Functionalized Silanes for the Preparation of Siloxane-Anchored Monolayers[†]

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Siloxane-anchored monolayer films are best prepared by the self-assembly of trichlorosilanes. The moisture sensitivity and chemical reactivity of the trichlorosilane moiety complicates the synthesis and purification of the ω-functionalized alkyltrichlorosilanes that are the building blocks for functionalized monolayer surfaces. Obtaining these materials is facilitated by using trialkoxysilanes as synthetic intermediates. They offer superior stability with respect to various synthetic operations. This allows the flexibility to incorporate the silane functionality at various stages of a multistep synthesis. This relative stability has also allowed us to develop a general approach to their purification by chromatography (using $Si(OCH_3)_4$ as an additive), making them useful in removing undesired side products. Ultimately, the usefulness of the alkoxysilanes is also evidenced in the ease with which they can be converted into the trichlorosilanes, as needed for monolayer self-assembly. Trichloroacetyl chloride has proven to be the optimal reagent for this transformation.

Introduction

The past 20 years have seen growing interest[1] in self-assembled monolayers (SAMs) as uniformly structured surfaces offering a rich testing ground for developing new tools for probing surface structure and as informative models for surface organization phenomena. The incorporation of chemical functionality distal to the monolayer anchoring sites allows for systematic variation of the chemical and physical properties of the exposed SAM surface and makes the SAMs into powerful tools for controlled surface modification by providing uniform surfaces with particular charge or reactivity. Schematic treatment of SAM-forming monomers highlights three domains: a terminal functional group which ultimately defines the exposed surface functionality, a hydrocarbon chain (typically polymethylene) to promote monolayer packing and organization, and an anchoring group responsible for the specific chemical interactions with the substrate.

Among the various anchoring group chemistries available, the relatively robust nature of siloxane-anchored SAMs and their convenient attachment to a wide range of hydroxyl- and/or oxide-bearing surfaces makes them particularly attractive for surface modification in a variety of applications. Such systems are mostly based on molecules where the anchoring group is a silicon atom with electronegative ligands, typically halides and/or alkoxides, and most favorably three such groups. To facilitate the formation of true monolayers, two additional constraints apply: (a) the interchain packing of polymethylene chains of 11 carbons or more promotes the formation of close-packed monolayers;[2] (b) the use of the halosilanes (typically $SiCl_3$) rather than alkoxysilanes also increases the likelihood of monolayer rather than multilayer formation.[3]

The synthesis of the requisite long-chain alkyl trichlorosilanes most often involves installing the $SiCl_3$ group as the last step, because of its incompatibility with further synthetic manipulation. Silane incorporation is done either by hydrosilylation (using $HSiCl_3$) of a terminal olefin or by Grignard reaction of an alkyl halide with $SiCl_4$. Thus, any such synthesis will be problematic if other functionality in the molecule is incompatible with these procedures, or if the silane incorporation step produces a mixture of products requiring purification other than simple distillation (e.g., chromatography).

We have developed an approach that has allowed us to successfully synthesize pure samples of functionalized trichlorosilanes (**1**) that would otherwise be inaccessible.
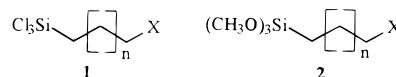
It involves using a $Si(OCH_3)_3$ moiety as a masked form of the $SiCl_3$ group, performing all necessary synthetic and chromatographic manipulations, and then replacing $Si(OCH_3)_3$ with $SiCl_3$. The advantage of the trimethoxy material (**2**) lies in its stability relative to the $SiCl_3$ analogue. This allows it to withstand the reaction conditions required for many chemical transformations. It has also allowed us to develop an effective general procedure for chromatographic purification of these materials. We report herein: (1) effective procedures for installing the $Si(OCH_3)_3$ unit and for its conversion into $SiCl_3$, (2) a sampling of reactions which manipulate the X group at the remote molecular terminus and yet are tolerated by the $Si(OCH_3)_3$ moiety, and (3) an effective method for the chromatographic purification of compounds **2** so as to ultimately provide pure samples of the corresponding trichlorosilanes (**1**).

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(1) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: London, 1991.

(2) Jin, Z. H.; Vezenov, D. V.; Lee, Y. W.; Zull, J. E.; Sukenik, C. N.; Savinell, R. F. *Langmuir* **1994,** *10,* 2662−2671.

(3) See for example: (a) Tsukruk, V.; Luzinov, I.; Julthongpiput, D. *Langmuir* **1999,** *15,* 3029−3032; (b) Dunaway, D.; McCaley, R. L. *Langmuir* **1994,** *10,* 3598−3606; (c) Kurth, D. G.; Bein, T. *Langmuir* **1993,** *9,* 2965−2973.

Results

Installation of Si(OCH$_3$)$_3$ groups is achieved by treating an alkyltrichlorosilane with methanol (in NEt$_3$/CH$_2$Cl$_2$), conditions that do not allow for acid build up in a way that could adversely affect the alkoxysilane or other sensitive functionality. Alternatively, hydrosilylation of an alkene (typically a terminal olefin) with HSi(OCH$_3$)$_3$ is typically done using chloroplatinic acid as a catalyst. Though this is often a clean reaction, a common side reaction in this process involves reduction wherein the silane acts as a hydride donor.[4]

Reactions 1−3 (below) show a sampling of reactions that we have successfully performed in the presence of a Si(OCH$_3$)$_3$ group.[5] Neither the active metal nor the ZnBr$_2$ byproduct harm the silane (reaction 1); so too for the heterogeneous reductive amination in reaction 3. Reaction 2 allowed us to circumvent the decomposition of the dimethylphosphonate group when subjected to hydrosilylation using HSiCl$_3$ and its instability to Grignard conditions which precluded silane incorporation by that route.
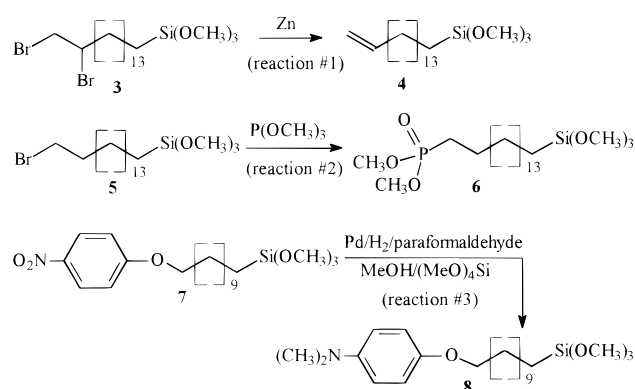
Silica gel chromatography of trichlorosilanes (**1**) is impossible and even with trimethoxysilanes (**2**) material recovery is problematic. However, for **2**, this can be dramatically improved by adding 0.5−1.0% (CH$_3$O)$_4$Si to the eluting solvent. The impact of this additive on the chromatographic separation is usually modest, whereas, if the (CH$_3$O)$_4$Si is not added, a 40−60% reduction in material recovery (depending on the scale) is to be expected. This chromatographic approach was successfully tested on compounds **3**−**8** and it permitted the successful synthesis of trichlorosilane **11** by the two steps shown below. This takes advantage of the chromatography of **10** to obtain a pure product.
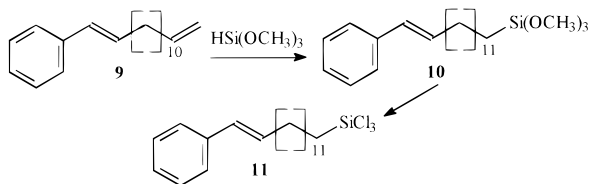
The conversion of Si(OCH$_3$)$_3$ units into SiCl$_3$ units is well-precedented in the literature and has been achieved with a wide range of chloride-containing electrophiles.[6]

(4) (a) Keinan, E.; Greenspoon, N. *Isr. J. Chem.* **1984**, *24*, 82−87; (b)Lukevich, E. *Russ. Chem. Rev.* **1977**, *46*, 264−269.

(5) A related reference where Si(OCH$_3$)$_3$ is shown to be stable to the hydrolysis of an imide with hydrazine and to the reductive removal of a trityl group is: Effenberger, F.; Heid, S. *Synthesis* **1995**, 1126−1130.

(6) Eaborn, E. *Organosilicon Compounds*; Butterworths: London, 1960; Weber, P. W. *Silicon Reagent for Organic Synthesis*; Springer-Verlag: Berlin/Heidelberg/New York, 1983.

These reagents differ greatly in their reactivity (ranging from reaction in minutes at room temperature to reactions requiring days at elevated temperatures). They also vary in the kinds of side products produced and how they can be removed. We have found that trichloroacetyl chloride (CCl$_3$COCl, neat, 70−100 °C) is superior to reagents previously reported. It is sufficiently reactive so as to give trichlorosilanes (**1**) in good yield, but it is not so active an electrophile so as to attack other functionalities (including very electron-rich aromatic rings (e.g., **8**)). Moreover, its reactions are easy to purify. Typically, the SiCl$_3$ compounds (**1**) produced in this way require only evaporation of unreacted CCl$_3$COCl and of the CCl$_3$-COOCH$_3$ byproduct.

Discussion

The challenge in obtaining clean samples of trichlorosilanes (**1**) stems from a number of sources. The instability of the trichlorosilyl group dictates its installation at the end of a synthesis and prevents its purification by chromatography. Since both Grignard and hydrosilylation reactions are prone to yield side products (e.g., from unwanted reduction processes, among others), the inability to purify the silane product is serious, particularly when trying to achieve the high purity needed to guarantee uniform monolayer composition. Also, synthetic transformations with incomplete selectivity (such as the process used to make **11**, above) demand the removal of other reaction components.

With respect to these considerations, trialkoxysilanes (**2**) offer significant advantages in allowing chromatographic purification. The addition of a small amount of Si(OCH$_3$)$_4$ to passivate the silica gel greatly improves material recovery without severely harming chromatographic effectiveness. The amenability of the alkoxy compounds to chromatography is consistent with the observation that whereas RSiCl$_3$ compounds do not move at all on silica gel TLC plates, the corresponding RSi-(OCH$_3$)$_3$ materials elute normally. Initial attempts at preparative silica gel chromatography of compounds **2** were disappointing in that while pure material could be obtained, material recovery was very poor. The idea of using Si(OCH$_3$)$_4$ arose when we observed particularly good material recovery in isolating compound **8**. The Si(OCH$_3$)$_4$ that had been added to the reductive amination to prevent hydrolysis of **8** was shown to be responsible and a general method was developed. Specifically, adding Si(OCH$_3$)$_4$ to the chromatography solvent protects the alkyltrialkoxysilanes from adventitious hydrolysis while it passivates the chromatographic support.

Another application for the chromatographic purification of compounds **2** is their use in the recovery of partially polymerized and/or decomposed samples of trichlorosilanes (**1**). Effective recovery is achieved by reacting the crude chlorosilane mixture with methanol (to yield impure **2**), followed by chromatography and then conversion back into pure trichlorosilane (**1**).

The other feature of compounds **2** is their resilience in the face of a wide range of reaction conditions. The reduction of a 1,2-dihalide with zinc (used to convert **3** into **4**), the Arbuzov reaction used to make phosphonate **6**, and the reductive amination that produced **8**, are all good examples of the usefulness of this stability. In a slightly different, but complementary fashion, the synthesis of **10** and/or **11** relies on the selective hydrosilylation of a terminal olefin in the presence of a styrenyl unit. This selectivity is enhanced by doing the hydrosilylation under the mild conditions described in the Experimental Section.

However, obtaining pure material is only possible with chromatography; the ability to chromatograph **10** is the key.

Ultimately, the usefulness of compounds **2** also depends on having effective routes by which they can be converted into compounds **1**. There are many reagents capable of this transformation. The advantages of Cl₃CCOCl have been described above. We have sampled five of the reagents described in the literature[7] and found them wanting. The less active reagents (SiCl₄, CH₃COCl, and ClCOCOCl) all were reacted for 3−4 days at 70 °C and gave incomplete conversion (50−80%) as well as some mixed chloroalkoxy silane products which were difficult to completely remove. The more reactive reagents (PCl₅ and SOCl₂) were effective at room temperature but evidenced problems in the purification of the silane product and were also aggressive enough electrophiles so as to be incompatible with other sensitive functionality in the molecule (e.g., **8**). The inert, easy-to-remove nature of the Cl₃CCO₂CH₃ side product, along with the cost-effectiveness and relative convenience of the Cl₃CCOCl (70−100 °C; 2−3 days), combine to recommend it as the best reagent for this purpose.

Conclusion

We have reported the use of trimethoxysilyl units as masked trichlorosilyl moieties permitting synthetic manipulations and chromatography that facilitate the synthesis and purification of the alkyltrichlorosilanes that are the key to functionalized siloxane-anchored monolayer formation. It has long been recognized that siloxane-anchored SAMs are particularly robust, but the preparative difficulties associated with the silanes have been a major impediment to their widespread use. Implementation of the methodologies described herein should change this situation by making the pure trichlorosilane monomers more readily accessible.

Experimental Section

Materials. All reagents and solvents were obtained (unless otherwise specified) from Aldrich Chemical Co. and used as is. Water was deionized and then distilled in an all glass apparatus. CH₂Cl₂ was dried by distillation under N₂ from P₂O₅. CH₃OH was dried by distillation under N₂ from magnesium turnings. Et₃N was dried by distillation from CaH₂. THF was dried by distillation under N₂ from Na/benzophenone.

Methods. NMR spectra were recorded on a Bruker DPX 300 Spectrometer (units δ, ppm; referenced to TMS for ¹H-NMR and to CDCl₃ for ¹³C-NMR) in CDCl₃ solvent. Mass spectra were recorded on a Finnigan model 400 using CI with methane as the reagent gas. Distillation conditions are reported as the pot-temperature of the Kugelrohr oven. Column chromatography used silica gel 60 (230−400 mesh) and was done under a positive pressure of nitrogen. *Caution*: Addition of Si(OCH₃)₄ to the chromatography solvent and its removal by evaporation both demanded particular care because of its toxicity and potential hazards (including possible blindness). Similar care was exercised in the use of SiH(OCH₃)₃.

Syntheses. *General Procedures for RSiCl₃/RSi(OCH₃)₃ Interconversion; R = C₁₈H₃₇;* **1** *and* **2**, *n = 15, X = CH₃. From* **1** *to* **2**: Into a dry 250-mL flask equipped with a pressure-equalized addition funnel, a magnetic stirring bar, and a N₂ inlet were placed 2 g (5.18 mmol) of octadecyltrichlorosilane and 10 mL of dry CH₂Cl₂. The solution was cooled to 0 °C. The funnel was

charged with 10 mL of dry CH₃OH, 5 mL of dry Et₃N, and 10 mL of dry CH₂Cl₂, which was added to the flask, dropwise, over 20 min. The reaction mixture was stirred for an additional 3 h as the solid ammonium salt formed. The resulting mixture was evaporated to dryness under N₂ and 25 mL of hexane was added. The resulting slurry was filtered and the clear solution was evaporated to give the crude trialkoxysilane product which was purified by chromatography (silica gel; hexane/diethyl ether/Si(OCH₃)₄ 100:15:1): yield 1.61 g (72%). This material was identical, by ¹H-NMR, to the known material.[8a]

From **2** *to* **1**: Into a 20-mL pressure tube containing a magnetic stirring bar were placed octadecyltrimethoxysilane (582 mg, 1.56 mmol) and 10 mL of freshly distilled Cl₃CCOCl (*Lachrymator*). The tube was sealed, placed in an oil bath maintained at 100 °C and heated for 48 h (or 3 days at 70 °C). The progress of the reaction was monitored by ¹H-NMR, that is, disappearance of OCH₃ at 3.6 ppm and of CH₂Si at 0.65 ppm, and the appearance at 3.9 ppm of methyl trichloroacetate. Removal of volatiles at reduced pressure produced a clear liquid product: yield 0.54 g (90%). This material was identical, by ¹H-NMR, to the known material.[8b]

*1,2-Dibromo-16-(trimethoxy)hexadecane (***3***).* Compound **3** was prepared in 4 steps. A flame-dried three-neck 100-mL flask, equipped with a pressure-equalizing addition funnel, a reflux condenser with a N₂ inlet, and a magnetic stirring bar, was charged with Mg turnings (5 g, 208 mmol). The addition funnel was charged with a solution of ω-undecenyl bromide (6 g, 25.9 mmol)[9] in 30 mL of dry THF. A portion of this solution (5 mL) was added to the flask, and it was gently warmed. Once Grignard formation began, the rest of the solution was added over a period of 30 min, followed by an additional 1 h of reflux, while Grignard formation was monitored by TLC (silica gel/hexane). The solution was then cooled to room temperature. To another two-neck 250-mL flame-dried flask, fitted with a pressure-equalizing addition funnel, magnetic stirring bar, and N₂ inlet, was added 100 mL of THF and 5-bromo-1-pentene (6.0 g, 40.3 mmol). This solution was cooled in an ice/salt bath to −10 °C The Grignard reagent from the first flask was transferred to the addition funnel by syringe. It was then added dropwise to the flask. A solution of LiCl (170 mg) and CuCl₂ (270 mg) in THF (10 mL) was then added to the reaction flask. The resulting mixture was stirred at −10 °C for 12 h. Ether (150 mL) was added to the flask, and the entire contents were transferred to a separatory funnel. The organic solution was washed twice with saturated aqueous NH₄Cl and once with saturated aqueous NaCl, dried over MgSO₄, and concentrated on a rotovap. After distillation (120 °C, 0.3 mm), pure 1,15-hexadecadiene (3.5 g, 61%) was obtained. This material was identical, by ¹H-NMR, to that reported in the literature.[10] Observed ¹H-NMR δ: 1.2−1.34 (m, 20H), 1.94−2.0 (m, 4H), 4.85−4.95 (m, 4H), 5.71−5.80 (m, 2H).

In a dry 500-mL two-neck round-bottom flask equipped with a magnetic stirring bar was placed 1,15-hexadecadiene (5.0 g, 22.5 mmol) and 300 mL of CCl₄. The solution was cooled in an ice/salt bath to 0 °C. To this was added a solution of Br₂ (3.2 g, 20 mmol) and 100 mL of CCl₄ by a syringe pump over 4 h. The reaction mixture was then stirred for an additional 2 h. The resulting solution was concentrated to yield a mixture (8 g) of product, starting material, and doubly brominated diene. Purification by chromatography (silica gel/hexane) yielded the following: starting material (1.5 g) and 1,2,15,16-tetrabromo-hexadecane (1.5 g) along with the desired 1,2-dibromo-15-hexadecene (3.5 g, 41%): ¹H-NMR δ: 1.21−1.36 (m, 20H), 1.70−1.73 (m, 1H), 1.94−2.01 (m, 3H), 3.53−3.60 (m, 1H), 3.64 (t, *J* = 10 Hz, 1H), 3.81−3.89 (dd, *J* = 10, *J* = 4.5 Hz, 1H), 4.09−4.10 (m, 1H), 4.84−4.96 (m, 2H), 5.74−5.80 (m, 1H).

In a 20-mL pressure tube containing a magnetic stirring bar were placed 1,2-dibromo-16-hexadecene (3 g, 7.85 mmol), HSiCl₃ (4 mL), and 0.15 mL of a 4% solution of H₂PtCl₆·6H₂O in *i*-PrOH. These reagents were all manipulated in a nitrogen atmosphere. The tube was placed in an oil bath maintained at 60 °C and heated for 24 h. The progress of the reaction was monitored by

(7) (a) CH₃COCl: Ladenburg, A. *Liebigs Ann.* **1872**, *164*, 300; (b) ClCOCOCl: Gerrard, W.; Kilburn, K. D. *J. Chem. Soc.* **1956**, 1536; (c) SiCl₄: Eaborn, C. *J. Chem. Soc.* **1949**, 2755; (d) PCl₅: Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509; (e) SOCl₂: McGregor, R. R.; Warrick, E. L. U. C. Patent Chem. Abstr. 40 592, 1946; and Frohn, H. J.; Giesen, M.; Klose, A.; Lewin, A.; Bardin, V. V. *Organomet. Chem.* **1996**, *506*, 155−164.

(8) Aldrich Library of NMR Spectrum: (a) 1(3), 665 C; (b) 1(3), 651 C.

(9) Balachander, N.; Sukenik, C. N. *Langmuir* **1990**, *6*, 1621.

(10) Schlosser, M.; Bossert, H. *Tetrahedron* **1991**, *47*, 6287−6292.

following the disappearance of olefinic protons by ^{1}H-NMR. After the reaction was complete, the contents of the tube were transferred (under N$_2$) to a 50-mL round-bottom flask. Excess HSiCl$_3$ was removed by evaporation and crude 1,2-dibromo-16-(trichlorosilyl)hexadecane (3 g), suitable for conversion to **3**, was obtained. The SiCl$_3$ material (2 g, 4.33 mmol) was converted to the Si(OCH$_3$)$_3$ material (**3**) by using the standard methanol/Et$_3$N/CH$_2$Cl$_2$ procedure (above): yield 1.6 g (73%). ^{1}H-NMR δ: 0.65 (t, J = 7.7 Hz, 2H), 1.26–1.796 (m, 24H), 2.109 (m, 1H), 2.127 (m, 1H), 3.57 (s, 9H), 3.56–3.63 (t, J = 10 Hz,1H), 3.82–3.87 (dd, J = 10 Hz, J = 4.5 Hz, 1H), (m, 1H), 4.17–4.18 (m, 1H). The crude material was suitable for debromination to **4**.

16-(Trimethoxysilyl)-1-hexadecene (4). In a dry 250-mL round-bottom flask equipped with a magnetic stirring bar and a reflux condenser were placed 10 mL of THF, 20 mL of methanol, and activated Zn (6 g, 92.3 mmol). To this was added **3** (1.5 g, 2.98 mmol), and the mixture was heated at reflux while the progress of the reaction was monitored by TLC (silica gel/hexane). After 3 h, the reaction mixture was cooled and concentrated under nitrogen. Hexane (100 mL) was added and the slurry was filtered under nitrogen. The solvent was removed on a rotovap. The crude product was purified by Kugelrohr distillation (180 °C, 0.05 mm): yield 0.6 g (59%). ^{1}H-NMR δ: 0.65 (t, J = 7.7 Hz, 2H), 1.25 (m, 24 H), 2.02 (m, 2H), 3.57 (s, 9H), 4.94 (m, 2H), 5.80 (m, 1H).

Compound **4** (0.5 g, 1.74 mmol) was converted into its SiCl$_3$ analogue (**1**, n = 12; X = CH=CH$_2$) by the Cl$_3$CCOCl procedure (above). It was isolated by Kugelrohr distillation (160 °C, 0.05 mm): yield 0.2 g (32%). This material was identical to that reported in the literature[5,11] which was obtained by Grignard reaction with SiCl$_4$. Observed ^{1}H-NMR δ: 5.78–5.87 (m, 1H), 4.92–5.04 (m, 2H), 2.01–2.06 (m, 2H), 1.28–1.6 (m, 26H).

1-Bromo-16-(trimethoxysilyl)hexadecane (5). Compound **5** was prepared from 1-bromo-16-(trichlorosilyl)hexadecane (2 g, 6 mmol)[5,11] using the methanol/Et$_3$N/CH$_2$Cl$_2$ procedure (above): yield 1.2 g (61%). ^{1}H-NMR δ: 0.65 (t, J = 7.7 Hz, 2H), 1.25–1.4 (m. 26H), 1.85 (m, 2H), 3.56 (s, 9H), 3.4 (t, J = 7 Hz, 2H). Crude product was suitable for preparing **6**.

1-(Dimethylphosphonate)-16-(trimethoxysilyl)hexadecane (6). In a dry 100-mL two-neck round-bottom flask equipped with an N$_2$ inlet, magnetic stirring bar, and a reflux condenser was placed **5** (2 g, 3.97 mmol) and trimethylphosphite (5 g, 40.3 mmol). The reaction was heated (130 °C, 24 h) under a stream of nitrogen. Excess trimethylphosphite was evaporated and the crude product was purified by Kugelrohr distillation (200 °C, 0.09 mm): yield 1.6 g (79%). ^{1}H-NMR δ: 0.65 (t, J = 7.7 Hz, 2H), 1.2–1.8 (m, 30H), 3.6 (s, 9H), 3.7–3.8 (d, J = 10.8 Hz, 6H).

1-p-Nitrophenoxy-11-(trimethoxysilyl)undecane (7). Compound **7** was obtained in two steps. Into a dry 500-mL flask equipped with a magnetic stirring bar, a reflux condenser, and a drying tube were placed 300 mL of acetone and ω-undecenyl mesylate[9] (14.13 g, 57 mmol) and potassium carbonate (7.9 g, 57 mmol) and *p*-nitrophenol (7.91 g, 57 mmol). The reaction was heated at reflux for 3 days and monitored by TLC (hexane:ethyl acetate 90:10). It was cooled to room temperature and concentrated on a rotovap. Ether was added and the solution was transferred to a separatory funnel, where it was washed with cold water, 5% NaOH and saturated aqueous NaCl. The solution was then dried with MgSO$_4$, filtered, and concentrated on a rotovap. The ω-undecenyl *p*-nitrophenyl ether was obtained as a yellow solid and purified by chromatography (silica gel/hexane:ethyl acetate 90:10): yield 11.12 g (67%). ^{1}H-NMR δ: 8.09 and 6.86 (AA'XX' system, 4H), 3.96 (t, J = 6.5 Hz, 2H), 1.74 (m, 2H), 2.04 (m, 2H), 1.32–1.47 (m, 12H), 4.92–5.04 (m, 2H), 5.8–5.92 (m, 1H). ^{13}C-NMR δ: 114.17; 139.18; 33.8; 29.17; 29.399; 29.293; 29.1; 28.97; 28.92; 25.91; 68.9; 164.26; 114.4 (2C); 125.92 (2C); 141.33.

In a 20-mL pressure tube containing a magnetic stirring bar were placed ω-undecenyl *p*-nitrophenyl ether (2.97 g, 10.2 mmol), HSi(OCH$_3$)$_3$ (10 mL), and 0.15 mL of a 4% solution of H$_2$PtCl$_6$·6H$_2$O in *i*-PrOH. These reagents were all manipulated in a nitrogen atmosphere. The tube was heated in an oil bath maintained at 60 °C for 72 h. The progress of the reaction was

monitored by the disappearance of an olefinic proton by ^{1}H-NMR. After the reaction was completed, the contents of the tube were transferred to a 50-mL round-bottom flask and excess HSi(OCH$_3$)$_3$ was evaporated under nitrogen. The product (**7**) was used without further purification: yield 3.91 g (88%). ^{1}H-NMR δ: 8.09 and 6.86 (AA'XX' system, 4H), 3.96 (t, J = 6.5 Hz, 2H), 3.48 (s, 9H), 1.75 (q, J = 6.6 Hz, 2H), 1.38–1.20 (m, 16H), 0.56 (t, J = 7.7 Hz, 2H). ^{13}C-NMR δ: 50.3 (3C); 9.01; 22.46; 32.98; 29.42; 29.37; 29.34; 29.17; 29.1; 28.83; 25.77; 68.75; 164.13; 114.25 (2C); 125.71 (2C); 141.13.

1-(p-Dimethylaminophenoxy)-11-(trimethoxysilyl)undecane (8). Into a dry 100-mL flask equipped with a magnetic stirring bar were placed 1-(*p*-nitrophenoxy)-11-(trimethoxysilyl)undecane (3.9 g, 9 mmol), CH$_3$OH (30 mL), Si(OCH$_3$)$_4$ (10 mL), *p*-formaldehyde (0.92 g, 28 mmol), and Pd 10% activated on carbon (2.01 g). The flask was evacuated (to 10 mm) and its atmosphere was replaced with nitrogen. It was then evacuated again and filled with hydrogen at atmospheric pressure by a plastic balloon. This evacuation/H2-fill procedure was repeated three times. The reaction mixture was then stirred for 36 h during which the hydrogen-filled balloon maintained a hydrogen atmosphere over the reaction. The resulting mixture was filtered under nitrogen and the filtrate was concentrated. The crude product was purified by chromatography (silica gel/hexane:diethyl ether 3:1): yield 1.1 g (30%). MS *m/e* 411 (calcd.), 411.280 (found). ^{1}H-NMR δ: 6.83 (d, J = 9.3 Hz, 2H), 6.73 (d, J = 9.2 Hz, 2H), 3.9 (t, J = 6.6 Hz, 2H), 3.57 (s, 9H), 2.86 (s, 6H), 1.74 (q, J = 6.7 Hz, 2H), 1.27–1.5 (m, 16H), 0.65 (t, J = 7.7 Hz, 2H). ^{13}C-NMR δ: 50.42 (3C); 10.8; 22.54; 33.09; 29.54; 29.45; 29.41; 29.39; 29.2; 26.03; 68.62; 151.56; 115.4 (2C); 114.93 (2C); 145.51.

Compound **8** (200 mg, 486.6 mmol) was converted into its SiCl$_3$ analogue using the Cl$_3$CCOCl procedure (above). Excess Cl$_3$CCOCl was removed by evaporation and 1-(*p*-dimethylaminophenoxy)-11-(trichlorosilyl)undecane (as its HCl salt) was washed (under nitrogen) with three 10-mL portions of hexane. ^{1}H-NMR δ: 7.59 (d, J = 9.14 Hz, 2H), 6.88 (d, J = 9.1 Hz, 2H), 3.89 (t, J = 6.45 Hz, 2H), 3.95 (d, J = 4.39 Hz, 6H), 1.7 (m,2H), 1.56–1.1 (m, 18H).

ω−Undecenyl Cinnamyl (9). A flame-dried three-neck 250-mL flask equipped with a pressure-equalizing additional funnel, a reflux condenser with a nitrogen inlet, and a magnetic stirring bar was charged with Mg turnings (3.85 g, 160 mmol). The addition funnel was charged with a solution of undecenyl bromide (5.05 g, 21.8 mmol) in 30 mL of dry THF. A portion of this solution (10 mL) was added to the flask, and it was gently warmed. Once Grignard formation began, the rest of the solution was added over a period of 30 min. After the contents of the flask were heated at reflux for an additional 2 h, the reaction was shown to be complete by TLC (silica gel/hexane). The resulting solution was cooled to room temperature. To another two-neck 500-mL flame-dried flask, fitted with a pressure-equalizing additional funnel, magnetic stirring bar, and nitrogen inlet was added 100 mL of dry THF and cinnamyl chloride (4.47 g, 29 mmol). This solution was cooled in an ice/salt bath to −20 °C. The Grignard reagent from the first flask was transferred to the addition funnel by syringe. It was then added to the flask. A solution of 170 mg of LiCl, 270 mg of CuCl$_2$, and 10 mL of THF was added to the reaction flask (the solution was a green color). The resulting mixture was stirred at −20 °C overnight. Ether (100 mL) was added to the flask, and the entire contents were transferred to a separatory funnel. The organic solution was washed twice with saturated aqueous NH$_4$Cl and once with saturated aqueous NaCl, dried over MgSO$_4$, and concentrated on a rotovap. The crude product was purified by chromatography (silica gel/hexane): yield 2.35 g (40%). ^{1}H-NMR δ: 1.24–1.48 (m, 16H), 2.2–2.05 (m, 2H), 2.16–2.23 (m, 2H), 4.9–5.0 (m, 2H), 5.8–5.82 (m, 1H), 6.24–6.34 (m, 2H), 7.17–7.34 (m, 4H). ^{13}C-NMR δ: 114.15; 139.28; 35.5; 33.88; 29.6; 29.58; 29.45; 29.29; 29.22; 29.01; 129.75; 126.78; 138; 125.95 (2C); 128.44 (2C); 127.63.

11-(Trimethoxysilyl)-undecenyl-cinnamyl (10). In a 20-mL pressure tube containing a magnetic stirring bar were placed ω-undecenyl cinnamyl (1.014 g, 3.75 mmol), 1.5 mL of HSi(OMe)$_3$, 10 mL of CCl$_4$, and 0.15 mL of a 4% solution of H$_2$PtCl$_6$·6H$_2$O in *i*-PrOH. These reagents were all manipulated in a nitrogen atmosphere. The reaction mixture was stirred at 60 °C for 18 h. After the reaction was complete, the contents of the tube were

(11) (a) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *99*, 235; (b) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.

transferred to a 50-mL round-bottom flask and excess $HSi(OMe)_3$ was distilled off. A portion of the crude product (250 mg) was purified by chromatography (silica gel/hexane:diethyl ether:Si-$(OCH_3)_4$ 100:15:1): yield 130 mg. ^{1}H-NMR δ: 0.65 (t, $J = 7.7$ Hz, 2H), 1.26–1.46 (m, 20H), 2.18–2.2 (m, 2H), 3.56 (s, 9H), 6.19–6.34 (m, 2H), 7.18–7.35 (m, 5H).

*11-(Trichlorosilyl)-undecenyl-cinnamyl (**11**).* Compound **11** was prepared from **10** (100 mg) by the standard Cl_3CCOCl procedure (above); excess reagent and byproducts were evaporated and the product was analyzed by ^{1}H-NMR δ: 1.3–1.6 (m, 20H), 2.2–2.24 (m, 2H), 6.23–6.43 (m, 2H), 7.2–7.39 (m, 5H).