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Synthesis of Supercritical Carbon Dioxide Soluble Perfluorinated Dendrons for Surface Modification

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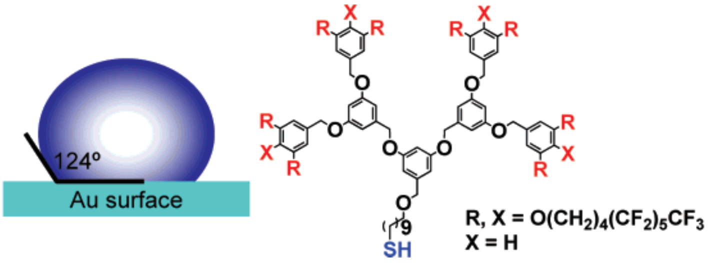

The rational design, synthesis, and characterization of a series of novel perfluorinated dendrons **14a**,**b**, **25a**,**b**, **26a**,**b,** and **18** are described. The dendrimers were designed to have a thiol at the focal point for attachment to a gold surface to enable the fabrication of self-assembled monolayers (SAMs). Perfluorinated tails were attached to the periphery to provide solubility in supercritical carbon dioxide, and to increase the hydrophobicity and the stability of self-assembled monolayers formed. Mitsunobu reactions were utilized to provide high-yielding steps allowing large-scale production of the novel dendrimers.

Introduction

The hydrophobicity of a solid surface is important for many applications, for example, in self-cleaning and antifogging windows and snow or raindrop repelling surfaces.[1] There has also been increased interest in hydrophobic surfaces in the biotechnology sector for use in self-cleaning surfaces for DNA and protein microarrays[2] and for use in microfluidic channels.[3,4]

Dendrimers are highly branched three-dimensional macromolecules with controlled structures, a single molecular weight, and flexibility for tailored functionalization.[5] The aim of the work presented below was to synthesize novel dendrons, which have fluorinated end-groups with a thiol at the focal point for attachment to a gold surface. The chemisorption of Fréchet-type dendrons has only been investigated by a small number of groups[6−11] and fluorinated dendrons have never been studied

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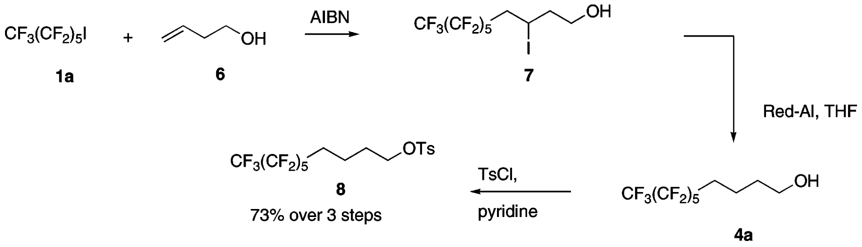
SCHEME 1. Synthesis of Fluorinated Side Chains



before. Gorman et al. have reported that dendritic systems cannot lead to well-organized close-packed surfaces.[8] However, Zhang et al. have reported that polyether dendron thiols can lead to patterned stripes with nanometer-sized features and long-range order.[6,11] It therefore seems that the organization of dendrons on surfaces is not well understood. The durability of self-assembled monolayers (SAMs) of thiols on gold is known to be enhanced by the introduction of fluorocarbon terminal groups in the case of linear alkanethiol molecules.[12,13] Additionally, it has been reported that the fluorination of alkyl-terminated dendritic molecules improves the stability of hexagonal columns induced by the perfluorinated supramolecular structures.[14,15] Therefore, it is expected that SAMs formed by using the novel fluorinated dendrons will provide stable surfaces. Another advantage of using a dendron is that if a pinhole was to form in the monolayer by the removal of a dendron from the surface, the highly branched dendrons should branch out to cover the hole. Furthermore, owing to the higher molecular weight of dendrons compared with a simple *n*-alkanethiolate, the molecules are less volatile and therefore the surfaces formed should be more thermally stable. The high molecular weight and the branched nature of a dendrimer, combined with the low surface energy should enable us to fabricate a surface that is physically and thermally stable as well as providing an appropriate degree of hydrophobicity.

Supercritical carbon dioxide ($scCO_2$), readily accessible with a T_c of 31 °C and P_c of 73 atm, has excellent potential for achieving the goal of an environmentally friendly, economical reaction medium. It is abundant, inexpensive, nonflammable, nontoxic, and environmentally benign.[16] CO_2 has a high solubility for many nonpolar and some polar small organic molecules. However, it is a very poor solvent for most high molecular weight molecules under readily achievable conditions. Fluorinated compounds, such as those described in this paper, have low solubilities in most organic solvents but can be processed in halogenated solvents. The disadvantages of these solvents include their toxicity, price, and adverse impact on the atmosphere. However, fluorinated macromolecules are soluble in $scCO_2$.[17] Additionally, it has been shown that SAMs can be formed with a greater overall chain density and at a faster rate by using compressed CO_2 as a solvent instead of common organic solvents.[18−20] With these factors in mind, CO_2-soluble fluorinated dendrons were designed and synthesized for the formation of stable hydrophobic SAMs. Although, zero-generation perfluorinated dendritic wedges and perfluorinated dendrons with one alkyl chain per monomer have been synthesized before,[14,15,21−27] perfluorinated dendrons with a large density of perfluorinated alkyl chains have never been synthesized, largely due to the steric hindrance and decreased reactivity that the large and electronegative fluorine atoms provide. In this report we describe, for the first time, the large scale synthesis of perfluorinated dendrons with high fluorine content. Additionally, the properties of the SAMs formed by these perfluorinated dendrons are reported. The SAMs formed in $scCO_2$ show superior chemical and thermal stability compared to SAMs formed in conventional organic solvents.

Results and Discussion

Dendrimers can be synthesized in two ways: one is the divergent method where the molecule is built up from the inside,[28] and the other is Fréchet's convergent method where the molecule is synthesized from the outside.[29] One of the problems associated with the divergent method is that as the dendrimer generation increases, the number of reactive centers increases. Therefore, the number of reactions involved in one step increases exponentially. If incomplete reaction occurs, then the number of impurities increases. In the case of the convergent method, since the number of reactive centers remains constant as the dendrimer generation increases, this problem is avoided. With this in mind, the dendrons were synthesized by using the convergent methodology.

The first step in the sequence of reactions was the synthesis of the semifluorinated side chain for the end-groups of the dendron. Two routes were investigated: 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,

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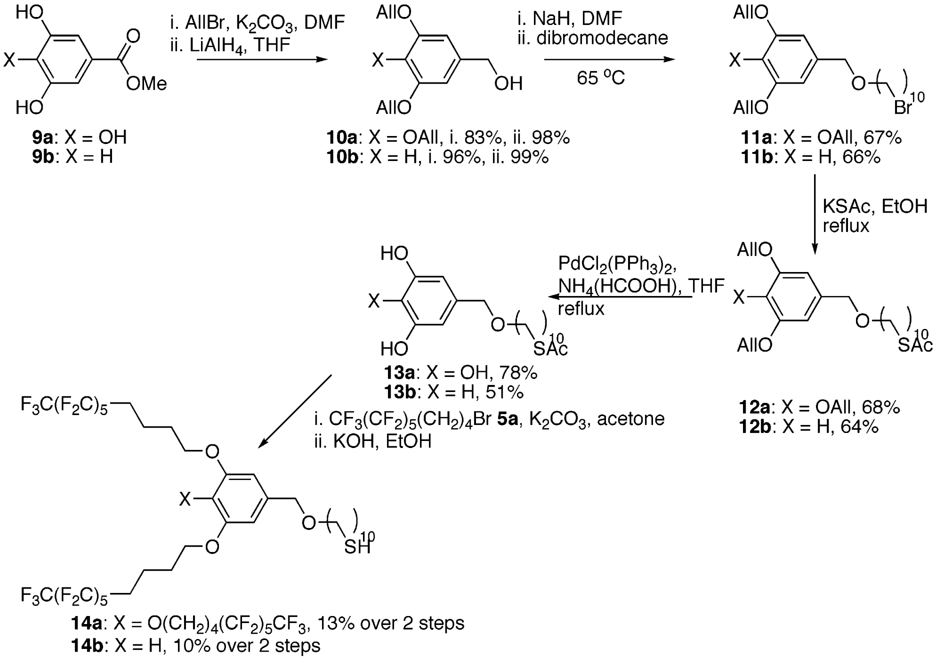
SCHEME 2. Synthesis of the Zero-Generation Dendrons 13a and 13b



4*H*,4*H*-perfluorodecyl bromide **5a** and 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorotetradecyl bromide **5b** were synthesized following a similar route to that described by Johansson et al.[26] shown in Scheme S1 in the Supporting Information; Scheme 1 outlines an alternative route for the synthesis of tosylate **8**, which provided the perfluorinated side chain in a greater yield. The key step in both routes is the radical addition of a perfluoroalkyl iodide to an olefin.[30] The route started with 3-butene-1-ol **6** for the radical addition reaction to yield alcohol **7**. Using sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al) as a reducing agent instead of $LiAlH_4$ allows removal of iodine under milder conditions and in higher yield. Finally the alcohol **4a** was transformed quantitatively into the tosylate **8**. This alternative route allowed the synthesis of the fluorinated side chain with a yield of 73% over three steps compared with the original route, which only gave a 50% yield. Furthermore, the tosylate **8** can be easily prepared on a multigram scale (25.8 g synthesized).

Scheme 2 outlines the synthesis of the zero-generation dendron thiols **14a** and **14b**. Initially, a totally convergent method was attempted but failed. The reasons for this are discussed in the Supporting Information. Methyl 3,4,5-trihydroxybenzoate **9a** and methyl 3,5-dihydroxybenzoate **9b** were protected by using allyl bromide in DMF at 60 °C with K_2CO_3 as a base. This afforded the protected methyl esters in excellent yields of 83% and 96%, respectively. The allyl group was chosen as the protecting group owing to its ease of attachment, stability over the required functional group manipulations, and ease of removal. Other protecting groups were also attempted but failed. These are described in the Supporting Information.

Reduction of the methyl esters with $LiAlH_4$ provided alcohols **10a** and **10b** in good yields of 98% and 99%, respectively. The next step involved the formation of the ethers **11a** and **11b** by the alkylation of the alkoxides with 3 equiv of dibromodecane followed by nucleophilic addition of thioacetate to allow the introduction of the thiol focal point, giving thioacetates **12a** and **12b** in good yield. Initial studies examined the introduction of the thioacetate side chain in a single step from alcohol **10a** and **10b**. However, the thiol protecting group proved to be unstable under the basic conditions of NaH and DMF. Therefore, the thiol focal point was introduced in a stepwise manner as shown. An alternative method was also investigated for the introduction of the thioacetate and the route is shown in Scheme S2 in the Supporting Information. This route was only used for the synthesis of **12b** and not **12a**, but allowed the synthesis of the intermediate in a similar yield to that of the first route but at lower temperatures and with the use of less material, making the synthesis more amenable to large-scale reactions.

The last step toward the synthesis of precursor **13a** and **13b** was the removal of the allyl groups in **12a** and **12b**, which involved the isomerization of the allyl group to an enol ether followed by acid hydrolysis. A number of catalysts were attempted for the isomerization which included a Pd catalyst and $RhCl_3$. However, in all cases the cleavage of the allyl groups was unsuccessful, even though we did find evidence for migration of the double bond. Finally, we found that the use of $PdCl_2(PPh_3)_2$ with $NH_4(HCOOH)$ and with THF as solvent yielded **13a** and **13b** in 78% and 51%, respectively.[31]

Unfortunately, the deprotection protocol with the Pd catalyst in the presence of $NH_4(HCOOH)$ gave rise to reactions with variable yields which made it very difficult to transfer the reaction onto a larger scale. An efficient deprotection method of allyamines with malonate as a soft nucleophile was described by Mortreux et al. with Ni(0) and Pd(0) as a catalyst.[32] This mild method was used for deprotection of the allylether in **12b** and to generate the desired dihydroxy thioacetate **13b** in 70% yield (Scheme 3). Interestingly, the deprotection was found to proceed only in the presence of both transition metals Ni and Pd. Also the presence of a catalytic amount of Et_4NBF_4 and an

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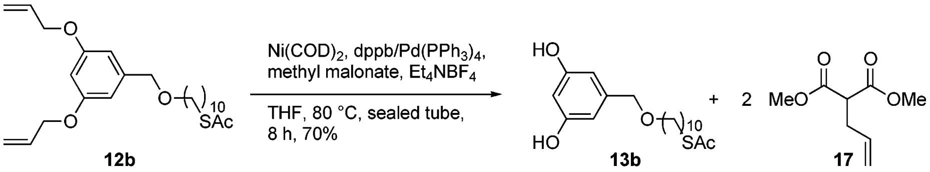
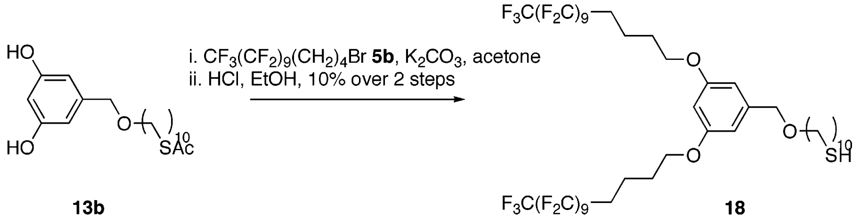
SCHEME 3. Deprotection of the Allylether with Methyl Malonate to Achieve Coupling Precursor 13b



dppb = *bis*-diphenylphosphinobutane
NiCOD = Nickel(0)cyclooctadiene

SCHEME 4. Synthesis of the Zero-Generation Perfluorinated Dendron 18



excess of methyl malonate was necessary to improve the yield of dihydroxy thioacetate **13b**.[33]

The final steps in the synthesis of the zero-generation dendrons involved alkylation of phenolate anions derived from **13a** and **13b** followed by deprotection of the thiol group. Alkylation of thioacetates **13a** and **13b** with perfluorobromide **5a** in refluxing acetone containing K_2CO_3 gave the esters in low yield. This is due to either the suppression of reactivity of the bromoalkane by the electron-withdrawing fluorine atoms and/or the unwanted premature cleavage of the thioester of the thiol derivative under the basic conditions. The final step involving the deprotection of the thiol derivatives under basic conditions provided the zero-generation dendron thiols **14a** and **14b**. The basic conditions required short reaction times of approximately 10 min at room temperature. This method was preferred to acidic conditions, which require refluxing for over 12 h. It has been reported that basic conditions give disulfide side products but this was not observed in the present work.[34]

The synthesis of the zero-generation dendron thiol **18** with a longer fluorinated side chain is shown in Scheme 4. It has been reported that the length of the perfluorinated unit attached to an *n*-alkanethiol could affect the hydrophobicity of the surface.[13,35] Therefore, dendron thiol **18** was synthesized as a comparison with dendrimer thiol **14b**. The synthetic route is very similar to that previously described. Alkylation of the common intermediate **13b** followed by deprotection of the thiol gave dendron thiol **14b** in a yield of 10%. The alkylation step was poor yielding as explained previously. In this case, acid deprotection of the intermediate thioacetate was attempted as a comparison. This provided thiol **18** in higher yields as observed by TLC. This shows that the deprotection can be carried out under either basic or acidic conditions indicating the high flexibility of the thioester, and both methods have been performed for larger generation dendrimers.

With the zero-generation dendrons **14a**, **14b**, and **18** in hand, the synthesis of the larger generation dendrons was attempted. To use the common intermediate **13b**, while at the same time keeping to the convergent dendrimer synthesis methodology as much as possible, the zero-generation dendron bromides **20a** and **20b** were synthesized as shown in Scheme 5.

Methyl 3,4,5-trihydroxybenzoate **9a** and methyl 3,5-dihydroybenzoate **9b** were alkylated with 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecyl bromide **5a** in DMF at 65 °C with K_2CO_3 as base. Subsequent reduction with $LiAlH_4$ afforded the benzyl alcohols **19a** and **19b** in excellent yields. Bromination with CBr_4 and PPh_3[29] in the presence of DIPEA in dichloromethane provided the zero-generation dendrimer bromides **20a** and **20b** as required.

Similarly, the first-generation dendron bromides **23a** and **23b** were synthesized as shown in Scheme 5. Alkylation of 3,5-dihydroxybenzyl alcohol **21** with bromides **20a** and **20b** followed by bromination yielded the first-generation bromides **23a** and **23b** in moderate yields. Acetone was chosen as the solvent for alkylation instead of DMF due to its ease of removal. The first-generation dendron **22b** was also synthesized by using the Mitsunobu reaction[36] as shown in Scheme 5. The Mitsunobu reaction allows a short and efficient route to build up the dendrimer and works well even on a multigram-scale synthesis. Reduction of ester to the corresponding alcohol with $LiAlH_4$ proceeded in 71% yield providing dendron **22b** in an overall 63% yield as compared to 48% with the Fréchet methodology.

The final steps in the synthesis of the dendron thiols **25a**, **25b**, **26a**, and **26b** involved the coupling of the intermediate **13b** with the appropriate benzyl bromides. Scheme 6 shows the last stages in the preparation of second-generation dendrimer thiols **25a** and **25b**. Alkylation followed by acid deprotection afforded the thiols **25a** and **25b** in 10% and 12% yields, respectively. The yields of the alkylation steps were again low and may be ascribed to the labile thiol protecting group and the destabilizing effect of the fluorine atoms.

Scheme 7 shows the final stages in the synthesis of the second-generation thiols **26a** and **26b**. The same reagents as before were used in these steps. The alkylation steps involved gave higher yields than those steps of **25a** and **25b**. This may be due to the fact that the fluorinated groups are now sufficiently far from the electrophilic center that the destabilizing effect on the transition state is significantly reduced.

The previously successful Mitsunobu reaction conditions for alkylation of phenols were exploited to prepare dendrons **25a**

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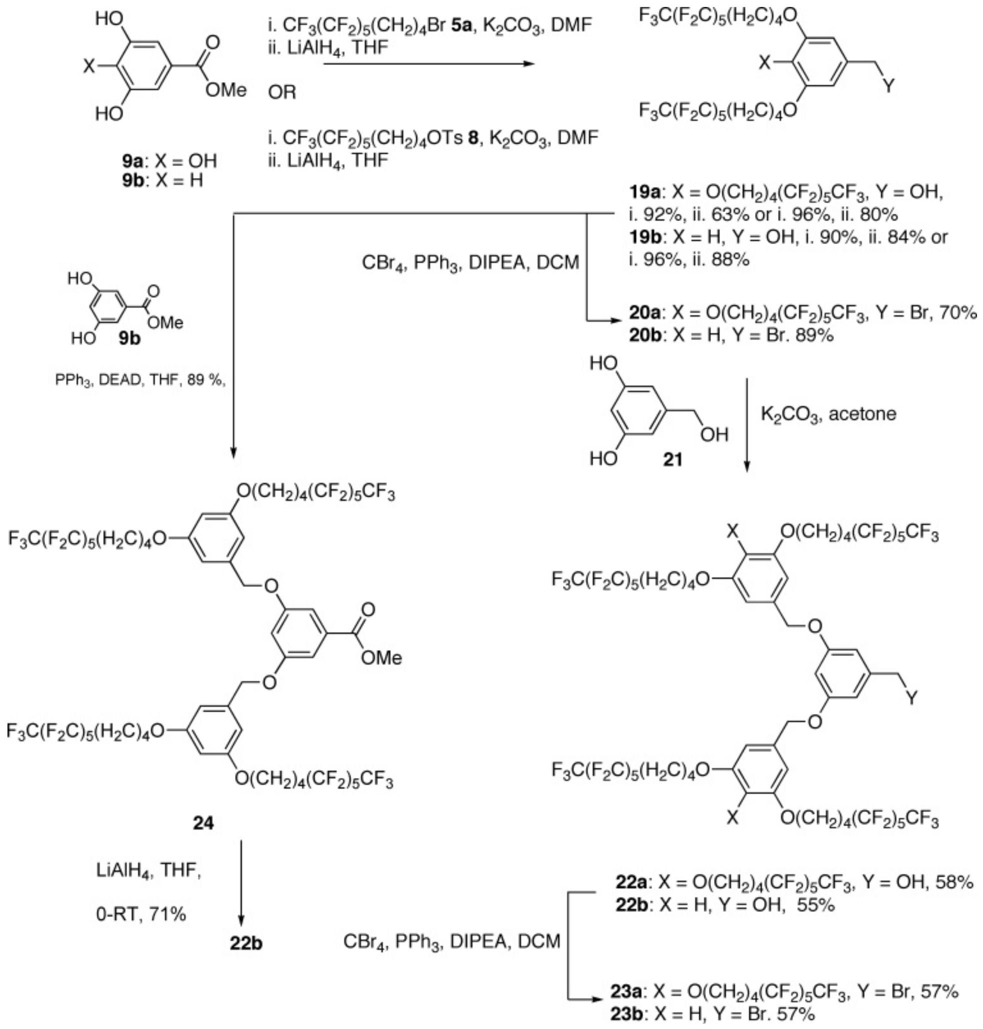
SCHEME 5. Synthesis of the Zero- and First-Generation Dendrons



and **26b** (Schemes 6 and 7, respectively). Dendron **25a** was synthesized by the coupling of the intermediate **13b** with benzyl alcohol **22b**. It was realized that the initial acidic deprotection of the thioacetate into the thiol was inadequate to improve the yield. Thus the synthetic strategy was tuned toward the conditions of basic deprotection. This gave the final dendron **25a** in 66% yield, which is a significantly better yield than the route with the benzyl bromide **20a**. Similarly, dendron **26b** was synthesized by using the same conditions in 76% yield.

Formation of Self-Assembled Monolayers. The synthesized perfluorinated dendrons were then evaluated in the formation of self-assembled monolayers (SAMs) on gold. SAMs were prepared in a conventional solvent by placing a freshly evaporated Au substrate (200 nm Au, 20 nm Cr as an adhesion layer, on Si/SiO$_2$) in a 1 mM solution of the dendrons in CH$_2$Cl$_2$ at 25 °C for 1 h. It was expected that larger dendrons might show slower kinetics, as Peterlinz et al. have observed chain length dependent kinetics.[37] However, longer deposition times did not lead to observable changes in thickness or contact angle. Typical results for contact angles and ellipsometrically determined thickness values of the different generation dendrons are reported in Table 1. Not surprisingly, a comparison between the dendron series **14a**, **25a**, and **26a** and the series **14b**, **25b**, and **26b** shows that the hydrophobicity of the monolayers exhibits a slight increase with dendron generation and also that the hydrophobicity increases with the number of perfluoroalkyl chains per dendritic branch. Furthermore, Table 1 also shows the variation in water contact angle with respect to the length of the perfluoroalkyl chain on the dendron, therefore comparing the contact angles between surfaces formed with dendrons **14b** and **18**. The contact angles are considerably higher for monolayers formed with dendron **18** (119°/110° for θ_a/θ_r) compared with monolayers formed with dendron **14b** (109°/101°). This is to be expected as it has been reported that the increase in fluorinated units in an *n*-alkylthiolate SAM increases the hydrophobicity of the surface.[13]

TABLE 1. The Ellipsometry Thickness and Water Contact Angles of Monolayers of Dendrons 14a, 14b, 25a, 25b, 26a, 26b, and 18 Formed in CH$_2$Cl$_2$, Compressed CO$_2$, and Octafluorotoluene

	thickness (Å)				contact angle (θ_a/θ_r) (deg)		
	CH$_2$Cl$_2$	CO$_2$	OFT	theor.[a]	CH$_2$Cl$_2$	CO$_2$	OFT
14a	7.6	22.0		33	112/103	120/111	
25a	13.2	39.9		39	116/103	118/102	
26a	20.1	42.3		45	118/105	126/114	
14b	10.5	24.5	9.7	32	109/101	117/114	98/88
25b	14.0	38.7	10.7	45	113/104	120/115	106/96
26b	21.8	43.1	13.2	46	114/116	123/116	100/95
18	20.7	28.6	7.0	39	119/110	124/113	107/98

[a] Theorectical values obtained from MM2 calculations.[38]

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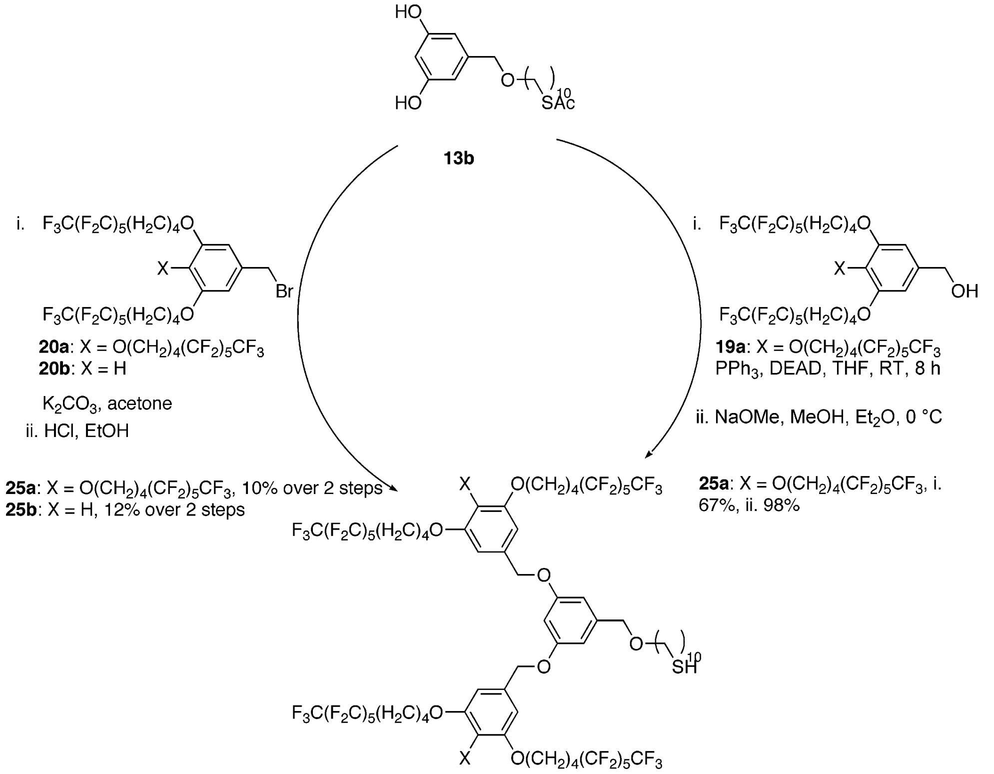
SCHEME 6. Synthesis of First-Generation Dendrons 25a and 25b



As mentioned, solvent molecules can greatly affect the kinetics of SAM formation as well as their properties. We therefore investigated dendron SAM formation in octafluorotoluene (OFT) and compressed CO_2, which are good solvents for fluorinated compounds. For the experiments with CO_2, the gold surfaces were placed into a 10 cm^3 CO_2 vessel along with the dendron thiols **14a**, **14b**, **25a**, **25b**, **26a**, **26b**, and **18** (0.01 mmol). Liquid CO_2 was passed into the vessel, the temperature was raised to 40 °C, and the pressure was adjusted by the further addition of CO_2 until a pressure of 1000 psi was obtained. After 1 h, the pressure of the vessel was released and the surfaces were cleaned of any excess physisorbed dendrons by rinsing with liquid CO_2. Surprisingly, we found that SAMs formed in OFT (or in mixtures of OFT with CH_2Cl_2) showed markedly lower contact angles and ellipsometry values, indicating that the SAMs were more disordered when deposited from OFT (Table 1).

The ellipsometric thicknesses of the monolayers formed in CH_2Cl_2, OFT, and CO_2 are summarized in Table 1 and the theoretical value of the extended length of the dendrons is included as a comparison. The theoretical value was obtained by performing MM2 optimization calculations on the molecules.[38] The MM2 calculations are those of free molecules in the gas phase rather than of molecules restricted on a surface, and therefore do not predict actual monolayer thickness measurements. This could be addressed by further work on the theory of macromolecule−surface interactions. Nevertheless, the values give an indication of how large the molecules are. These results suggest that for the monolayers formed in CH_2Cl_2 and OFT, the monolayers are not complete and/or the dendrons are not fully extended whereas the monolayers formed in CO_2 are probably complete and fully extended. The changes in ellipsometry thicknesses are matched by the changes in contact angles.

TABLE 2. The Hexadecane Contact Angles and Water Contact Angle Hystereses of Monolayers of Dendrons 14b, 25b, 26b, and 18

	hexadecane contact angle (deg)			hysteresis		
	CH_2Cl_2	CO_2	OFT	CH_2Cl_2	CO_2	OFT
14b	38	60	51	0.13	0.05	0.17
25b	34	71	49	0.15	0.08	0.17
26b	37	66	52	0.03	0.11	0.09
18	48	72	51	0.14	0.17	0.15

The hexadecane contact angles of SAMS formed from linear perfluoroalkyl chains vary between 77° and 83°.[13] Semifluorinated SAMs are expected to show high hexadecane contact angles because of the weak and nonideal dispersive interactions between hydrocarbons and fluorocarbons. However, the hexadecane contact angles of the monolayers formed in CH_2Cl_2 and OFT presented in Table 2 are low and are in the range of those expected from a linear alkyl chain SAM. The low contact angles observed in the present work may be due to the increased disorder on the surface of these dendron monolayers. However, the hexadecane contact angles of the monolayers formed in CO_2 are large, indicating that the monolayers formed in CO_2 are more tightly packed than those formed in organic solvents.

The contact angle hystereses of the monolayers formed in the various solvents are summarized in Table 2. For comparison, the contact angle hysteresis[39] of a monolayer of $CF_3(CF_2)_9(CH_2)_{11}SH$ on gold formed in CH_2Cl_2 is 0.08. The general trend for the data appears to be that the hystereses are highest for monolayers formed in OFT and lowest for monolayers formed

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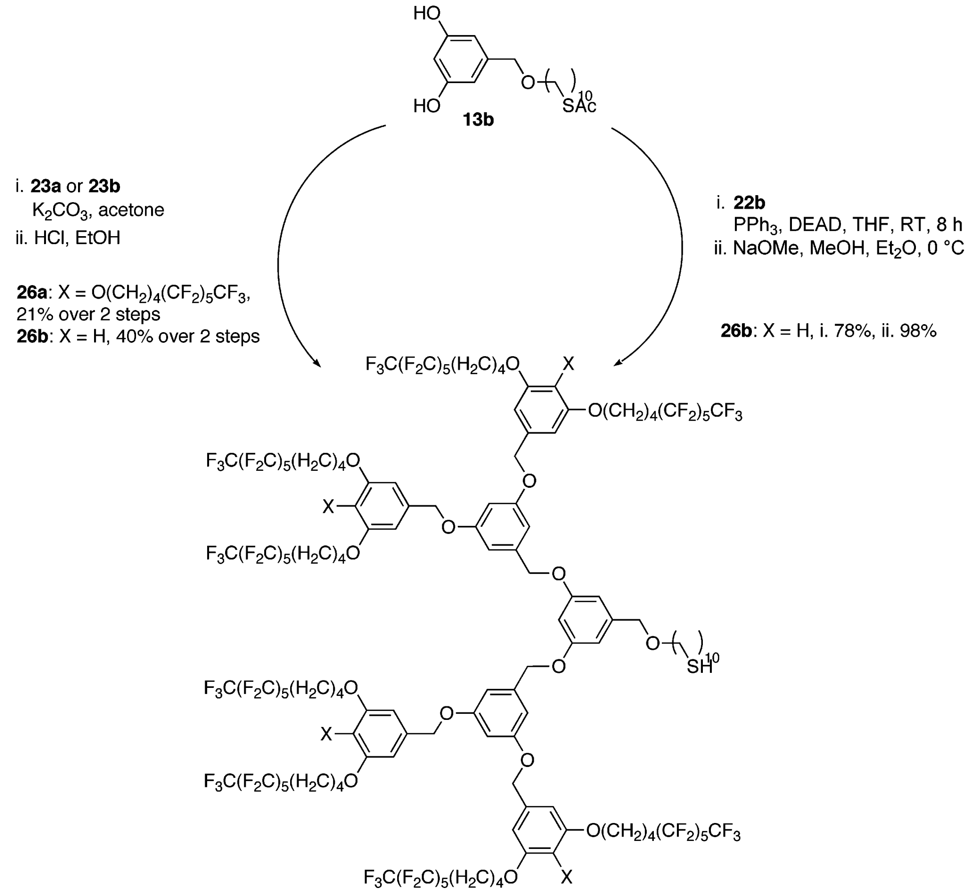
(38) Obtained with Chem3D Pro 8.0 by CambridgeSoft.

(39) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

SCHEME 7. Synthesis of Second-Generation Dendrons 26a and 26b



in CO$_2$, again illustrating that these SAMs exhibit the densest packing. It has been reported by Yan et al.[40] that polar solvents give rise to more densely packed *n*-alkylthiol monolayers. However, the dielectric constant of CO$_2$ is similar to that of OFT and significantly lower than that of CH$_2$Cl$_2$. The observed denser packing can be explained by considering that CO$_2$ is considerably smaller in size compared with OFT, therefore perhaps allowing tighter packing of the molecules on the surface.

One of the major drawbacks for practical use of thiolate monolayers as protective coatings on gold is their limited stability when heated in air or solvents. To study the thermal stability of the dendron monolayers, the monolayers of dendrons **14b**, **25b**, **26b**, and **18** formed in CH$_2$Cl$_2$, OFT, and CO$_2$ were incubated for 1 h in air in an oven at 150 °C or in DMSO solvent at 150 °C. It had been reported that the thermal stability of a monolayer increases with the length of the monomer used to form the SAM. Hence it was envisaged that the fluorinated dendrons would show increasing stability with dendron generation, and would also show greater stability than a linear alkyl SAM. Semifluorinated linear alkyl SAMs show up to 74% decrease of hexadecane contact angles after incubation for 1 h at 150 °C.[13] However, all dendron monolayers deposited from CHCl$_2$ or OFT show total desorption. This would mean that the dendron monolayers are less thermally stable than the linear perfluoroalkyl SAMs. In contrast, the monolayers formed in CO$_2$ proved to be more robust and the ellipsometry and contact angle results of the monolayers before and after thermal and chemical treatment are summarized in Table 3. After treatment, the monolayers have reduced significantly in thickness but the water contact angles remained high, especially after the thermal treatment. During the incubation, some of the dendrons may desorb from the surface thereby reducing the packing density of the monolayer, allowing the dendritic branches to spread over the surface giving rise to the reduction in ellipsometry thickness and contact angle, and an increase in hysteresis.

TABLE 3. The Ellipsometry Thickness and Water Contact Angle Before and After Thermal and Solvent (DMSO) Treatment

	thickness (Å)			water contact angle (deg)		
	before	thermal	chemical	before	thermal	chemical
14b	24.5	10.7	11.3	117/114	114/98	93/82
25b	38.7	25.1	7.7	120/115	116/105	92/86
26b	43.1	26.8	22.0	123/116	117/108	92/85
18	28.6	11.2	11.0	124/114	123/110	112/101

Conclusion

In conclusion, we have prepared a number of thiol-terminated dendritic wedges with perfluorinated tails. By exploring different reaction conditions, we were able to follow a (mostly) convergent route to prepare these dendritic wedges on a gram scale. In this synthetic work, generations 0, 1, and 2 were synthesized and the number of perfluorinated tails per end-group was varied. Additionally, SAMs formed with the perfluorinated macromolecules were studied. The SAMs formed in scCO$_2$ showed increased robustness compared to when the SAMs were formed

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(40) Yan, D.; Saunders, J. A.; Jennings, G. K. *Langmuir* **2000**, *16*, 7562.

in conventional organic solvents. We believe that the dendron-based SAMs provide a new and interesting route to structurally different monolayers.

Experimental Section

A typical procedure for the large-scale synthesis of a thiol-terminated perfluorinated dendron is as follows:

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-3-iodo-decan-1-ol (7). To a Schlenk tube were added perfluorohexyl iodide **1a** (20 g, 45 mmol), 3-buten-1-ol **6** (3.9 g, 54 mmol), and AIBN (0.37 g, 2.2 mmol). The reaction mixture was degassed by the freeze−pump−thaw method (repeated 3 times) and heated to 80 °C under nitrogen atmosphere. After being stirred for 2 h, it was cooled to room temperature, another portion of AIBN (0.37 g, 2.2 mmol) was added, and the solution was heated again to 80 °C. After being stirred for 3 h the reaction mixture was poured directly into warm *n*-hexane (100 mL) and crystallized overnight in the fridge. The precipitated white solid was collected, washed with small portions of *n*-hexane, and dried under reduced pressure to give the alcohol (20 g, 87%) as white crystals: mp 45−48 °C (from *n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.6 (br s, 1H), 1.99−2.11 (m, 2H), 2.83−3.06 (m, 2H), 3.78−3.93 (m, 2H); NMR spectra agreed with values quoted in the literature.[41]

1*H*,1*H*,2*H*,2*H*,2*H*,3*H*,4*H*,4*H*-Perfluorodecan-1-ol (4a). To a magnetically stirred solution of sodium bis(2-methoxyethoxy)-aluminum hydride (70 wt % solution in toluene, 36 g, 123 mmol) in anhydrous diethyl ether (500 mL) was added alcohol **7** (34 g, 65 mmol) dissolved in anhydrous diethyl ether (100 mL) dropwise at room temperature under a nitrogen atmosphere. After 3 h of stirring at room temperature, 2 M HCl aqueous solution (300 mL) was added dropwise. The organic layer was then separated, washed with brine (150 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography (1:1 hexane:EtOAc) to give alcohol **4a** (23 g, 91%) as a colorless viscous liquid: ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.43 (br s, 1H), 1.62−1.76 (m, 4H), 2.04−2.18 (m, 2H), 3.70 (t, J = 6.0 Hz, 2H); NMR spectra agreed with values quoted in the literature.[34]

3,5-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecan-1-yloxy)-benzyl Alcohol (19b). To a magnetically stirred solution of perfluorinated alcohol **4a** (23 g, 58 mmol) and pyridine (11 mL, 79 mmol) in DCM (250 mL) was added *p*-toluenesulfonyl chloride (15 g, 79 mmol) in an ice/water bath under a nitrogen atmosphere. The reaction mixture was then stirred for 1 h in an ice/water bath and overnight at room temperature. After completion of the reaction, the DCM solution was concentrated under reduced pressure and the resulting slurry was purified by flash chromatography (5:1 hexane:EtOAc) to give tosylate **8** (26 g, 81%) as a white solid.

To a magnetically stirred clear solution of tosylate **8** (5.46 g, 10 mmol) and 3,5-dihydroxy benzoate **9b** (0.78 g, 4.6 mmol) in dry DMF (18 mL) was added K_2CO_3 (1.8 g, 13 mmol) and the mixture was heated to 65 °C for 8 h. The solution was then cooled to room temperature and ether (100 mL) and water (100 mL) were added. The aqueous phase was extracted with ether (3 × 100 mL) and the collected organic phase was washed with brine (3 × 50 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (1:10 ethyl acetate:hexane v/v) to give the ester (4.05 g, 96%) as a white solid: R_f 0.44 (3:1 hexane:EtOAc); mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (s, 2H), 6.36 (s, 1H), 4.63 (s, 2H), 3.99 (t, J = 8.0 Hz, 4H), 2.16 (m, 4H), 1.89−1.80 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 143.4, 120.4, 118.3, 116.0, 113.1, 111.0, 108.6, 105.0, 100.5, 67.2, 65.3, 30.6, 29.2, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.1 (m, 6F), −114.7 (m, 4F), −122.1 (m, 4F), −123.1 (m, 4F), −123.8 (m, 4F), −126.4 (m, 4F); $\upsilon_{\max}$ ($CHCl_3$) 3458, 1636, 1472 cm^{-1}; *m/z* (EI) 888.1155 [$M^+ \cdot C_{27}H_{22}F_{26}O_3$ requires *M* 888.1154], 890 [M^+, 3%], 889 (34), 888 (100), 887 (9), 886 (24). Anal. Calcd for $C_{27}H_{22}F_{20}O_3$; C, 36.5; H, 2.5. Found: C, 36.9; H, 2.4.

3,5-Bis[3,5-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecan-l-yloxy)benzyloxy]benzyl Alcohol (22b). Diisopropyl azodicarboxylate (0.67 mL, 3.3 mmol) was slowly added to a stirred solution of alcohol **19b** (2.94 g, 3.3 mmol), 3,5-dihydroxy ester **9b** (0.28 g, 1.7 mmol), and PPh_3 (0.87 g, 3.3 mmol) in THF (6.6 mL) at room temperature. After being stirred overnight at room temperature the reaction mixture was purified directly by flash chromatography (10:1 hexane/EtOAc) to give ester **33** (2.83 g, 89%) as a white solid. To a magnetically stirred slurry of $LiAlH_4$ (0.15 g, 3.4 mmol) in anhydrous THF (2 mL) was added ester **24** (3.2 g, 1.68 mmol) dissolved in anhydrous THF (5 mL) dropwise at 0 °C under a nitrogen atmosphere. After 4 h of stirring at room temperature, the reaction was quenched by dropwise addition of water (0.35 mL), 0.5 N NaOH (0.35 mL), and water (1 mL) to give a white precipitate. The reaction mixture was filtered trough celite and washed with diethyl ether and then the filtrate was concentrated under reduced pressure. The residue was extracted with diethyl ether (3 × 50 mL) and the organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (3:1 hexane:EtOAc) to give alcohol **22b** (2.25 g, 71%) as a white solid: R_f 0.14 (5:1 hexane: EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (s, 2H), 6.56 (s, 4H), 6.52 (s, 1H), 6.39 (s, 2H), 4.96 (s, 4H), 4.64 (s, 2H), 3.98 (t, J = 6.0 Hz, 8H), 2.11 (m, 8H), 1.95−1.84 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 160.1, 143.4, 139.2, 120.4, 118.3, 116.0, 113.2, 110.7, 108.6, 105.7, 105.1, 101.3, 100.6, 70.0, 67.2, 65.3, 30.7, 28.6, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.1 (m, 12F), −114.7 (m, 8F), −122.2 (m, 8F), −123.1 (m, 8F), −124.2 (m, 8F), −126.4 (m, 8F); $\upsilon_{\max}$(film) 3442, 1636, 1456 cm^{-1}; *m/z* (FAB) 1904 [M + Na^+, 60%], 1881 (60), 1741 (75), 1157 (95), 1048 (100), 871 (l00), 218 (l00).

3,4,5-Tris(prop-2-en-1-yloxy)benzyl Alcohol (10a). To a flame-dried 100-mL three-necked flask equipped with a pressure equalized dropping funnel under N_2 was added THF (20 mL) and $LiAlH_4$ (1.3 g, 34 mmol). Methyl 3,4,5-tris(prop-2-en-l-yloxy)benzoate **9a** (5.2 g, 17 mmol) was dissolved in THF (20 mL) and added dropwise to the $LiAlH_4$ slurry. The reaction mixture was stirred for 3 h. The reaction was quenched by the dropwise addition of water (1 mL), followed by sodium hydroxide solution (15% aqueous; 1 mL) and water (3 mL) to give a white precipitate. The reaction mixture was filtered and the mixture was concentrated under reduced pressure. The residue was extracted with ether (20 mL) and the organic phases were dried ($MgSO_4$). Purification by flash chromatography (3:1 hexane:EtOAc) furnished the alcohol **10a** (4.63 g, 98%) as a yellow oil: R_f 0.21 (1:1 hexane:EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.50 (s, 2H), 5.97 (m, 3H), 5.11 (m, 6H), 4.49 (d, J = 6.0 Hz, 6H), 4.40 (s, 2H), 2.90 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 152.5, 136.8, 134.6, 133.4, 117.5, 117.2, 105.9, 74.1, 69.8, 65.0; $\upsilon_{\max}$ (film) 3392, 2871, 1649, 1594, 1505 cm^{-1}; *m/z* (ES) 294.1704 [$(M + NH_4)^+ \cdot C_{16}H_{24}NO_4$ requires *M* 294.1704], 294 [$(M + NH_4)^+$, 100%], 277 (66), 259 (98), 235 (15), and 58 (14).

3,5-Bis(prop-2-en-l-yloxy)benzyl Alcohol (10b). To a flame-dried 100-mL three-necked flask equipped with a pressure equalized dropping funnel under N_2 was added THF (60 mL) and $LiAlH_4$ (1.86 g, 49.0 mmol). The ester **9b** (6.08 g, 24.5 mmol) was dissolved in THF (60 mL) and added dropwise to the $LiAlH_4$ slurry. The reaction mixture was stirred for 3 h. The reaction was quenched by the dropwise addition of water (1 mL), followed by sodium hydroxide solution (15% aqueous; 1 mL) and water (3 mL) to give a white precipitate. The reaction mixture was filtered and the mixture was concentrated under reduced pressure. The residue was extracted with ether (20 mL) and the organic phases were dried ($MgSO_4$). Purification by flash chromatography (1:1 hexane:EtOAc) furnished the alcohol **10b** (5.34 g, 99%) as a yellow oil: R_f 0.38 (1:1 hexane:EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.52 (s, 2H), 6.42 (s, 1H), 6.03 (m, 2H), 5.34 (dd, J = 6.0 and 12.0 Hz, 4H),

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(41) Cheng, X.; Das, M. K.; Diele, S.; Tschierske, C. *Langmuir* **2002**, *18*, 6521.

4.55 (s, 2H), 4.49 (d, $J = 6.0$ Hz, 4H), 2.28 (br s, 2H); NMR spectra agreed with literature.[42]

[3,5-Bis(prop-2-en-l-yloxy)benzyloxy]decanyl 10-Thioacetate (12b). To a magnetically stirred clear solution of 1,10-decane bistosylate **15** (6.1 g, 12.6 mmol) in dry THF (50 mL) was added KH (30 wt % suspension in mineral oil, 1.9 g, 12.6 mmol) at room temperature. 3,5-Bis-allyloxy benzyl alcohol **10b** (1.9 g, 8.6 mmol) in dry THF (10 mL) was then added dropwise at room temperature. After 20 min, saturated aqueous NH_4Cl (50 mL) was added carefully at 0 °C followed by DCM (100 mL). The aqueous phase was extracted with DCM (3 × 50 mL) and the organic phase washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography (6:1 hexane:EtOAc) to give tosylate **16** (2.9 g, 70%) as a yellow oil. To a magnetically stirred clear solution of tosylate **16** (2.9 g, 5.97 mmol) in dry DMF (12 mL) was added KSAc (0.86 g, 7.55 mmol) at room temperature with stirring overnight. Then ether (40 mL) and Ac_2O (0.7 mL) were added and the solution was stirred for 1 h at room temperature. Water (10 mL) was then added. The aqueous phase was extracted with ether (3 × 70 mL) and the combined organic phase was extracted with brine (3 × 70 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography (6:1 hexane: EtOAc) to give thioacetate **12b** (1.88 g, 73%) as a yellow oil: R_f 0.28 (1:1 hexane:EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.42 (s, 2H), 4.31 (s, 2H), 3.45 (t, $J = 6.0$ Hz, 2H), 2.85 (t, $J = 6.0$ Hz, 2H), 2.31 (s, 3H), 1.64−1.49 (m, 4H), 1.38−1.18 (m, 12H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 171.6, 144.4, 131.5, 129.8, 108.0, 72.9, 70.4, 30.9, 30.6, 29.4, 29.3, 29.2, 29.0, 28.7, 26.0, 21.0, 14.2; υ_{max} (film) 3450, 2930, 1686 cm^{-1}; m/z (EI) 431 [$(M + H)^+$, 60%], 279 (30), 234 (40), 222 (50), 208 (40), 174 (50), 154 (l00). Anal. Calcd for $C_{25}H_{38}O_4S$: C, 69.1; H, 8.8. Found: C, 68.8; H, 8.8.

[3,5-Bis(hydroxy)benzyloxy]decanyl 10-Thioacetate (13b) To a sealed tube were added thioacetate **12b** (1.0 g, 2.3 mmol), methyl malonate (1.8 g, 13.8 mmol), and THF (6.5 mL). The reaction mixture was degassed by the freeze−pump−thaw method (repeated 3 times), $Pd(Ph_3)_4$ (50 mg), NiCOD (50 mg), and dppb (50 mg) were added, and the mixture was heated to 80 °C under nitrogen atmosphere. After the mixture had stirred for 4 h at 80 °C the reaction was monitored by TLC and another portion of $Pd(Ph_3)_4$ (50 mg) was added. Depending on the reaction progress, it was necessary to add more $Pd(PPh_3)_4$ to the reaction mixture as long as the starting material **12b** could be detected by TLC. After all the starting material **12b** was consumed, water (10 mL) and ether (20 mL) were added. The aqueous phase was extracted with ether (3 × 70 mL) and the combined organic phase was washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash chromatography (gradient 6:1 to 3:1 hexane:EtOAc) to give thioacetate **12b** (0.57 g, 70%) as a yellow oil: R_f 0.32 (1:1 hexane:EtOAc); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.41 (d, $J = 2.0$ Hz, 2H), 6.27 (t, $J = 2.0$ Hz, 1H), 5.35 (br s, 2H), 4.40 (s, 2H), 3.47 (t, $J = 6.5$ Hz, 2H), 2.87 (t, $J = 8.0$ Hz, 2H), 2.34 (s, 3H), 1.63−1.54 (m, 4H), 1.34−1.27 (m, 12H); ^{13}C NMR (100 MHz, $CDC1_3$) δ 157.0, 141.4, 107.0, 102.0, 72.4, 70.5, 30.7, 29.6, 29.5, 29.3, 29.2, 29.2, 28.9, 28.7, 26.0, 23.0; υ_{max} (film) 3392, 2929, 2856, 1690, 1665, 1605, 1455 cm^{-1}; m/z (ES) 355.1938 [$(M + H)^+ \cdot C_{19}H_{31}O_4S$ requires M 355.1943], 355 [$(M + H)^+$, 50%], 250 (68), 233 (58), 206 (31), 140 (32), 125 (100). Anal. Calcd for $C_{l9}H_{30}O_4S$: C, 64.4; H, 8.5. Found: C, 64.6; H, 8.6.

(3,5-Bis{3,5-bis[3,5-bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecan-1-yloxy)benzyloxy]benzyloxy}benzyloxy)decanyl 10-Thiol (26b). Diisopropyl azodicarboxylate (0.23 mL, 1.18 mmol) was slowly added to a stirred solution of alcohol **22b** (2.25 g, 1.18 mmol), 3,5-dihydroxybenzyloxy thioacetate **13b** (0.16 g, 0.45 mmol), and PPh_3 (0.31 g, 1.18 mmol) in THF (5.0 mL) at room temperature. After being stirred overnight at room temperature the mixture was then concentrated under reduced pressure to half of the solvent and purified directly by flash chromatography (gradient 8:1 to 7:1 hexane:EtOAc) to give the dendron thioacetate (1.44 g, 78%) as a yellow oil.

The dendron thioacetate (1.44 g, 0.35 mmol) was solved in Et_2O (6 mL) and MeOH (2.4 mL) and NaH (120 mg, 5.0 mmol) were added at 0 °C then the misture was stirred for 1 h. Next AcOH (1.8 mL) was added dropwise at room temperature and the precipitated solid was dissolved by adding water (5 mL) and Et_2O (20 mL). The mixture was extracted with ether (3 × 20 mL) and the combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography (ether) yielded the thiol **26b** (1.41 g, 98%) as a bright yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 4H), 6.60 (s, 2H), 6.56 (s, 10H), 6.54 (s, 1H), 6.39 (s, 4H), 4.95 (s, 12H), 4.45 (s, 2H), 3.98 (t, $J = 5.5$ Hz, 16H), 3.49 (t, $J = 7.0$ Hz, 2H), 2.49 (m, 2H), 2.10 (m, 16H), 1.86−1.81 (m, 32H), 1.55 (m, 4H), 1.34−1.26 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 160.1, 159.9, 141.3, 139.3, 139.1, 120.4, 115.7, 113.7, 113.2, 109.7, 108.7, 106.4, 106.1, 105.8, 101.5, 101.1, 100.8, 72.7, 70.7, 70.0, 67.2, 66.8, 31.9, 30.6, 29.7, 29.5, 29.4, 28.3, 26.2, 24.6, 22.7, 20.4, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.1 (m, 24F), −113.7 (m, 16F), −122.2 (m, 16F), −122.7 (m, 16F), −123.6 (m, 16F), −126.5 (m, 16F); υ_{max} (film) 2979, 2931, 1560, 1455 cm^{-1}; m/z (MALDI-TOF) 4083 [$(M + K^+$, 20%], 2308 (20), 1972 (100), 1952 (35), 1741 (20).

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Supporting Information Available: General experimental and spectroscopic data for compounds **4a**,**b**, **5a**,**b**, **10**−**14a**,**b**, **15**, **18**, **19**−**20a**,**b**, **22**−**23a**,**b**, and **25**−**26a**,**b**; relevant ellipsometric and characterization data; and schemes for alternative syntheses of **5a**,**b** (Scheme S1) and **12b** (Scheme S2) and an unsuccessful route to **13b** (Scheme S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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[42] Leveque, L.; Le Blanc, M.; Pastor, R. *Tetrahedron Lett.* **1998**, *39*, 8857.