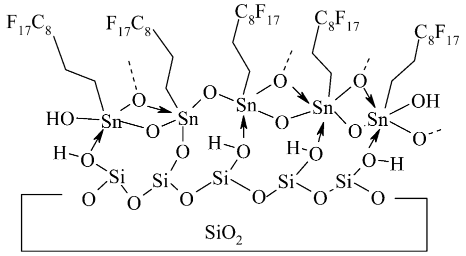
(31) (a) Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, *8*, 1120. (b) Angst, D. L.; Simmons, G. W. *Langmuir* **1991**, *7*, 2236. (c) McGovern, M. E.; Kallury, K. M. R.; Thompson, M. *Langmuir* **1994**, *10*, 3607. (d) Vallant, T.; Kattner, J.; Brunner, H.; Mayer, U.; Hoffmann, H. *Langmuir* **1999**, *15*, 5339. (e) Resch, R.; Grasserbauer, M.; Friedbacher, G.; Vallant, T.; Brunner, H.; Mayer, U.; Hoffmann, H. *Appl. Surf. Sci.* **1999**, *140*, 168.

(32) (a) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (b) Prabusankar, G.; Murugavel, R. *Organometallics* **2004**, *23*, 5644.

(33) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: Boston-San Diego-New York-London-Sydney-Tokyo-Toronto, 1987.

Scheme 4



conditions with the reference compound **2**, whereby a density as high as 2.8 chain•nm^{-2} can be reached. This discrepancy reveals a denser grafted layer in $\mathrm{G}_{\mathbf{2}}^{0.44}$ than in $\mathrm{G}_{\mathbf{1}}^{0.28}$. Indeed, the chain density in $\mathrm{G}_{\mathbf{2}}^{0.44}$ is comparable to those reported for SAMs prepared from alkyltrichlorosilanes, i.e., 4−5 chains•nm^{-2},[7,34] taking into account the difference between the cross-sectional areas of alkyl and fluoroalkyl chains which have been estimated to be 18 and 27 Å^2, respectively. According to the works of Hoffman et al.[31d,e] and on the basis of the role of water in the grafting processes, these different behaviors toward silica might be due to the slower hydrolysis rate of **1** which would favor polycondensation reactions in solution and, therefore, diminish surface reactions. This was confirmed by the results of experiments carried out in the presence of controlled water amounts. Indeed, as the final loading (2.2 chains•nm^{-2}) does not depend on the small water amount introduced, water probably increases the hydrolysis rate of **1,** favoring the surface reactions and, consequently, formation of a denser fluorinated chain layer.

Whatever the molecular precursor used, thermal decomposition of the samples studied clearly occurs in two main steps. A first explanation might be the reaction of organotin fragments with siloxane bridges during the TGA analyses leading to formation $-\mathrm{Si}-(\mathrm{CH_2})_2(\mathrm{CF_2})_7\mathrm{CF_3}$ entities which would decompose at ca. 500 °C. Nonetheless, the ^{29}Si MAS and CP-MAS spectra of samples calcined at 400 °C showed no signal of $\mathrm{O_3Si}-(\mathrm{CH_2})_2(\mathrm{CF_2})_7\mathrm{CF_3}$ sites, which precludes this hypothesis. This thermolytic behavior is therefore more likely due to the presence of different kinds of grafted species. First, the low-temperature decomposition process around 350−400 °C might be related to areas where the layer would be less dense and much more poorly organized, as previously proposed in the case of the surface modification of silica or glass beads with octadecyltrichlorosilane.[29,35] It might be alternatively due to the coexistence of (i) species strongly attached to the silica surface via Si−O−Sn bonds (Scheme 3) and (ii) cross-linked organotin oligomers with noncondensed hydroxyl functionalities which would be weakly anchored to the oxide support (Scheme 4). Furthermore, the reactivity differences between **1** and **2** also affect the thermal stability of the resulting materials. Even though the decomposition processes observed in both cases were very similar, the chemisorbed species in $\mathrm{G}_{\mathbf{2}}^{0.19}$ and $\mathrm{G}_{\mathbf{2}}^{0.44}$ indeed appeared to be more thermally stable than in $\mathrm{G}_{\mathbf{1}}^{0.19}$ and $\mathrm{G}_{\mathbf{1}}^{0.44}$. In addition, for similar loading, $\mathrm{G}_{\mathbf{1}}^{0.19}$ decomposed 50−70 °C earlier than $\mathrm{G}_{\mathbf{2}}^{0.19}$. This difference might be related to a weaker $\mathrm{Si_{bulk}}-\mathrm{O}-\mathrm{Sn}-\mathrm{C}$ attachment in $\mathrm{G}_{\mathbf{1}}^{y}$ compared to the $\mathrm{Si_{bulk}}-\mathrm{O}-\mathrm{Si}-\mathrm{C}$ linkage in $\mathrm{G}_{\mathbf{2}}^{y}$.

Conclusion

Chemical functionalization of silica surfaces has been efficiently achieved thanks to a new precursor molecule (1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)trihex-1-ynyltin(IV). Irreversible chemisorption or grafting of the precursor molecule occurred in solution at room temperature through three hex-1-yne molecules being cleaved off from the tin atom, coupled to the formation of $-\mathrm{Si_{bulk}}-\mathrm{O}-\mathrm{Sn}-\mathrm{C}$ linkages, leading to a fluorinated chain loading as high as 0.28 mmol•g^{-1}, i.e., 1.7 chain•nm^{-2}. The grafting process likely involved prehydrolysis of the precursor in solution prior to reaction of the species formed with the oxide surface. After drying, the resulting modified silica powders are thermally stable up to 350 °C under dry air. Preliminary experiments indicated that this method can be generalized to get fluoroalkyl chain thin layers grafted onto a silicon wafer.[36]

Work is currently in progress to modify nanocrystalline semiconducting oxide with dye-substituted trialkynylorganotins[37] in order to prepare dye-sensitized hybrid materials which could be used in photoelectrochemical solar cells.

Experimental Section

General Procedures, Starting Materials, and Instrumentation. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk lines under a nitrogen atmosphere or under vacuum. Toluene and THF were distilled from sodium benzophenone ketyl prior to use. Dichloromethane and *n*-pentane were distilled over $\mathrm{CaH_2}$. Carbon tetrachloride was distilled over $\mathrm{P_2O_5}$. All solvents were stored over activated 4-Å molecular sieves under a nitrogen atmosphere. Tin tetrachloride (Acros) was distilled under reduced pressure just before use. 1*H*,1*H*,2*H*-Heptadecafluorodec-1-ene (Fluka) and (1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)trichlorosilane, **2** (Gelest), were used as purchased. Tricyclohexyltin hydride was synthesized according to the literature method.[38] The oxide substrates were Biosepra 100 silica (Biosepra) and Kieselgel Merck Type 10181 (Aldrich, 24,217-9) showing BET surface areas of 100 and 675 m^2•g^{-1}, respectively.

Solution NMR analyses were performed on a Bruker AC-250 spectrometer or a Bruker DPX 200 spectrometer. ^{1}H NMR spectra were recorded at 250 MHz, while ^{13}C NMR spectra were obtained at 62.9 MHz. Chemical shifts were referenced internally using the residual nondeuterated protosolvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. Tin-carbon coupling constants (Hz) are given in brackets. Solution ^{119}Sn NMR spectra were recorded at 74.6 MHz (reference $\mathrm{Me_4Sn}$) and solution ^{19}F NMR spectra at 188.3 MHz (reference $\mathrm{CFCl_3}$).

Infrared spectra (KBr pellets or disks) were recorded in the absorption mode using a FTIR Perkin-Elmer spectrophotometer.

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[34] Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

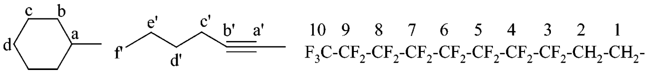
[35] Wang, R.; Wunder, S. L. *Langmuir* **2000**, *16*, 5008.

[36] Compound **1** (10^{-3} M in $\mathrm{CCl_4}$) was reacted with a silicon wafer (Si/$\mathrm{SiO_2}$) overnight at room temperature. After washing a water-repellent surface was obtained: contact angle of water $\theta > 100°$; F/Sn atomic ratio = 16 from XPS data.

[37] Vilaça, G.; Barathieu, K.; Jousseaume, B.; Toupance, T.; Allouchi, H. *Organometallics* **2003**, *22*, 4584.

[38] Jaumier, P. Ph.D. Thesis, University Bordeaux 1, 1997.

Mass spectrometry data were collected with a VG Autospec-Q working in the electronic impact mode. Elemental analyses were carried out in the Centre of Chemical Analysis of the CNRS (Vernaison, France).



(1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl)tricyclohexyltin, 4. In a Schlenk tube a mixture of tricyclohexyltin hydride (7 g, 19 mmol), 1*H*,1*H*,2*H*-heptadecafluorodec-1-ene (10 g, 22.4 mmol), and AIBN (0.4 g, 1.9 mmol) was heated to 110 °C for 24 h. After cooling to room temperature, the white solid was dissolved in petroleum ether (400 mL) and the solution obtained was filtered. After evaporation of the solvent, the residue was recrystallized from absolute ethanol to give the desired compound. Column chromatography (eluent petroleum ether) was necessary to remove trace amount of ethanol and yielded 10.91 g (yield 69.4%) of a white powder. Mp = 83 °C.

^{1}H NMR ($CDCl_3$): δ 0.8 (m, 2H, H_1), 1.2−1.9 (m, 33H, $H_{a,b,c,d}$), 2.2 (m, 2H, H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −5.4 ([220], C_1), 26.3 ([334], C_a), 27.1 ([13], C_d), 28.6 (t, $^2J_{C-F}$ = 24, C_2), 29.2 ([55], C_c), 32.3 ([17], C_b), 110−120 (C_{3-10}). ^{19}F NMR ($CDCl_3$): δ −81.0 (t, ^{3}F, $^3J_{F-F}$ = 13, F_{10}), −115.3 (m, 2F), −115.5 (m, 2F), −121.9 (m, 6F), −122.2 (m, 2F), −126.4 (m, 2F). ^{119}Sn NMR ($CDCl_3$): δ −65.1 (s). IR (KBr pellets) ν (cm^{-1}) = 1243, 1216, 1154, 553, 516. High-resolution MS-EI (*m*/*z*) calcd 815.286203; found 815.286334 (M^+). Anal. Calcd for $C_{28}H_{31}F_{17}Sn$: C, 41.56; H, 3.86; F, 39.91. Found: C, 41.48; H, 3.83; F, 38,72.

(1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl)trichlorotin, 3. To a solution of **2** (9.78 g, 12 mmol) in 30 mL of dry dichloromethane was added slowly tin tetrachloride (3.28 g, 12.6 mmol) under nitrogen. The reaction mixture was then refluxed overnight. After evaporation of the solvent, the residue was extracted for 2 h with a 1:1 mixture of acetonitrile:*n*-pentane (200 mL). The phases were separated under nitrogen, and the acetonitrile solution was extracted with *n*-pentane (3 × 40 mL). Evaporation of the acetonitrile solution gave the trichloride, which was distilled in a Kugelrohr apparatus (bp 100 °C (0.01 mmHg)). A white solid (3.28 g, yield 50%) was thus obtained. Mp 90 °C.

^{1}H NMR ($CDCl_3$): δ 2.3 (t, 9, 2H, H_1), 2.6 (m, 2H, H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.0 (t, $^3J_{C-F}$ = 5, C_1), 26.3 (t, $^2J_{C-F}$ = 23, C_2), 105−123 (C_{3-10}). ^{19}F NMR ($CDCl_3$): δ −81.0 (t, ^{3}F, $^3J_{F-F}$ = 13, F_{10}), −115.3 (m, 2F), −115.5 (m, 2F), −121.9 (m, 6F), −122.2 (m, 2F), −126.4 (m, 2F). ^{119}Sn NMR ($CDCl_3$): δ −2.9 (s). IR (KBr pellets) ν (cm^{-1}) = 1244, 1202, 1151, 516. High-resolution MS-EI (*m*/*z*) calcd 672.207792; found 672.207852 (M^+). Anal. Calcd for $C_{10}H_4F_{17}Sn$: C, 17.87; H, 0.60; F, 48.05; Cl, 15.82; Sn, 17.66. Found: C, 19.19; H, 0.51; F, 46.27; Cl, 15.34; Sn, 17.58.

(1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl)trihex-1-ynyltin, 1. In a three-necked flask under nitrogen, 9.7 mL (24.3 mmol) of 2.5 M butyllithium in hexane was slowly added at 0 °C to a solution of 2.32 g (28.3 mmol) of hex-1-yne in THF (30 mL). After the solution was stirred at room temperature for 15 min, the resulting solution was transferred via cannula to a funnel and added dropwise at −80 °C to 3.8 g (5.65 mmol) of **2** dissolved in THF/toluene (1/1; 30 mL). The mixture was allowed to return to room temperature and then heated at 60 °C for 15 h. After filtration over dried $MgSO_4$ under nitrogen and evaporation of the solvent, the crude product was purified by column chromatography on Florisil (eluent CH_2Cl_2). A yellow oil was thus isolated (3.24 g, 4 mmol). Yield: 71%.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, [7], 9H, $H_{f'}$), 1.3−1.5 (m, 14H, $H_{e',d'}$ and H_1), 2.2 (t, [7], 6H, $H_{c'}$), 2.3 (m, 2H, H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 3.8 (C_1), 13.5 ($C_{f'}$), 19.8 ([8], $C_{c'}$), 21.9 ($C_{e'}$), 27.2 (t, C_2, $^2J_{C-F}$ = 24), 30.5 ([4], $C_{d'}$), 75.7 ([600], $C_{a'}$), 113.2 ([90], $C_{b'}$), 110−130 (C_{3-10}). ^{19}F NMR ($CDCl_3$): δ −81.0 (t, ^{3}F, $^3J_{F-F}$ = 13, F_{10}), −115.3 (m, 2F), −115.5 (m, 2F), −121.9 (m, 6F), −122.2 (m, 2F), −126.4 (m, 2F). ^{119}Sn NMR ($CDCl_3$): δ -242 (tt). IR (KBr pellets) ν (cm^{-1}) = 2161, 1244, 1154, 555, 516. High-resolution MS-EI (*m*/*z*) calcd 809.109805; found 809.109515 (M^+). Anal. Calcd for $C_{28}H_{31}F_{17}Sn$: C, 41.56; H, 3.86; F, 39.91. Found: C, 41.48; H, 3.83; F, 38.72.

Grafting Procedure. Biosepra 100 silica (0.5 g), first dried for 2 h at 200 °C, was reacted with a solution of the precursor molecule (**1**, **2,** or **3**) in CCl_4 (25 mL) prepared in order to introduce coupling agent amounts ranging from 0.2 to 1.23 mmol per gram of silica support. After stirring at a fixed temperature (5, 20, or 60 °C) for various times (2, 7, 17, or 48 h), the reaction mixture was allowed to settle for 4 h. The supernatant was then removed via a cannula, and the resulting powder was washed with CCl_4 (3 × 40 mL) and dried overnight under vacuum at 50 °C. For each experimental condition investigated, three different experiments were conducted in parallel in order to assess the reproducibility.

The amount of chemisorbed fluorinated chain in each sample was determined according to two methods: (i) by careful integration of the CF_2, CF_3 stretching vibration bands (1243, 1215, and 1153 cm^{-1}) observed in the solution IR absorption spectra (recorded by using a universal liquid IR cell OMNICELL purchased from Eurolabo) of the grafting solution before and after reaction; (ii) by elemental analysis. Similarly, the amount of *n*-hex-1-yne released was estimated by careful integration of the C_{sp}−H stretching vibration band (3314 cm^{-1}) observed in the solution IR absorption spectrum recorded after reaction. The integration value obtained was calibrated against the one of a *n*-hex-1-yne solution in CCl_4 of known concentration.

$G_1^{0.19}$: XPS data (at %) F, 22.4; C, 17.1; O, 39.7; Si, 19.4; Sn, 1.3.

Anal. Calcd for 0.19 mmol·g^{-1}: Sn, 2.0; C, 2.1; F, 5.6. Found: Sn, 2.0; C, 2.5; F, 6.2.

$G_1^{0.28}$: XPS data (at %) F, 25.5; C, 15.7; O, 38.4; Si, 18.6; Sn, 1.8.

Anal. Calcd for 0.28 mmol·g^{-1}: Sn, 2.9; C, 2.9; F, 7.8. Found: Sn, 2.8; C, 3.7; F, 8.8.

$G_2^{0.19}$: XPS data (at %) F, 24.3; C, 14.3; O, 41.9; Si, 19.5.

Anal. Calcd for 0.19 mmol·g^{-1}: C, 2.3; F, 6.1. Found: C, 3.7; F, 8.8

$G_2^{0.44}$: Anal. Calcd for 0.44 mmol·g^{-1}: C, 4.7; F, 12.6. Found: C, 5.5; F, 13.0.

Multinuclear Solid-State NMR Studies. Solid-state NMR measurements were carried out on a Bruker Avance 250 spectrometer operating at 62.90, 89.12, and 49.70 MHz for ^{13}C, ^{117}Sn, and ^{29}Si, respectively. Chemical shifts were referenced to external adamantane, also used to establish the Hartmann−Hahn conditions, for ^{13}C (38.56 ppm with respect to TMS), tetracyclohexyltin for ^{117}Sn (−97.35 ppm with respect to $(CH_3)_4Sn$), and tetramethylsilane in $CDCl_3$ solution (0 ppm) for the ^{29}Si nuclei. Standard ZrO_2 rotors (7 mm) were used, and spinning rates were between 4000 and 5000 Hz. Typically a contact time of 2 ms, a relaxation delay of 2, and 30 000 scans were used for ^{117}Sn CP-MAS, while ^{13}C CP-MAS spectra were recorded with a 1.5 ms contact time, a relaxation delay of 4, and 2000 scans. MAS ^{29}Si spectra were recorded with a relaxation delay of 5 s and 2000 scans, while CP-MAS spectra were recorded with contact times varying from 2 to 8 ms and 2000 scans. The Hartmann−Hahn condition for ^{1}H−^{29}Si cross-polarization was set on kaolinite.[39] The ^{29}Si spectra were deconvoluted by total-line-shape (TLS)[40] fitting using PERCH software.[25]

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[39] Rocha, J.; Klinowski, J. *J. Magn. Reson.* **1990**, *90*, 567.

X-ray Photoelectron Spectroscopic Studies. XPS spectra were recorded with a 220i-XL ESCALAB from VG. Powders were pressed onto indium foils and put under UHV to reach the 10^{-8} Pa range. The nonmonochromatized Mg X-ray source was used at 200 W as well as a flood gun to compensate for the nonconductive samples. The spectra were calibrated in relation to the C1s binding energy (284.6 eV), which was applied as an internal standard. Fitting of the high-resolution spectra were provided through the ECLIPSE program from VG.

TGA-MS Studies. Thermal analyses were carried out on a Netzsch STA simultaneous analyzer. Thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses were recorded in the range 50−650 °C under air or helium flow at a heating rate of 10 $°C \cdot min^{-1}$. Mass analyses were performed on a Thermostar Balzers Instruments quadrupole spectrometer. Powder samples were placed in alumina crucibles. Electron impact mass spectra (70 eV) were continuously recorded and stored with scans from 3 to 300 amu. Each scan was recorded in 0.5 s with a delay time of 0.1 s.

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Supporting Information Available: Figures of XPS survey and thermogravimetric (under air) analyses of the modified silica powders. This material is available free of charge via the Internet at http://pubs.acs.org.

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