DOI: 10.1002/ejoc.201000151

Grafting Organic n-Semiconductors to Surfaces: (Perfluoro-*p*-terphenyl-4-yl)alkanethiols

Björn Schüpbach,[a] Michael Bolte,[a] Michael Zharnikov,[b] and Andreas Terfort*[a]

Keywords: Aromatic substitution / Helical structures / Monolayers / Nucleophilic substitution / Perfluoroarene / Self-assembly

Perfluoroterphenyl, an organic n-semiconductor, has been derivatized by short ω-mercaptoalkyl chains to permit the formation of self-assembled monolayers on semiconductor and coinage metal substrates. Because the perfluoroaryl rings are prone to nucleophilic attack, strategies for the introduction of the side chains had to be developed that avoid the use of any nucleophiles. Keeping this in mind, the respective derivatives with one, two, and three methylene groups in the alkyl linker could be obtained in good yields. The crystal structure of one of the intermediates, (perfluoroterphenyl-4-yl)methanol, exhibits a parallel arrangement of the molecules as well as a helical structure of the perfluoroterphenyl part, which is in contrast to the structure found for most nonfluorinated terphenyl derivatives. Using Au(111) as a test substrate, it could be demonstrated that all three thiols form dense monolayers with a pronounced odd–even effect governed by the parity of the number of methylene groups in the alkyl chain.

Introduction

The advent of organic semiconducting materials promises further miniaturization of logic circuitry, with the ultimate aim of generating single-molecule switches and transistors. Whereas the latter goal is likely not to be reached in the near future, the use of organic materials in low-cost electronic applications such as printable electronics is close to mass fabrication. The advantages of organic materials are – among others – their mechanical flexibility as well as their low-cost and convenient processing, which is often made possible through solution chemistry or low-temperature vapor deposition. In contrast to silicon-based circuitry, which usually requires massive slabs of single-crystalline silicon, the use of organic materials is restricted to the functional parts of the circuitry, usually deposited onto cheap, inert substrates such as glass or even polymer foils. Their application as thin films makes the whole setup comparatively cheap, so that their use in disposable electronic labeling of consumer products can even be considered.

Progress in this and related fields requires the design of suitable organic materials, which are mostly semiconductors, and investigation of the electronic properties of the respective films. One current problem in this area is the lack of organic n-type semiconductors. As a typical feature, organic semiconductors carry a number of conjugated double bonds,[1] resulting in the diminished band gap necessary for their conduction behavior. At the same time, this also results in energetically relatively high-lying highest occupied molecular orbitals (HOMO), making defect-electrons ("holes") the typical charge carrier (p-conduction). To obtain an alternative, n-type semiconductor behavior, the valence states should be lowered to some extent, which can be typically achieved by the introduction of electron-withdrawing moieties, such as cyano groups or fluorine atoms. This has recently been very elegantly demonstrated by the work of Kato and Yamabe,[2] who showed that the perfluoro-derivatives of tetracene and pentacene exhibit almost the same charge carrier mobility as the nonfluorinated materials, but with a different charge carrier type.[3] Surprisingly, to the best of our knowledge, the much simpler perfluoro-oligophenyls have only been used as n-semiconducting materials in one study, where an excellent charge carrier mobility was reported for OLED setups.[4] In contrast to the relatively demanding syntheses of the perfluoroacenes, the access to the perfluorooligophenyls is much less complicated.[5] Nevertheless, the reports[4,5] give only the syntheses of the parent compounds: Neither their structural properties nor the directed syntheses of functional derivatives have been described yet. In our effort to study ultra-thin films of organic semiconductors, we considered it of interest to (1) synthesize such functionalized perfluoro-oligophenyl derivatives, (2) determine their molecular structure, and (3) deposit them onto surfaces.

In this paper, we restrict ourselves to the chemistry of perfluoroterphenyl and its derivatives, since we consider it to be representative of the higher perfluoro-oligophenyls.

[a] Institut für Anorganische und Analytische Chemie, Universität Frankfurt,
Max-von-Laue-Straße 7, 60438 Frankfurt, Germany
Fax: +49-69-798-29188
E-mail: aterfort@chemie.uni-frankfurt.de
[b] Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany

These molecules should be functionalized with short ω-mercaptoalkyl chains for their attachment to gold and silver surfaces, making them closely related to a well studied group of substances carrying a nonfluorinated oligophenyl moiety and short ω-mercaptoalkyl chains.[6] This relationship promises to result in the formation of highly ordered films, which are necessary in any electronic application, because the order in the bi- and terphenylalkanethiolate monolayers were found to be much higher than those in analogous films without the alkyl linker. Additionally, the exact structure and density of these self-assembled monolayers (SAMs) are greatly affected by the parity of the number of methylene groups in the alkyl chain (i.e., an odd–even effect), which has been related to the bonding configuration of the anchoring groups, which differs on gold and silver.[7] It is of interest to determine whether the perfluorinated homologues also form such highly ordered films and also whether they show the same odd–even effect. This not only opens the door for very fundamental investigations into charge transport in organic molecules,[8] but could also enable their use in ultra-thin film devices, such as self-assembled monolayer field-effect transistors (SAMFETs).[9]

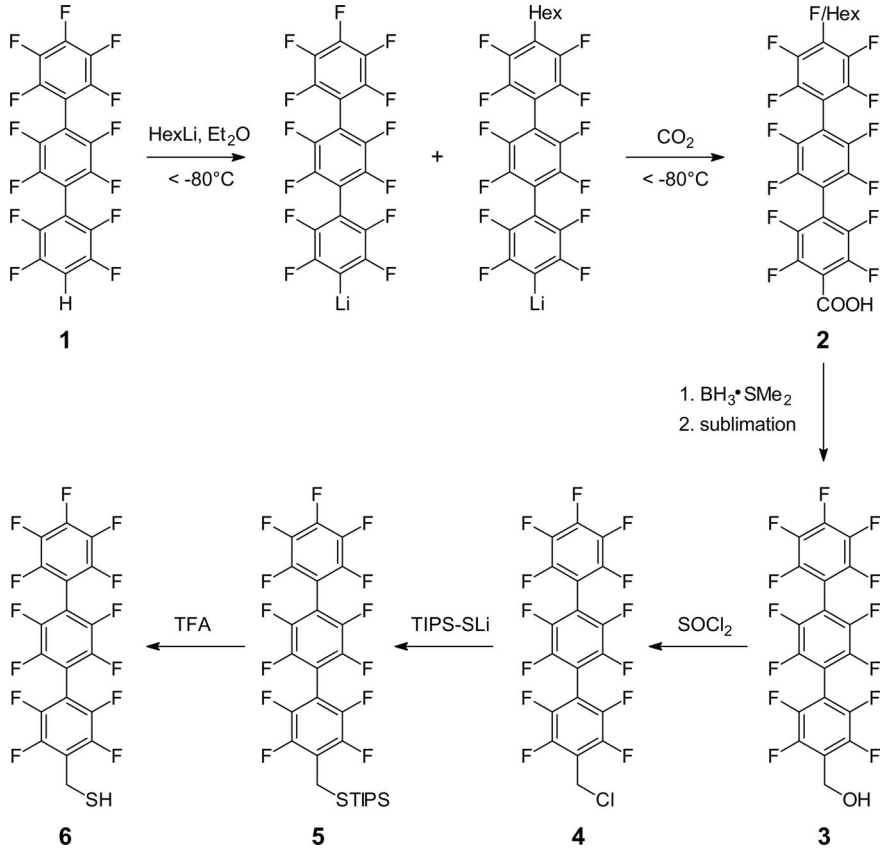
Results and Discussion

The main challenge in this project was to establish suitable synthetic approaches, because the chemistry of perfluoro-oligophenyls significantly differs from that of the respective nonfluorinated oligophenyls. In contrast to regular aromatic systems, the typical synthetic entry into this class of substituted perfluoroarenes involves substitution with hard nucleophiles.[10] It therefore seemed favorable to use the known perfluoroarene, perfluoroterphenyl,[5,11] as starting material, since the nucleophilic substitutions preferably take place at the 4-positions of the outer perfluorophenyl rings, which should provide the correctly substituted derivatives.[12]

Unfortunately, in our hands, no selective mono-substitution with a carbon nucleophile could be established: With *n*-butyllithium as a model reagent, even with sub-stoichiometric amounts, up to four alkyl groups were introduced into the perfluoroterphenyl system, with most of the starting material remaining unchanged. Presumably the reason for this is two-fold: On one hand, the solubility of the starting material is not very high, in particular at low temperatures, so that only the dissolved molecules react. On the other hand, the substituted rings experience a lowered reactivity, whereas the electronic situation in the other rings hardly changes, opening the opportunity for further nucleophilic attack. This is in pronounced contrast to the well established substitution chemistry of the parent compound, hexafluorobenzene. The use of less reactive Grignard reagents, in this case allylmagnesium bromide in tetrahydrofuran (THF), resulted in the formation of some of the desired 4′-substituted product, but also gave significant amounts of an insoluble byproduct, together with unreacted starting material. In contrast, when diethyl ether was used as solvent, no reaction took place. These difficulties led to the decision to reverse the coupling chemistry and, instead, use the fact that highly fluorinated (but not perfluorinated) arenes are easily metallated due to their relatively high thermodynamic acidity.[13] The respective starting compound, 4′-H-tridecafluoroterphenyl (**1**), can be prepared by the oligomerization of pentafluorobenzene,[5] a procedure that could be successfully scaled up to the 25 g range. The deprotonation of this compound by the action of alkyllithium is accompanied by the statistical alkylation reaction as in the case of perfluoroterphenyl, but this reaction can be controlled to some extent by performing the reaction at a temperature between –80 °C and –90 °C in diethyl ether (in THF the formation of an insoluble byproduct dominates). Nevertheless, it turned out to be advantageous to use *n*-hexyllithium instead of *n*-butyllithium, since this facilitates the removal of the by-products in the later stages of the synthesis (Scheme 1).

As mentioned before, derivatives with a range of alkyl chain lengths between the perfluoroterphenyl unit and the sulfur atom should be synthesized. For the introduction of a single carbon atom, the lithiated species was treated with carbon dioxide, resulting in the formation of the respective carbonic acid. The separation of the product from the 4′′-hexylated by-product was not feasible at this stage (the carbonic acid has previously been described in the literature[14]), so the mixture was directly converted into the respective benzylic alcohols by the action of borane–dimethylsulfide complex. It is worth mentioning that lithium aluminum hydride cannot be used for the reduction because the exchange of fluorine atoms by hydrogen atoms could not be excluded due to the high affinity of lithium and aluminum for fluoride.[15] The mixture of benzylic alcohols was separable by gradient sublimation, followed by two recrystallization steps, giving the desired perfluoroterphenyl-4′-ylmethanol (**3**) in a reasonable yield of 56%.

During the sublimation step, tiny crystals suitable for X-ray diffraction were obtained; a schematic view of the crystallographic structure is shown in Figure 1.[16] To the best of our knowledge, this is the first structural characterization of a perfluorinated oligophenyl derivative with more than two phenyl rings. As in the case of the perfluorinated biphenyls,[17] the phenyl rings in this system are not coplanar but twisted by about 56° with respect to each other due to the steric demand of the fluorine atoms. A striking feature is the torsion angle between the first and the third perfluorophenyl rings. Whereas in most nonfluorinated *p*-terphenyl derivatives at least these two rings are coplanar[18] (only two exceptions could be found, see ref[19]), the twist angle between the outermost two rings in **3** amounts to about 113°, resulting in a helical structure. Two neighboring molecules show inverse helicity, so the entire bulk structure is achiral. Note that helicity has also been found for perfluoroalkyl chains in densely packed 2D and 3D materials, whereas nonfluorinated alkyl chains often adopt an all-*trans* conformation under such conditions, rendering them basically planar.[20] From a geometrical point of view, this helicity means that there is no preferential plane within this



Scheme 1. Synthesis of (perfluoroterphenyl-4-yl)methanethiol (**6**). The introduction of the side-chain (in this case C_1) should be performed at low temperatures to minimize alkylation and self-condensation. Hexyllithium was used in the metallation step because this permits more facile removal of the alkylated side-products by sublimation.

aromatic system, which is of importance for spectroscopic investigations and might even result in a more isotropic charge-carrier mobility in the layers or even in the bulk material.

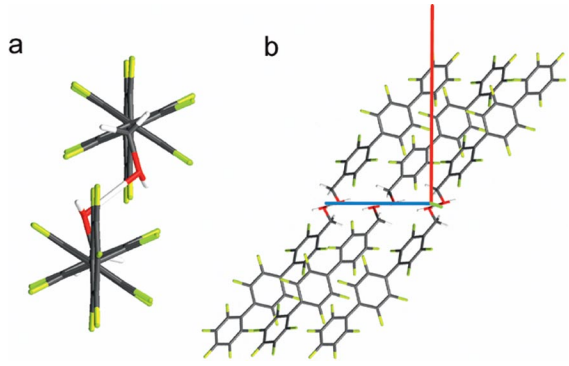


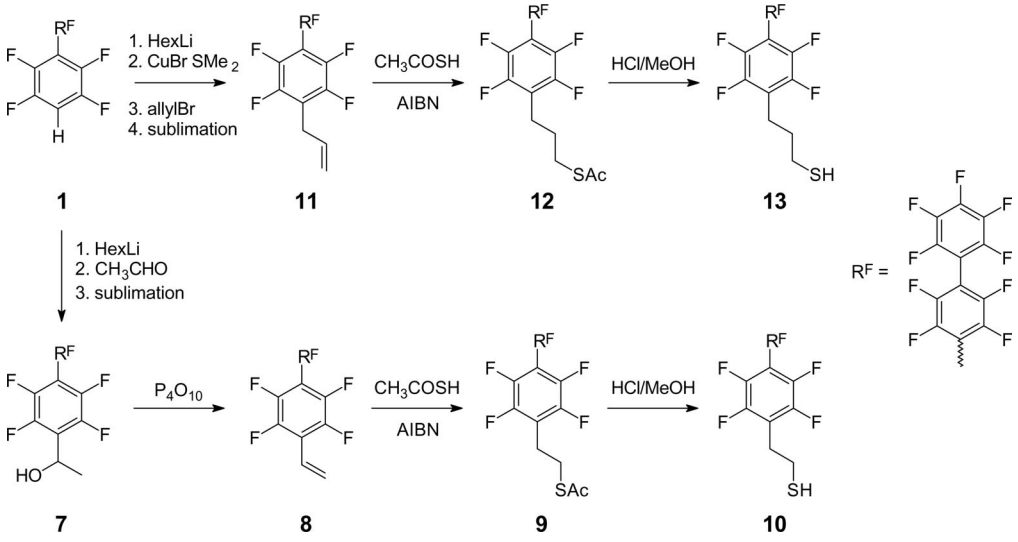
Figure 1. X-ray crystal structure of benzylic alcohol **3**. (a) The view along the axes of the asymmetric unit illustrates the helical conformation of the perfluoroterphenyl unit. (b) In the molecular arrangement, the oxygen atoms are basically located in the *b*/*c* plane (blue and green line), with the perfluoroterphenyl units tilted about 47° with respect to the *a* axis (red line). This may hint at the orientation adopted by the respective thiol in a monolayer.

In the asymmetric unit, two of the molecules are held together by a hydrogen bond between the OH groups. The non-participating hydrogen atom is equally disordered over both oxygen atoms. It is worth mentioning that the oxygen atoms in the crystal of **3** are basically within the *b*/*c* plane of the unit cell. This can be considered to be similar to the situation within a self-assembled monolayer of thiolates on gold, where all the sulfur atoms are placed in the plane of the SAM-substrate interface. Thus, one might expect that the tilt angle of the molecules within the crystal [47° with respect to the *a* axis, which in the orthorhombic system (space group *Pbcn*) is also the "surface normal" for the *b*/*c* plane] will also be observed in the respective SAMs – if no other influences, such as the bending potential around the sulfur atom,[7] occur. With a length of the *b* vector of 9.05 Å and a length of the *c* vector of 8.14 Å, and two asymmetric units within this plane, an average area of 36.8 $Å^2$ for each molecule results. For the respective SAM, this would be a comparably low packing density, which is thermodynamically not favored [in nonfluorinated terphenylalkanethiolate SAMs, the areas per molecule are about 21.6 $Å^2$ (odd number of methylene groups) and 27 $Å^2$ (even number of methylene groups)[6b]]. In this regard, a rearrangement of the perfluoroterphenylalkanethiol molecules to adopt a higher packing density is quite likely. This will be discussed in more detail in the section on monolayer characterization below.

For the introduction of the sulfur atom, the benzylic alcohol **3** was first converted into the respective benzylic chloride **4** by the action of thionyl chloride (Scheme 1). This compound turned out to be quite sensitive and decomposed upon attempted recrystallization, although sublimation in high vacuum was possible. Thus, the reaction with lithium triisopropylsilylthiolate (TIPS-SLi) was performed with crude **4**. The TIPS-SLi is one of only a few reagents that do not attack the perfluoroarene rings, in contrast to, for example, thioacetate, presumably due to steric reasons. The resulting silyl thioether **5** was then cleaved by the action of trifluoroacetic acid in dichloromethane, yielding the desired thiol **6**, which was purified by gradient sublimation. Note that this strategy avoids nucleophiles as far as possible, and when nucleophiles are used, only carefully selected molecules were chosen.

For the synthesis of the thiol with two methylene groups between the perfluoroterphenyl unit and the sulfur atom, again, the lithium salt of **1** was used as reagent, in this case to form the 1-hydroxyethyl derivative **7** by reaction with acetaldehyde (Scheme 2). To avoid nucleophilic attack of the intermediate lithium alkoxide at other perfluoroarenes, the reaction temperature had to be kept below –40 °C. Again, hexylated by-products were removed by a combination of chromatography and gradient sublimation to yield 83% of **7**. From this alcohol, water was eliminated by the action of phosphorus pentoxide at elevated temperature to provide 4′-vinylperfluoroterphenyl (**8**), which was then used as a substrate for the radical addition of thioacetic acid. The radical route avoids the generation of nucleophilic species reactive enough to substitute fluorine atoms. This is also true for the final deprotection step, where the resulting thioacetate (**9**) was cleaved by the action of hydrochloric acid in methanol. The ethanethiol derivative **10** thus became available in 45% yield over four steps. A similar strategy was used for the synthesis for the thiol with three methylene groups (**13**). By first transforming the lithium salt of **1** into the respective copper(I) compound, followed by reaction with allyl bromide, one reaction step could be omitted, since the alkene **11** became directly available for the radical thioacetylation. The thioacetate **12** was again cleaved using hydrochloric acid/methanol, with a moderate yield of only 46% in the final step. We therefore also tried to use dimethylamine, a well-established reagent for the cleavage of thioesters,[21] but could only obtain a product in which the fluorine atom at the 4′′-position had been replaced by a dimethylamino group, with the thioester function still intact. This is a striking example of the relative reactivity of the C–F bonds in perfluorooligophenyls.

To test the capability of these molecules to form densely packed monolayers, we used ellipsometry as a well-established tool. Whereas for thicker films, this method can determine the thickness and the refractive index of a film independently, for monomolecular films, one of these parameters has to be known to determine the second. Usually, the refractive index of the film is assumed to be equal to the bulk refractive index.[22] Since the bulk refractive index for perfluorinated oligophenyl derivatives is also not known, we used the Brewster angle to determine a representative bulk refractive index. For this, a compact sample of **11** with a highly reflective planar surface was formed by means of a commercial press typically used to make infrared (IR) pills. Using an optical two-circle goniometer set-up (Multiskop, Optrel, Germany), a Brewster angle of 55.85° was determined at 632.8 nm, the same wavelength as that used by the ellipsometer (SE400, Sentech, Germany). The resulting refractive index of 1.475 is in the anticipated range between that of perfluorinated alkanes (1.35) and that of typical nonfluorinated arenes (1.55). Because we considered the influence of the substitution at the alkyl chain likely to be small, we used this refractive index value for all three thiolate monolayers. The monolayers were deposited from 0.1 mM ethanolic solutions of the respective thiols by immersing the Au(111) substrates for 24 h. The purged and



Scheme 2. Synthetic scheme for the formation of the (perfluoroterphenyl-4-yl)alkanethiols with two (**10**) and three methylene groups (**13**). In these cases, radical addition of thioacetic acid was utilized for the introduction of the sulfur atoms.

dried monolayers showed thicknesses of 18.2 ± 0.2 (**6**), 16.8 ± 0.5 (**10**), and 19.8 ± 0.8 Å (**13**), respectively. These data hint at the presence of densely packed monolayers with a pronounced odd–even effect as has also been described for the nonfluorinated analogues of these molecules.[6,7] By combining these values with the molecular lengths, the tilt angles of the molecules in the monolayers can be estimated to be about 0 (**6**), 30 (**10**), and 10° (**13**), respectively. The value for **10** compares well with the tilt angle found in the crystal structure of **3**, suggesting a similar packing of the perfluoroterphenyl units in this monolayer, whereas molecules of **6** and **13** presumably adopt a much more upright conformation than predicted by the crystal structure of **3**. This orientation would correspond to a much closer packing and clearly hints at different factors (bending potential at the sulfur atoms, van-der-Waals interactions between the molecules) that either act synergistically or antagonistically.[7] The alkyl chains clearly act as mediators for these forces, because only the number of methylene groups and, thus their parity, differs between these three kinds of molecules. More detailed investigations using IR spectroscopy, X-ray photoemission, and X-ray absorption spectroscopy, etc., will be performed to gain additional insight.

Conclusions

In summary, we have developed a synthetic route to a very promising class of molecules for the fabrication of novel self-assembled monolayers, which may find use in organic or even molecular electronics. The strict avoidance of common nucleophiles, while performing the key steps at very low temperatures, e.g., for the reactions of the lithiated starting compound **1** with the carbon electrophiles, turned out to be essential for the success of this chemistry. With this in mind, all three thiols **6**, **10**, and **13** are now available through relatively short synthetic sequences with good yields.

The opportunity to obtain the crystal structure of a perfluoroterphenyl derivative for the first time gave insight into many previously unanticipated molecular features, such as the helical arrangement of the phenyl rings and the relatively high tilt angle of the molecular axes with respect to the layers formed by these molecules. The thickness of the monolayers of **10** (even number of methylene groups) suggests that this tilt angle is also adopted in the SAMs, whereas in the other two films, the molecules (with an odd number of methylene groups) presumably stand almost upright. This behavior would be analogous to that observed for the nonfluorinated terphenylalkane thiols. To understand the behavior of these molecules better, we are currently investigating the SAM-forming properties of these three thiols in more detail.

Experimental Section

General: All the procedures were carried out under complete exclusion of water and air using standard Schlenk techniques unless otherwise noted. The following NMR spectrometers were used: Bruker Avance 300, Bruker DRX 400, Bruker Avance 400, Bruker ARX 200, and Varian Gemini 2000. It is worth mentioning that due to the strong coupling of the fluorine to the carbon nuclei, the signals of the latter nuclei became often not visible in the ^{13}C NMR spectra. IR spectra were recorded either with a Bruker Vertex or a Nicolet 6700 FTIR spectrometer using the diamond-ATR technique. Mass spectra were recorded with a MAT 95 instrument from Finnigan or a Finnigan LTQ-FT from Thermo Fischer Scientific. Elemental analyses were performed with a Vario MICRO Cube instrument from Elementar-Analysensysteme (Hanau, Germany). Melting points were measured with a Büchi apparatus according to Dr. Tottoli.

Crystallography: Data were collected with a STOE-IPDS-II two-circle diffractometer employing graphite-monochromated Mo-K_α radiation (0.71073 Å) with ω-scans. Data reduction was performed with the X-Area software.[23]An empirical absorption correction was performed using the MULABS[24] option in PLATON.[25] The structure was solved by direct methods with SHELXS-90[26] and refined by full-matrix least-squares techniques with SHELXL-97.(4)[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon atoms were included at calculated positions and allowed to ride on their parent atoms. The hydroxyl hydrogen atom is disordered over two equally occupied positions.

4′-*H*-Tridecafluoroterphenyl (1): To achieve good yields, the quality of the KOH powder is critical. We used powdered KOH from commercial sources (Fluka) which was stored under nitrogen immediately after reception to prevent loss of quality by uptake of air humidity and CO_2.

Liquid ammonia (1 L) was produced by condensation of NH_3 gas in a 2 L four-necked flask and pentafluorobenzene (50.0 g, 298 mmol) was added before the cooling bath was removed. When the ammonia reached its boiling point, finely powdered KOH (20.0 g, 356 mmol) was added slowly under efficient mechanical stirring, resulting in vigorous boiling of the ammonia and partial solidification of the reaction mixture. After 1 h, solid NH_4Cl (49.4 g, 924 mmol) was carefully added, which again resulted in vigorous boiling of the ammonia. The ammonia was permitted to evaporate overnight. To the resulting solid, H_2O (300 mL) and the same volume of toluene were added and the mixture was heated to reflux. The hot mixture was filtered through a pad of kieselguhr to remove insoluble solids. After phase separation, the toluene was evaporated and the remaining solid was purified by gradient sublimation in vacuo to give **1** as a colorless solid (25.52 g, 54.98 mmol, 55%); m.p. 173–174 °C, 172–174 °C.[5] R_f = 0.69 (petroleum ether/CH_2Cl_2, 2:1). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.31 (tt, ^3J = 9.5, ^4J = 7.6 Hz, 1 H, 4-H) ppm. ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –136.60 to –138.20 (m, 10 F, F-2, F-6, F-3, F-5, F-2′, F-6′, F-3′, F-5′, F-2′′, F-6′′), –149.51 (t, ^3J = 20.7 Hz, 1 F, F-4′′), –160.00 to –160.40 (m, 2 F, F-3′′, F-5′′) ppm. MS (EI): *m*/*z* (%) = 464 (100) [M^+]. $C_{18}HF_{13}$ (464.18): calcd. C 46.58, H 0.22; found C 46.19, H 0.44.

Perfluoroterphenyl-4′-carboxylic Acid (2): A solution of **1** (10.03 g, 21.61 mmol) in dry diethyl ether (600 mL) was cooled to below –90 °C (nitrogen-cooled acetone/ethanol bath) before *n*-hexyllithium (21 mmol, 9.3 mL, 2.3 M in cyclohexane) were added under vigorous stirring. The temperature was raised slowly to reach –55 °C after 2 h, when some freshly broken lumps of dry ice were added. At –10 °C, approximately 10% H_2SO_4 (0.6 L) was added. After separation of the phases, the ethereal phase was washed once with very dilute H_2SO_4. Removing the solvent yielded a colorless

solid, from which traces of water were removed by coevaporation with dichloromethane. The product contained significant amounts of unchanged starting material as well as hexylated species and was used without further purification. Attempts to separate the carbonic acids from the nonpolar products by dissolution in bases yielded substitution products at the phenyl rings, so this strategy cannot be recommended. ^{19}F NMR ([D$_6$]DMSO, 282 MHz): δ = –136.75 to –140.00 (m, 10 F, F-2, F-6, F-3, F-5, F-2′, F-6′, F-3′, F-5′, F-2′′, F-6′′), –149.26 (t, ^3J = 21.9 Hz, 1 F, F-4′′), –160.52 to –160.79 (m, 2 F, F-3′′, F-5′′) ppm. HRMS (APCI$^-$): *m*/*z* calcd. (found): 462.9787 (462.9792), 98%, [$C_{18}F_{13}$]$^-$; 463.9865 (463.9870), 100%, [$C_{18}F_{13}H$]$^-$. IR (ATR): $\tilde{\nu}$ = 1720 (s, C=O), 1468 (s, C–F) cm^{-1}.

(Perfluoroterphenyl-4′-yl)methanol (3): The crude carboxylic acid **2** (all of the material obtained in the first step above) was dissolved in dry diethyl ether (100 mL). After addition of borane–dimethylsulfide complex (5.50 g, 72.4 mmol), the mixture was heated under reflux for 16 h. After cooling, excess borane was destroyed by careful addition of water (100 mL) followed by acidification with concentrated hydrochloric acid. The organic phase was washed with water twice. Evaporation of the solvent gave a crude product which contained significant amounts of **1** as well as the hexylated derivatives of **1** and **3**. Compound **1** and the hexyl derivative of **1** were removed by column chromatography over silica gel. These non-polar impurities were first eluted with petroleum ether/dichloromethane (20:1), then the product **3** and its hexyl derivative were eluted with pure dichloromethane. The latter two were separated by gradient sublimation. The almost pure **3** was crystallized twice from methylcyclohexane to afford pure **3** (5.97 g, 12.0 mmol, 56% over two steps) as a colorless solid. R_f = 0.31 (CH_2Cl_2); m.p. 179–183 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.94 (s, 2 H, C*H*$_2$), 2.03 (br. s, 1 H, OH) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –137.00 to –135.00 (m, 6 F), –138.08 to –138.43 (m, 2 F), –143.59 to –143.88 (m, 2 F), –149.78 (tt, ^3J = 21.1, ^4J = 3.0 Hz, 1 F, F-4′′), –160.33 to –160.70 (m, 2 F, F-3′′, F-5′′) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.5 (CH_2) ppm. MS (API$^-$): *m*/*z* (%) = 494 (100) [M]$^-$. HRMS (APCI$^-$): calcd. for [M]$^-$: 493.9971; found 493.9971 (100%). IR (ATR): $\tilde{\nu}$ = 3305 (br. d, m, O–H), 1472 (s, C–F), 1261 (m), 974 (s), 919 (s), 714 (m) cm^{-1}. $C_{19}H_3F_{13}O$ (494.21): calcd. C 46.18, H 0.61; found C 46.25, H 0.75.

(Perfluoroterphenyl-4′-yl)chloromethane (4): One droplet of DMF was added to a mixture of **3** (0.99 g, 2.0 mmol) and thionyl chloride (10 mL), and the mixture was then heated under reflux for 14 h. The excess thionyl chloride was removed in vacuo and the remaining solid was used directly without further purification; m.p. 173–175 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.76 (t, ^4J = 1.2 Hz, 2 H, CH_2) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –136.45 to –137.06 (m, 6 F), –137.10 to –137.34 (m, 2 F), –141.47 to –141.66 (m, 2 F), –149.31 (mt, ^3J = 20.8 Hz, 1 F, F-4′′), –159.97 to –160.24 (m, 2 F, F-3′′, F-5′′) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 34.5 (CH_2) ppm. MS (EI): *m*/*z* (%) = 477 (100) [$C_6F_5(C_6F_4)_2CH_2$]$^+$, 239 (28), 512 (25) [M]$^+$. $C_{19}H_2ClF_{13}$ (512.65): calcd. C 44.51, H 0.39; found C 44.79, H 0.57. IR (ATR): $\tilde{\nu}$ = 1469 (s, C–F), 972 (s) cm^{-1}.

Triisopropyl[(perfluoroterphenyl-4-yl)methylthio]silane (5): *n*-Butyllithium (2.6 mmol, 1.6 mL, 1.6 M in hexane) was added to a solution of triisopropylsilanethiol (0.80 g, 4.2 mmol) in dry THF (15 mL) at 0 °C. After stirring for 5 min, the solution of the thiolate was added to an ice-cooled solution of **4** (all of the material obtained in the previous step) in dry THF (30 mL). The reaction mixture was stirred at r.t. for 72 h, then the THF was removed and the remaining solid was partitioned between water and dichloromethane. The phases were separated and the organic solvent was evaporated. Further purification was accomplished by high vacuum distillation at 200 °C. The product thus obtained (0.62 g, 0.93 mmol, 47% over two steps) as an almost colorless solid still contained impurities, but was of sufficient purity for further transformations; m.p. 100–105 °C. R_f = 0.61 (petroleum ether/CH_2Cl_2, 5:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.93 (s, 2 H, CH_2), 1.51–1.29 [m, 3 H, C*H*(CH_3)$_2$], 1.29–1.15 [m, 18 H, CH(C*H*$_3$)$_2$] ppm. ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –137.14 to –138.18 (m, 6 F), –138.80 to –139.17 (m, 2 F), –142.72 to –143.06 (m, 2 F), –150.35 (tt, ^3J = 20.8, ^4J = 3.1 Hz, 1 F, F-4′′), –160.84 to –161.21 (m, 2 F, F-3′′, F-5′′) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 18.4 [*C*H(CH_3)$_2$], 17.1 (br. s, CH_2), 12.1 [CH(*C*H$_3$)$_2$] ppm. IR (ATR): $\tilde{\nu}$ = 2949 (m, aliph. C–H), 2869 (m, aliph. C–H), 1463 (s, C–F) cm^{-1}. MS (EI): *m*/*z* (%) = 477 (100) [$C_{18}F_{13}CH_2$]$^+$, 510 (53) [$C_{18}F_{13}CH_2SH$]$^+$, 623 (33) [$C_{18}F_{13}CH_2SSi\{CH(CH_3)\}_2$]$^+$, 666 (1) [M]$^+$. $C_{28}H_{23}F_{13}SSi$ (666.61): calcd. C 50.45, H 3.48, S 4.81; found C 49.97, H 3.21, S 5.38.

(Perfluoroterphenyl-4-yl)methanethiol (6): Trifluoroacetic acid (1.5 mL) was added to a solution of **5** (0.26 g, 3.9 mmol) in dry dichloromethane (10 mL). After 90 min stirring at r.t., the solvent was removed and the residue was redissolved in dichloromethane and washed with saturated sodium hydrogen carbonate. After evaporation of the solvent, the remaining crude product was purified by gradient sublimation in vacuo to give an almost colorless solid (0.17 g, 0.33 mmol, 85%); m.p. 159–161 °C. R_f = 0.36 (petroleum ether/CH_2Cl_2, 5:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.89 (d, ^3J = 8.6 Hz, 2 H, CH_2), 2.19 (t, ^3J = 8.6 Hz, 1 H, SH) ppm. ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –136.86 to –137.75 (m, 6 F), –138.21 to –138.55 (m, 2 F), –143.44 to –143.69 (m, 2 F), –149.95 (tt, ^3J = 20.9, ^4J = 2.9 Hz, 1 F, F-4′′), –160.51 to –160.88 (m, 2 F, F-3′′, F-5′′) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 15.2 (CH_2) ppm. MS (EI): *m*/*z* = 510 (10) [M]$^+$, 477 (100) [$C_{18}F_{13}CH_2$]$^+$. $C_{19}H_3F_{13}S$ (510.27): calcd. C 44.72, H 0.59, S 6.28; found C 44.72, H 0.83, S 6.29. IR (ATR): $\tilde{\nu}$ = 2164 (w, S–H), 1503 (s, C–F), 1466 (s, C–F) cm^{-1}.

1-(Perfluoroterphenyl-4′-yl)ethanol (7): To a solution of **1** (10.97 g, 23.64 mmol) in diethyl ether (1 L), *n*-hexyllithium (22 mmol, 9.5 mL, 2.3 M in cyclohexane) was added under vigorous stirring while the temperature was maintained below –80 °C. After slow (2 h) warming to –60 °C, acetaldehyde (4 mL, 70.8 mmol) was added to the solution. When the temperature reached –45 °C (1 h), the reaction was quenched by addition of diluted H_2SO_4. At r.t., the ethereal phase was separated and washed with water until neutral. Evaporation of the ether gave the crude product **7**, which contained 1-(4′′-hexylperfluoroterphenyl-4′-yl)ethanol as well as unchanged **1** and 4′-*H*-4′′-hexylperfluoroterphenyl. The latter two were removed by column chromatography over silica (petroleum ether / CH_2Cl_2, 20:1) followed by elution of **7** and its hexylated product with dichloromethane. The separation of **7** from the 1-(4′′-hexylperfluoroterphenyl-4-yl)ethanol was accomplished by gradient sublimation. The final product still contained some 1-(4′′-hexylperfluoroterphenyl-4-yl)ethanol and 1-(perfluoroquarterphenyl-4-yl)ethanol, both of which were observed in the mass spectra.

Yield of **7**: 9.66 g (19.0 mmol, 83%); colorless solid; m.p. 146–152 °C. R_f = 0.38 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.37 (q, ^3J = 6.7 Hz, 1 H, -C*H*OH-CH_3), 2.29 (br. s, 1 H, OH), 1.75 (d, ^3J = 6.7 Hz, 1 H, -CHOH-C*H*$_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –136.64 to –137.18 (m, 6 F), –137.85 to –138.11 (m, 2 F), –143.57 to –143.59 (m, 2 F), –149.43 (tt, ^3J = 20.9, ^4J = 3.1 Hz, 1 F, F-4′′), –160.04 to –160.28 (m, 2 F, F-3′′, F-5′′) ppm. ^{13}C NMR ($CDCl_3$, 62 MHz): δ = 147–125 (C–F), 62.8 (t, ^3J = 2.0 Hz, $CHOHCH_3$), 23.1 ($CHOHCH_3$) ppm. MS (AP$^-$): *m*/*z* (%)

= 508 (100) [M]$^-$, 574 (78) [$CH_3CHOH - (C_6F_4)_3 - (CH_2)_5CH_3^-$], 656 (23) [$CH_3CHOH - (C_6F_4)_3 - (C_6F_5)]^-$. HRMS (APCI$^-$): calcd. for [M]$^-$ 508.0127; found 508.0128 (100%). $C_{20}H_5F_{13}O$ (508.23): calcd. C 47.26, H 0.99; found C 47.36, H 1.25. IR (ATR): $\tilde{\nu}$ = 3344 (br. d, m, O–H), 2976 (w, C–H), 2933 (w, C–H), 1467 (s, C–F).

4′-Vinylperfluoroterphenyl (8): To a solution of **7** (0.75 g, 1.5 mmol) in methylcyclohexane (50 mL), P_4O_{10} (ca. 2 g, 7 mmol) was added and the reaction mixture was heated under reflux for 20 h. Full conversion of **7** was indicated by TLC. Water was added and the organic phase was separated. Evaporation of the methylcyclohexane gave the crude product, which was purified by gradient sublimation to give a colorless solid (0.63 g, 1.3 mmol, 87%); m.p. 149–150 °C. R_f = 0.83 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.79 (dd, ^3J = 18.0, ^3J = 11.8 Hz, 1 H -C*H*=CH_2), 6.25 (d, ^3J = 17.9 Hz, 1 H, -CH=CH_{trans}H$_{cis}$), 5.86 (d, ^3J = 11.8 Hz, 1 H, -CH=CH_{trans}-H_{cis}) ppm. ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –136.96 to –137.91 (m, 6 F), –139.60 to –140.02 (m, 2 F), –142.94 to –143.35 (m, 2 F), –150.00 (tt, ^3J = 20.9, ^4J = 3.2 Hz, 1 F, F-4′′), –160.52 to –160.90 (m, 2 F, F-3′′, F-5′′) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 147.0–136.0 (arom. C-F), 125.4 (t, ^3J = 7.9 Hz, C–CH=CH_2), 122.1 (C-CH=CH_2), 119.2 (t, ^2J = 13.4 Hz, C-CH=CH_2), 109.6 (t, ^2J = 18.3 Hz, quat. C), 108.1 (t, ^2J = 17.5 Hz, quat. C), 104.7 (t, ^2J = 18.8 Hz, quat. C), 102.0 (t, ^2J = 17.3 Hz, quat. C) ppm. MS (EI): *m*/*z* (%) = 490 (100) [M]$^+$. $C_{20}H_3F_{13}$ (490.22): calcd. C 49.00, H 0.62; found C 49.16, H 0.34.

2-(Perfluoroterphenyl-4′-yl)ethane-1-*S*-thioacetate (9): Compound **8** (1.31 g, 2.67 mmol), thioacetic acid (2.0 mL, 2.1 g, 28 mmol), and a small amount of AIBN in carbon tetrachloride (50 mL) were heated under reflux for 10 h. Then, a further portion of AIBN was added and reflux was continued for another 10 h. Full conversion of **8** was indicated by TLC. The carbon tetrachloride was removed in vacuo, giving crude **9**, which was purified by column chromatography over silica with a petroleum ether/dichloromethane gradient starting with 100:1. Finally, the product (1.14 g, 2.01 mmol, 75%) was purified by gradient vacuum sublimation to give an almost colorless solid; m.p. 139–141 °C. R_f = 0.83 (CH_2Cl_2), 0.22 (petroleum ether/CH_2Cl_2, 4:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.17–3.02 [m, 4 H, $(CH_2)_2$], 2.29 (s, 3 H, $COCH_3$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 194.8 (C=O), 30.5 (-CH_2CH_2-SAc), 27.8 [(-CH_2)$_2$-SCOCH_3], 23.4 (-CH_2CH_2-SAc) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz): δ = –136.72 to –137.10 (m, 4 F), –137.10 to –137.36 (m, 2 F), –138.47 to –138.70 (m, 2 F), –142.03 to –142.22 (m, 2 F), –149.57 (mt, ^3J = 20.9 Hz, 1 F, F-4′′), –160.14 to –160.38 (m, 2 F, F-3′′, F-5′′) ppm. MS (API$^-$): *m*/*z* (%) = 566.3 (100) [M]$^-$. $C_{22}H_7F_{13}OS$ (566.33): calcd. C 46.66, H 1.25, S 5.66; found C 46.83, H 1.21, S 5.72. IR (ATR): $\tilde{\nu}$ = 1686 (s, C=O), 1498 (s, C–F), 1462 (s, C–F) cm^{-1}.

2-(Perfluoroterphenyl-4′-yl)ethane-1-thiol (10): Degassed hydrochloric acid (20%, 20 mL) was added to a suspension of **7** (1.31 g, 2.31 mmol) in oxygen-free methanol (150 mL). The reaction mixture became clear upon heating to reflux. After 14 h at reflux, full conversion of **9** was indicated by TLC. The product was precipitated after cooling by addition of an equal volume of water and filtered off. The solid was washed thoroughly with water and redissolved in dichloromethane. The dichloromethane solution was washed with water and the solvents evaporated. Purification was accomplished by gradient vacuum sublimation to give a colorless solid (1.02 g, 1.95 mmol, 84%); m.p. 167 °C. R_f = 0.16 (petroleum ether), 0.39 (petroleum ether/CH_2Cl_2, 4:1). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.08 (t, ^3J = 7.2 Hz, 2 H, -C*H*$_2$-CH_2-SH), 2.86–2.72 (m, -CH_2-C*H*$_2$-SH), 1.48 (t, ^3J = 8.3 Hz, 1 H, -CH_2-CH_2-S*H*) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 28.1 (-CH_2CH_2-SH), 23.8 (-CH_2CH_2-SH) ppm. ^{19}F NMR ($CDCl_3$, 188 MHz): δ = –137.10 to –137.87 (m, 6 F), –138.81 to –139.19 (m, 2 F), –142.71 to –142.99 (m, 2 F), –149.99 (t, ^3J = 20.8 Hz, 1 F, F-4′′), –160.47 to –160.93 (m, 2 F, F-3′′, F-5′′) ppm. MS (API$^-$): *m*/*z* (%) = 524 (100) [M]$^-$. HRMS (APCI$^-$): calcd. for [M]$^-$ 523.9899; found 523.9898 (100%). $C_{20}H_5F_{13}S$ (524.30): calcd. C 45.82, H 0.96, S 6.12; found C 45.74, H 1.11, S 6.01. IR (ATR): $\tilde{\nu}$ = 2997 (w, aliph. C–H), 2959 (w, aliph. C–H), 2164 (w, S–H), 1469 (s, C–F) cm^{-1}.

4′-Allyltridecafluoroterphenyl (11): Under vigorous stirring, *n*-HexLi (8.05 mmol, 3.5 mL, 2.3 M in cyclohexane) was slowly added to a solution of **1** (3.29 g, 7.02 mmol) in absolute diethyl ether (200 mL), while maintaining a temperature below –90 °C. After slow (2 h) warming to –60 °C, CuBr · SMe_2 (1.50 g, 7.32 mmol) was added to the solution, followed by addition of allyl bromide (1.0 mL, 12 mmol). After stirring for 1 h, during which time the temperature rose to –55 °C, the cooling bath was removed. When the temperature reached 0 °C, water (200 mL) was added and the mixture was made slightly acidic by addition of HCl. The ethereal phase was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were deacidified by washing with water. The organic solvent was evaporated and the resulting solid was purified by gradient sublimation in vacuo to give the product as a colorless solid (2.34 g, 4.66 mmol, 66%); m.p. 114–116 °C. R_f = 0.69 (cyclohexane/CH_2Cl_2, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.2 (tdd, ^3J = 6.3, ^3J = 10.4, ^3J = 16.8 Hz, 1 H, CH_2-C*H*=CH_2), 5.22–5.12 (m, 2 H, CH_2-CH=C*H*$_2$), 3.62 –3.55 (md, ^3J = 6.3 Hz, 2 H, C*H*$_2$-CH=CH_2) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.3–120.8 (C-F), 132.3 (CH_2-CH=CH_2), 117.7 (CH_2-CH=CH_2), 27.3 (CH_2-CH=CH_2) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –136.75 to –137.60 (m, 6 F), –138.73 to –139.09 (m, 2 F), –142.78 to –143.16 (m, 2 F), –149.59 (t, ^3J = 20.85 Hz, 1 F, F-4′′), –160.04 to –160.45 (m, 2 F, F-3′′, F-5′′) ppm. MS (EI): *m*/*z* = 504 (100) [M]$^+$, 477 (68) [$C_{18}F_{13} - CH_2^+$]. $C_{21}H_5F_{13}$ (504.24): calcd. C 50.02, H 1.00; found C 50.15, H 1.30.

3-(Perfluoroterphenyl-4-yl)propane-1-*S*-thioacetate (12): A mixture of **11** (0.64 g, 1.3 mmol), thioacetic acid (1.0 mL, 14 mmol) and a small amount of AIBN was heated under reflux in carbon tetrachloride (40 mL). After 5 h, full conversion of **11** was indicated by TLC. The carbon tetrachloride was condensed into a cold trap and the remaining crude product was crystallized twice from methylcyclohexane. The pure product was washed with pentane and dried to give a colorless solid (0.58 g, 1.0 mmol, 79%); m.p. 136–139 °C. R_f = 0.47 (cyclohexane/CH_2Cl_2, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.98 [t, ^3J = 7.3 Hz, 2 H, -C*H*$_2$-CH_2-CH_2-S-(CO)CH_3], 2.92 [t, ^3J = 7.8 Hz, 2 H, -CH_2-CH_2-C*H*$_2$-S-(CO)CH_3], 2.37 [s, 3 H, -CH_2-CH_2-CH_2-S-(CO)C*H*$_3$], 1.97 [tt, -CH_2-C*H*$_2$-CH_2-S-(CO)CH_3, $^3J_1$ = $^3J_2$ = 7.5 Hz, 2 H, app. q] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.4 (C=O), 30.6 (CH_3), 28.9, 28.4 ($CH_2CH_2CH_2$-SAc), 22.3 ($CH_2CH_2CH_2$-SAc) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –136.66 to –137.06 (m, 4 F), –137.11 to –137.36 (m, 2 F), –138.61 to –138.85 (m, 2 F), –142.82 to –143.03 (m, 2 F), –149.52 (mt, ^3J = 20.9 Hz, 1 F, F-4′′), –160.06 to –160.33 (m, 2 F, F-3′′, F-5′′) ppm. HRMS (APCI$^-$): calcd. for [M]$^-$ 580.0161; found: 580.0160 (100%). $C_{23}H_9F_{13}OS$ (580.36): calcd. C 47.60, H 1.56, S 5.53; found C 47.94, H 1.87, S 5.77.

3-(Perfluoroterphenyl-4-yl)propane-1-thiol (13): To a suspension of **12** (0.84 g, 1.4 mmol) in oxygen-free methanol (70 mL), degassed 20% hydrochloric acid (5.0 mL) was added. The reaction mixture was heated to reflux for 48 h, then water (100 mL) was added and the methanol was distilled off in vacuo. From the remaining suspension, the product was extracted with CH_2Cl_2. This solution was deacidified by washing with water. Evaporation of the solvent gave

crude **13**, which was purified first by column chromatography over silica with a petroleum ether ether/dichloromethane gradient starting with 20:1, followed by gradient vacuum sublimation to give a colorless solid (0.35 g, 0.65 mmol, 46%); m.p. 126–128 °C. R_f = 0.63 (cyclohexane/CH_2Cl_2, 1:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.89 (t, ^3J = 7.6 Hz, 2 H, -CH_2CH$_2$CH$_2$-SH), 2.63 (dt, $^3J_1$ = $^3J_2$ = 7.40 Hz, 2 H, -CH$_2$CH$_2$CH_2-SH), 2.02–1.94 (m, 2 H, -CH$_2$CH_2CH$_2$-SH), 1.39 (t, ^3J = 8.0 Hz, 1 H, -CH$_2$CH$_2$CH$_2$-S*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.6 (t, ^2J = 18.3 Hz, C-4), 33.2 (CH$_2$CH$_2$CH$_2$-SH), 24.1 (CH$_2$CH$_2$CH$_2$-SH), 22.0 (CH$_2$CH$_2$CH$_2$-SH) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –137.16 to –137.91 (m, 6 F), –139.08 to –139.44 (m, 2 F), –143.32 to –143.61 (m, 2 F), –150.02 (tt, ^3J = 20.90, ^4J = 3.1 Hz, 1 F, F-4′′), –160.53 to –160.90 (m, 2 F, F-3′′, F-5′′) ppm. IR (ATR): $\tilde{\nu}$ = 2977 (w, aliph. C–H), 2938 (w, aliph. C–H), 2872 (w, aliph. C–H), 1471 (s, C–F) cm^{-1}. MS (EI): *m*/*z* = 538 (24) [M]$^+$, 504 (100) [$C_{18}F_{13}CH_2$–CH=CH$_2$]$^+$, 477 (48) [$C_{18}F_{13}CH_2$]$^+$. HRMS (APCI$^-$): calcd. for [M]$^-$ 538.0055; found 538.0060 (100%). $C_{21}H_7F_{13}S$ (538.32): calcd. C 46.85, H 1.31, S 5.96; found C 46.67, H 1.35, S 5.92.

Acknowledgments

The authors acknowledge the generous gift of several silanes by the Wacker AG. B. S. and A. T. appreciate the financial support by the Deutsche Forschungsgemeinschaft (DFG) through the graduate school 611 (“Functional materials”).

[1] a) J. E. Anthony, *Angew. Chem. Int. Ed.* **2008**, *47*, 452–483; b) J. Roncali, P. Leriche, A. Cravino, *Adv. Mater.* **2007**, *19*, 2045–2060.
[2] T. Kato, T. Yamabe, *J. Chem. Phys.* **2004**, *121*, 2356–2366.
[3] a) M. C. R. Delgado, K. R. Pigg, D. A. da Silva, N. E. Gruhn, Y. Sakamoto, T. Suzuki, R. M. Osuna, J. Casado, V. Hernandez, J. T. L. Navarrete, N. G. Martinelli, J. Cornil, R. S. Sanchez-Carrera, V. Coropceanu, J.-L. Bredas, *J. Am. Chem. Soc.* **2009**, *131*, 1502–1512; b) Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Inoue, S. Tokito, *Mol. Cryst. Liq. Cryst.* **2006**, *444*, 225–232.
[4] S. B. Heidenhain, Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, T. Mori, S. Tokito, Y. Taga, *J. Am. Chem. Soc.* **2000**, *122*, 10240–10241.
[5] A. A. Shtark, T. V. Chuikova, V. D. Shteingarts, *J. Org. Chem. USSR* **1984**, 960–966.
[6] a) W. Azzam, P. Cyganik, G. Witte, M. Buck, C. Wöll, *Langmuir* **2003**, *19*, 8262–8270; b) W. Azzam, A. Bashir, A. Terfort, T. Strunskus, C. Wöll, *Langmuir* **2006**, *22*, 3647–3655.
[7] a) H.-T. Rong, S. Frey, Y.-J. Yang, M. Zharnikov, M. Buck, M. Wühn, C. Wöll, G. Helmchen, *Langmuir* **2001**, *17*, 1582–1593; b) A. Shaporenko, M. Brunnbauer, A. Terfort, L. S. O. Johansson, M. Grunze, M. Zharnikov, *Langmuir* **2005**, *21*, 4370–4375; c) M. Zharnikov, S. Frey, H. Rong, Y.-J. Yang, K. Heister, M. Buck, M. Grunze, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3359–3362; d) P. Cyganik, K. Szelagowska-Kunstman, A. Terfort, M. Zharnikov, *J. Phys. Chem. C* **2008**, *112*, 15466–15473.
[8] a) D. L. Cheung, A. Troisi, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5941–5952; b) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J. Bredas, *Chem. Rev.* **2007**, *107*, 926–952.
[9] a) E. C. P. Smits, S. G. J. Mathijssen, P. A. van Hal, S. Setayesh, T. C. T. Geuns, K. A. H. A. Mutsaers, E. Cantatore, H. J. Wondergem, O. Werzer, R. Resel, M. Kemerink, S. Kirchmeyer, A. M. Muzafarov, S. A. Ponomarenko, B. de Boer, P. W. M. Blom, D. M. de Leeuw, *Nature* **2008**, *455*, 956–959; b) J. Collet, D. Vuillaume, *Appl. Phys. Lett.* **1998**, *73*, 2681–2683; c) S. R. Saudari, P. R. Frail, C. R. Kagan, *Appl. Phys. Lett.* **2009**, 95(2), 023301/1-023301/3; d) C. Bock, D. V. Pham, U. Kunze, D. Käfer, G. Witte, A. Terfort, *Appl. Phys. Lett.* **2007**, 91(5), 052110/1-052110/3.
[10] a) J. A. Godsell, M. Stacey, J. C. Tatlow, *Nature* **1956**, *178*, 199–200; b) W. J. Pummer, L. A. Wall, *Science* **1958**, *127*, 643–644; c) C. L. Cheong, B. J. Wakefield, *J. Chem. Soc. Perkin Trans. 1* **1988**, *12*, 3301–3305.
[11] D. D. Callander, P. L. Coe, J. C. Tatlow, *Tetrahedron* **1966**, *22*, 419–432.
[12] G. G. Yakobson, V. D. Shteingarts, A. I. Miroshnikov, N. N. Vorozhtsov, *Dokl. Akad. Nauk SSSR* **1964**, *159*, 1109.
[13] a) M. Schlosser, E. Marzi, *Chem. Eur. J.* **2005**, *11*, 3449–3454; b) M. Stratakis, P. G. Wang, A. Streitwieser, *J. Org. Chem.* **1996**, *61*, 3145–3150.
[14] D. D. Callander, P. L. Coe, J. C. Tatlow, R. C. Terrell, *J. Chem. Soc. C* **1971**, 1542–1547.
[15] D. J. Byron, A. S. Matharu, R. C. Wilson, *Liq. Cryst.* **1995**, *19*, 39–45.
[16] CCDC-759867 contains 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.
[17] a) W. B. Gleason, D. Britton, *Cryst. Struct. Commun.* **1976**, *5*, 483–488; b) M. J. Hamor, T. A. Hamor, *Acta Crystallogr., Sect. B* **1978**, *34*, 863–866.
[18] a) H. M. Rietveld, E. N. Maslen, C. J. B. Clews, *Acta Crystallogr., Sect. B* **1970**, *26*, 693–706; b) J. L. Baudour, Y. Delugeard, P. Rivet, *Acta Crystallogr., Sect. B* **1978**, *34*, 625–6258.
[19] a) P. Guionneau, J.-F. Letard, D. S. Yufit, D. Chasseau, G. Bravic, A. E. Goeta, J. A. K. Howard, O. Kahn, *J. Mater. Chem.* **1999**, *9*, 985; b) M. Tominaga, H. Masu, K. Yamaguchi, I. Azumaya, *Chem. Lett.* **2006**, *35*, 718–719.
[20] C. W. Bunn, E. R. Howell, *Nature* **1954**, *174*, 549.
[21] N. Ballav, B. Schuepbach, O. Dethloff, P. Feulner, A. Terfort, M. Zharnikov, *J. Am. Chem. Soc.* **2007**, *129*, 15416–15417.
[22] D. L. Allara, R. G. Nuzzo, *Langmuir* **1985**, *1*, 45–52.
[23] *X-Area. Area-Detector Control and Integration Software*, Stoe & Cie, Darmstadt, Germany, **2001**.
[24] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–35.
[25] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[26] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Received: February 3, 2010
Published Online: April 14, 2010

