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Articles

Polyphenylene Dendrimers with Pentafluorophenyl Units: Synthesis and Self-Assembly

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ABSTRACT: A series of polyphenylene dendrimers (PDs) incorporating additional pentafluorophenyl units have been synthesized. A key building block thereby is the tetrakis(pentafluorophenyl)cyclopentadienone, which serves as the end-capper for making the outer shells of the dendrimers. The variation of the peripheral pentafluorophenyl content was varied using desymmetrized tetraphenylmethane cores for the divergent construction of the dendrimers. The self-assembled nanostructures, prepared by drop-casting solutions of the second-generation species on highly oriented pyrolytic graphite (HOPG), have been investigated by *tapping mode* atomic force microscopy (AFM). Besides isotropic globular aggregates and percolated networks of nanometer size anisotropic objects, the herein presented dendrimers self-organize into micrometer long nanofibers. The formation of a certain morphology depends upon the amount of pentafluorophenyl rings at the periphery of the dendrimers. Furthermore, it has been observed that by the progressive blending of two dendrimers with different peripheral functionalities a certain control over the length of the formed nanofibers is possible.

Introduction

The self-assembly of functional molecules, as an alternative route for the fabrication of materials with properties that make them suitable for nanotechnology applications, has received increasing attention in recent years.[1] Whereas it is rather difficult to organize low molecular weight organic molecules into periodic macroscopic assemblies, macromolecules can be assembled into a large variety of ordered morphologies covering several length-scales. Dendrimers[2] constitute one of the major new developments in the field of macromolecules. As a result of their compact globular shape and easily controlled size and functionality, dendrimers constitute ideal molecular building blocks for a wide range of surface-related applications.[3] The study of self-assembled monolayers[4−7] of dendrimers on solid substrates enhanced the understanding of properties like shape and compressibility, that are only accessible through surface confinement. The utilization of monolayers assembled from tailor-made dendritic macromolecules for the production of functional materials for sensors[6,8,9] or for microelectronics[10] have recently been in the focus of application-oriented research. Similarly the globular shape and multifunctional periphery of dendrimers makes them well suited for the construction of self-assembled multilayer nanocomposite materials. By the synthetic design of the peripheral functionality, reversible interactions, such as hydrogen-bonding,[11] electrostatic effects,[5,12] and metal coordination[13] were successfully used as the driving force for the self-assembly process.

Polyphenylene dendrimers (PDs), which have been introduced and further developed in recent years by our group,[14] are a subclass of these macromolecules distinguished by unique properties such as high chemical and thermal stability and shape-persistence.[15] A broad variety of PDs of different generations (up to the sixth generation)[9] built around cores of different geometry and function (such as biphenyl,[16] tetraphenylmethane,[17] azobenzene,[18] or rylene dyes[19]) are available and have been extensively studied. The rigid molecular framework of PDs ensures a replication of the core geometry in the final macromolecules and leads to a rather narrow variation of the voids in their interior rendering them as ideal supramolecular building-blocks for sensors of volatile organic solvents with a high degree of reproducibility.[20] The shape-persistent polyphenylene scaffold allows the efficient shielding of the core[18] functionality as well as the topologically defined placement of functions on the periphery.[19,21]

The constitutional desymmetrization of these nanoparticles is accessible through the use of partially protected core building-blocks.[22] The resulting compounds have two segments of different functionality, e.g., one for binding a substrate and the others for sensing or further transformations. As such, a precise tailoring of the functional properties of these molecules is possible.

We have shown that, irrespective of their generation and core, these macromolecules self-assemble into micrometer long nanofibers[5] of high temporal and thermal but low mechanical stability. Thereby the peripheral functionalities of PDs play an

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important role. Thus, the self-assembly of dodecyl- and octyl-decorated polyphenylene dendrimers on a solid surface lead to ordered layers[7] rather than to nanofibers.

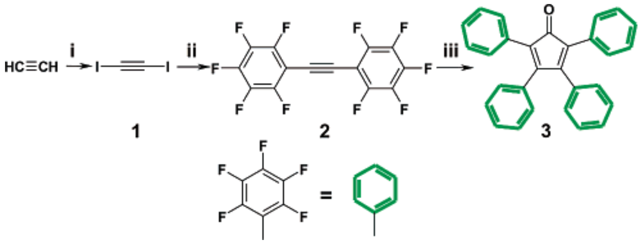
The stacking between aryl and perfluoroaryl units is an important type of aromatic−aromatic interactions that has been attracting rapidly growing interest in recent years.[23,24] This phenomenon has been studied extensively since Patrick and Prosser demonstrated in 1960 that a 1:1 mixture of benzene and hexafluorobenzene forms a solid complex that melts at 24 °C.[25] In contrast to the crystals of the individual components, which show a herringbone packing, this complex consists of face-to-face stacks of alternating benzene and hexafluorobenzene molecules. Crystallographic studies of several 1:1 complexes of perfluorinated aromatic compounds with non-fluorinated arenes have revealed similar stacking motifs of alternating component molecules.[24,26] This arrangement can be attributed to a quadrupolar interaction between electron-rich and electron-deficient aromatic rings.[27] The calculated binding energy between two aromatic rings (benzene and hexafluorobenzene) ranges from 15 to 20 kJ mol^{-1} [28]. Thus, this interaction has emerged as a very important driving force in crystal engineering and supramolecular chemistry which is comparable to that of many robust hydrogen-bonding motifs. However, little is known about the influence of phenyl/perfluorophenyl stacking upon the self-organization of dendrimers and up to now no studies dealing with this aspect are available. Looking for a functionality which has major impact upon intermolecular interactions during the self-assembly process, a new series of polyphenylene-dendrimers which comprise a variable number of pentafluorophenyl units on the periphery is introduced. Their self-assembly induced by slow evaporation of the solution onto a highly oriented pyrolytic graphite (HOPG) surface is examined by atomic force microscopy (AFM). The self-assembly is not restricted to dendrimers with a variable pentafluorophenyl content at the periphery but includes also blends with unfunctionalized polyphenylene dendrimers. The influence of the presence and the amount of the perfluorinated benzenes upon the morphologies obtained by the self-assembly on HOPG of these nanoparticles is discussed.

Results and Discussion

Synthesis. The synthesis of pentafluorophenyl substituted polyphenylene dendrimers is based on a divergent growth approach[17] and starts from a tetraphenylmethane core functionalized with free ethynyl groups. The Diels−Alder cycloaddition of tetraphenylcyclopentadienones bearing triisopropylsilyl-protected (T*i*PS) ethynyl groups to the core molecule, as well as the subsequent activation of the masked alkyne moieties are the two orthogonal reaction steps which are used in the iterative synthesis of the polyphenylene dendrimers.[17,29] In the present case, the key compound for the peripheral pentafluorophenyl-functionalization is represented by the tetrakis(pentafluorophenyl)cyclopentadienone (**3**, Scheme 1). **3** was obtained in moderate yields through the reaction of 1,2-diiodoethyne with pentafluorophenylcopper (formed from pentafluorophenylmagnesium bromide and cuprous iodide) and a subsequent conversion of the resulting bis(pentafluorophenyl)acetylene (**2**) with $Co_2(CO)_8$, according to previous reports.[30] The use of **3** in the final step of the divergent dendrimer synthesis led to the polyphenylene dendrimers **TdG$_1$F**, **TdG$_2$F**, and **TdG$_3$F** (see Scheme 2) with 16, 32, and 64 pentafluorophenyl units, respectively, in the outer rim.

The variation of the peripheral pentafluorophenyl content required the application of a synthetic strategy which permits the selective functionalization of the different dendrons of one dendrimer. Recently, it has been shown that starting from asymmetrically activated core molecules, shape-persistent nanoparticles with spatial separation of different functional groups at the periphery are accessible.[31] The key factor of this synthetic strategy is the selective synthesis of the different compartments within one dendrimer molecule. Accordingly the various desymmetrized T*i*PS-protected tetrakis(4-ethynylphenyl)methane cores **6**, **7**, and **8** (Scheme 3) have permitted the selective buildup of the dendritic structure at the unprotected ethynyl-groups, maintaining at the same time the option for a second dendritic growth after the cleavage of the initial T*i*PS functions. Thus, employing different functional tetraphenylcyclopentadienones in the two different stages of the dendrimer synthesis, nanoparticles with two different functions can be produced. In the present case, this strategy was used for the variation of the pentafluorophenyl/phenyl ratio at the dendrimer periphery. The partially T*i*PS-protected core building-blocks **6**, **7**, and **8** were formed by the treatment of **4** with a controlled amount of *n*-butyllithium at −78 °C followed by a quenching with triisopropylsilyl chloride (T*i*PS−Cl). The components of the statistical product mixture containing 1- (**6**), 2- (**7**), 3- (**8**), and 4-fold T*i*PS substituted derivatives were separated via column chromatography and used as separate starting compounds in a convergent dendrimer synthesis. The alternating Diels−Alder cycloadditions of tetraphenylcyclopentadienone **5** and tetrakis(pentafluorophenyl)cyclopentadienone **3** to **6**, **7**, and **8** produced in good yields the first-generation dendrimers with 4 (**TdG$_1$C$_3$F**), 8 (**TdG$_1$C$_3$F**) and 12 (**TdG$_1$CF$_3$**) pentafluorophenyl rings, respectively.

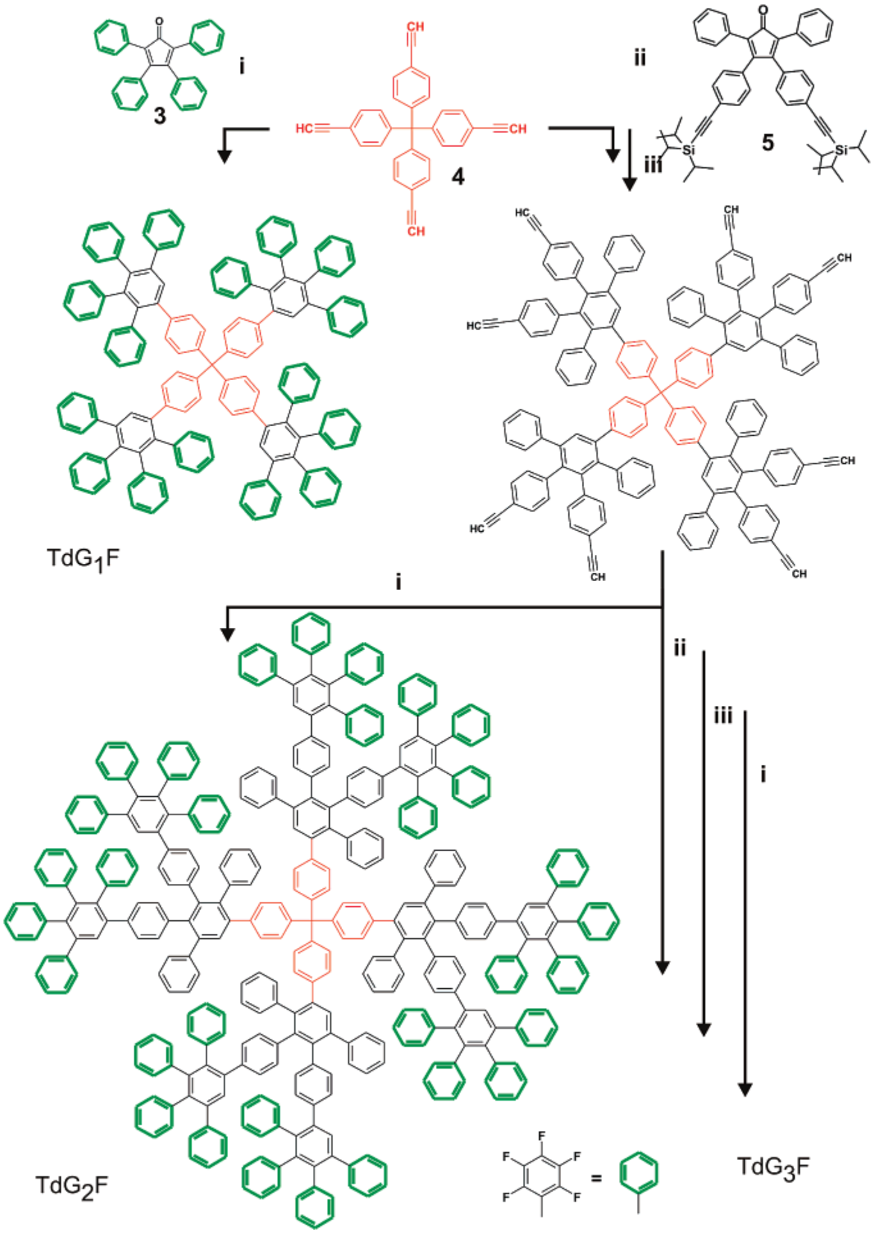
Scheme 1. Synthetic Route to Tetrakis(pentafluorophenyl)cyclopentadienone (3)[a]



[a] Key: (i) KI, NaOH, −20 °C/1 N NaClO (aq); (ii) C_6F_5Br, Mg, dry ether, 30 min reflux/CuI room temperature, 45%; (iii) $Co_2(CO)_8$, *o*-xylene, 142 °C, 54%.

The convergent synthesis of the second-generation dendrimers required the initial synthesis of the respective polyphenylene[29] (**9**) and pentafluorophenyl-decorated dendrons. However the synthesis of **9** involves a Knoevenagel condensation step in the presence of a strong base such as KOH or Bu_4NOH. This hinders the application of a similar synthetic procedure for the pentafluorophenyl substituted dendron due to undesired nucleophilic substitutions at the pentafluorophenyl rings. Therefore, a new synthetic design was employed using both, the convergent and the divergent synthetic protocols. First the pure polyphenylenic parts of the dendrimers were built up by the Diels−Alder cycloaddition of **9** to the free ethynyl groups of **6**, **7**, and **8** producing intermediate derivatives which still had 1, 2, and 3 T*i*PS-protected ethynyl groups, respectively, at the core. Subsequently, at these sites the pentafluorophenyl functionalized wedges were built up by the use of an iterative synthetic protocol consisting of an activation/deprotection step, the cycloaddition of **5** to the activated dienophiles, a second activation/deprotection step and the final Diels−Alder cycloaddition of **3** to the ethynyl-functionalized intermediates. Scheme 4 depicts this

Scheme 2. Synthesis of Pentafluorophenyl-Terminated Polyphenylene Dendrimers[a]



[a] Key: (i) 1.5 equiv of 3/C≡C bond, *o*-xylene, 142 °C, 75% for TdG_1F, 70% for TdG_2F, and 51% for TdG_3F; (ii) 1.5 equiv of 5/C≡C bond, *o*-xylene, 142 °C, 89%; (iii) 1 equiv of *n*Bu4NF /T*i*PS, THF, room temperature.

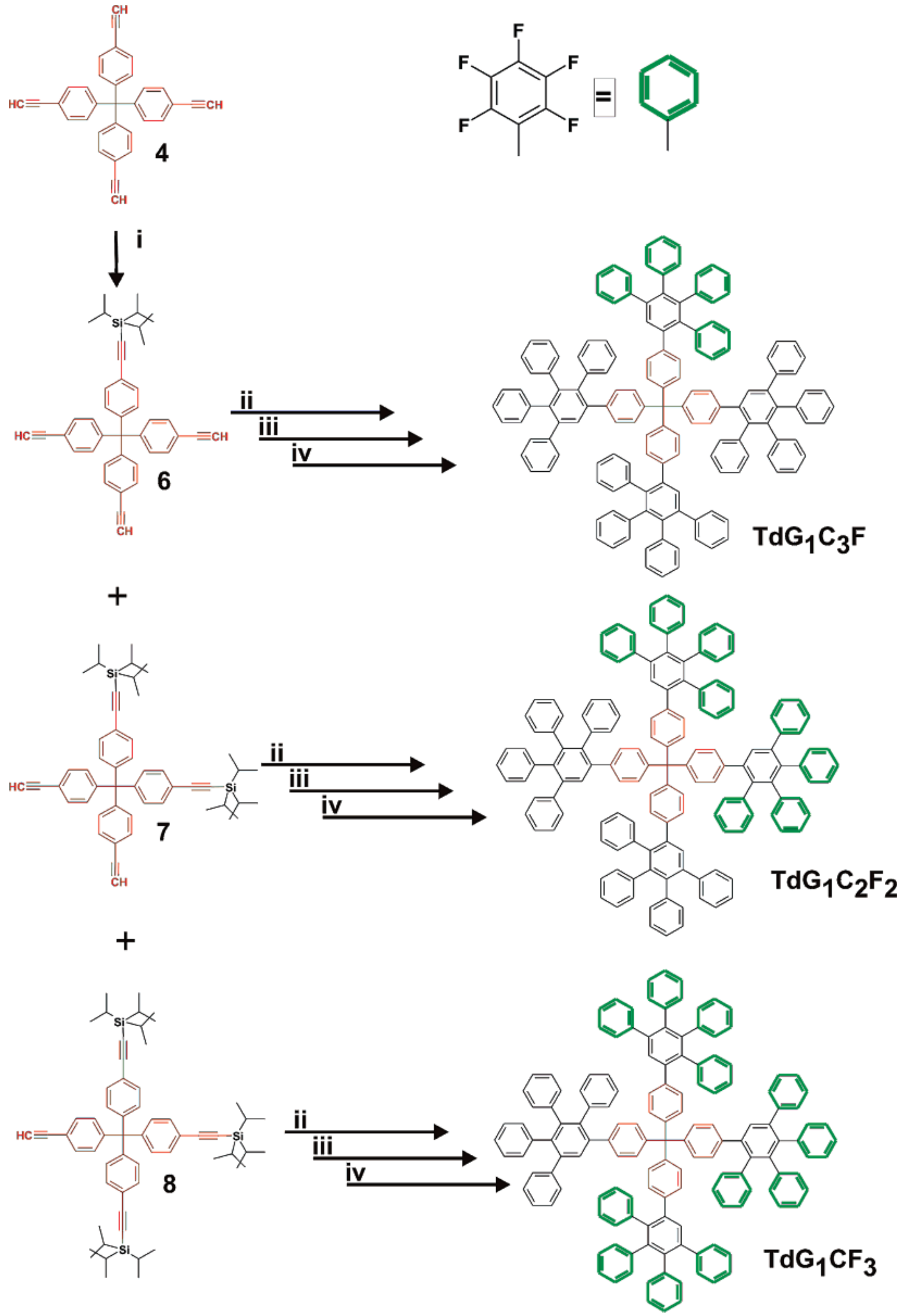
synthetic route for the case of the second-generation dendrimer with two pentafluorophenyl decorated dendrons ($\mathbf{TdG_2C_2F_2}$). To produce the pendants with one ($\mathbf{TdG_2C_3F}$) and three ($\mathbf{TdG_2CF_3}$) pentafluorophenyl functionalized wedges, respectively, identical synthetic strategies were used starting from the partially protected cores **6** and **8**, respectively.

All the presented dendrimers are soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, THF, toluene, and xylene. Therefore, their routine characterization by spectroscopic methods such as ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectroscopy is straightforward. Additionally, elemental analysis (EA), FD−MS, and MALDI−TOF−MS data were recorded and used for the unambiguous identification of the chemical structures and their purity. The first-generation dendrimers have molecular weights lower than 3300 g/mol, and were detected by FD−MS as single peaks. The MALDI−TOF measurements of $\mathbf{TdG_2F}$ and $\mathbf{TdG_3F}$ were performed in the presence of TCNQ as solid matrix, with the observation of *m*/*z* peaks which are exactly matching the calculated molecular weights. Similarly the MALDI−TOF spectra of the second-generation desymmetrized dendrimers $\mathbf{TdG_2CF_3}$, $\mathbf{TdG_2C_2F_2}$, and $\mathbf{TdG_2C_3F}$ were recorded in CH_2Cl_2 solution in the presence of silver or potassium salts. An exclusive *m*/*z* peak was detected for each dendrimer, which equals the sum of the calculated dendrimer molecular weight plus the weight of silver or potassium ion. The perfect agreement between calculated and experimentally determined *m*/*z* ratio confirms the monodispersity and the structural perfection of the synthesized dendrimers (see also Supporting Information).

Thermal and Chemical Stability. Thermogravimetric analyses (TGA) of the synthesized polyphenylene dendrimers revealed that the loss of weight under nitrogen occurred in the range 500−620 °C. This high thermal stability is characteristic of this type of dendrimers and was observed also in the case of the parent unfunctionalized polyphenylene dendrimers.

The composition of the periphery is easily altered by nucleophilic displacement reactions of the fluorines in the pentafluorophenyl groups of $\mathbf{TdG_1F}$. Hereby a set of reactions using aniline, thiophenol or 1,3-propanediamine as nucleophiles

Scheme 3. Synthesis of Desymmetrized First-Generation Dendrimers[a]

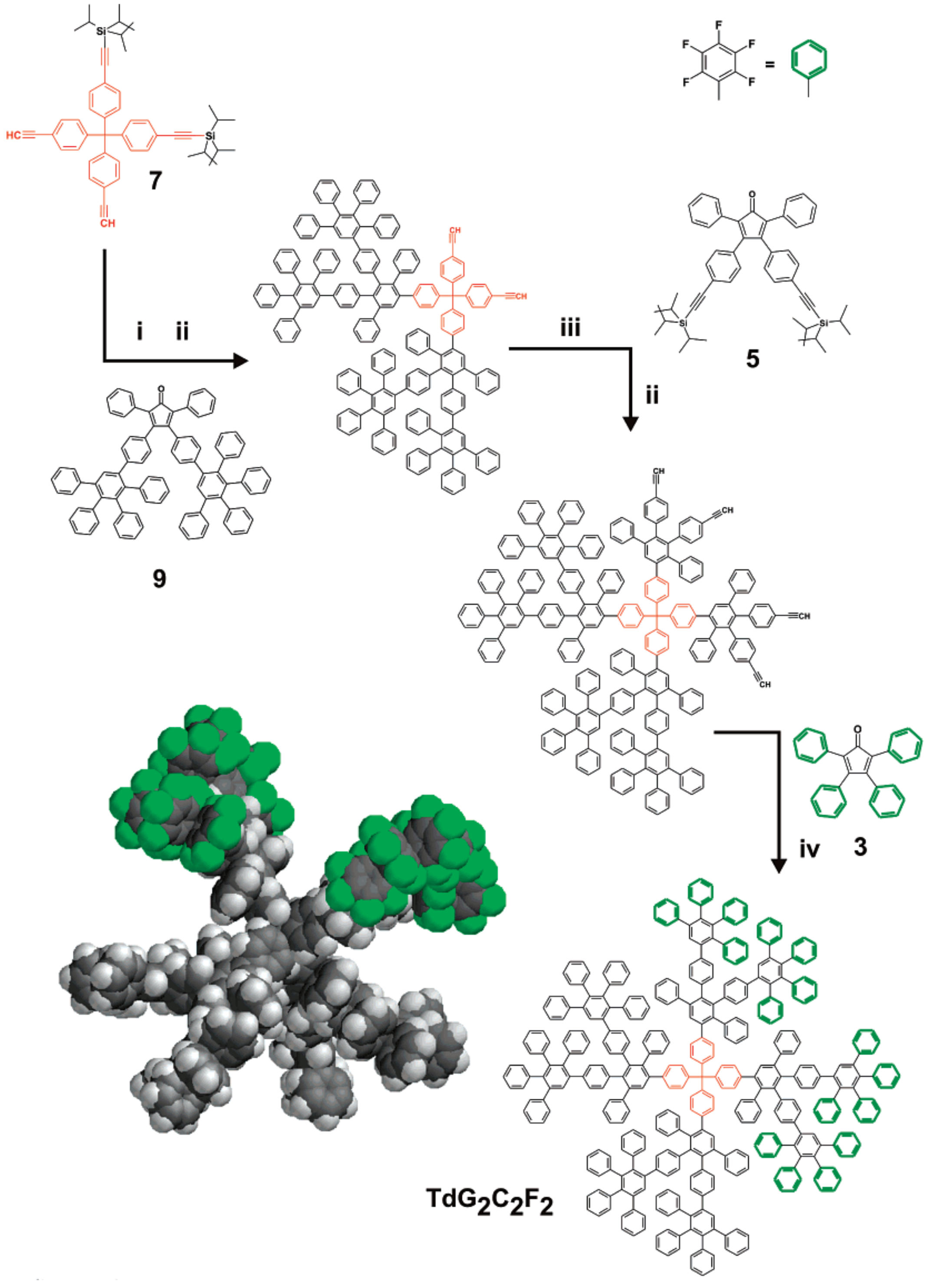


[a] Key: (i) 4 equiv. *n*BuLi, THF, −78 °C/ variable amounts of T*i*PS−Cl, room temperature; (ii) 1.5 equiv of 3/C≡C bond, *o*-xylene, 142 °C, 85% for TdG_1C_3F, 89% for TdG_1C_3F, and 90% for TdG_1CF_3; (iii) 1 equiv *n*Bu4NF /*Ti*PS, THF, room temperature, 88% (TdG_1C_3F), 87% (TdG_1C_3F), and 85% (TdG_1CF_3);(iv) 1.5 equiv of 5/C≡C bond, *o*-xylene, 142 °C, 92% (TdG_1C_3F), 86% (TdG_1C_3F), and 82% (TdG_1CF_3).

were performed in refluxing *o*-xylene for 48 h. In the case of the first two nucleophiles, the focus was upon the extent of substitution in view of a possible easy method for the a posteriori functionalization of these new materials. Additionally, in the case of the bifunctional 1,3-propanediamine, the degree of cross-linking of the separate nanoparticles was assessed.

Reactions with aniline and thiophenol showed that **TdG_1F** undergoes multiple nucleophilic substitutions, in both cases leading to product mixtures where up to 18 fluorine atoms were displaced by the used nucleophile. Likely, the first fluorine atoms to be displaced were the *p*-fluorines of each pentafluorophenyl ring. The higher reactivity of the *p*-fluorine position

Scheme 4. Synthesis of Desymmetrized Second-Generation Dendrimer TdG$_2$C$_2$F$_2$[a]



[a] Key: (i) 1.5 equiv of 9/C≡C bond, diphenyl ether, 190 °C, 80%; (ii) 1 equiv *n*Bu4NF /T*i*PS, THF, room temperature; (iii) 1.5 equiv of 5/C≡C bond, *o*-xylene, 142 °C, 91%; (iv) 1.5 equiv of 3/C≡C bond, *o*-xylene, 142 °C, 92%.

is well-known, and it has been successfully exploited also for the synthesis of perfluoroaromatic linear and hyperbranched polymers.[32] The above findings were confirmed by NMR spectroscopy and MALDI−TOF spectrometry. The analytical results showed that the pentafluorophenyl substituted polyphenylene dendrimers readily underwent nucleophilic substitution reactions, and led to products, which lost the initial monodispersity of the parent dendrimer.

In the case of the reactions with 1,3-propanediamine, besides the statistical substituted products of single dendrimers, cross-linked oligomeric species were observed. MALDI−TOF spectrometry and size exclusion chromatography (SEC) investigations proved the presence of species where up to six nanoparticles were bridged by the bifunctional nucleophile.

AFM Studies. AFM was used to examine the self-assembly of the synthesized second generation dendrimers on HOPG since it is a powerful tool to visualize the surface topography and to examine surface properties at the nanoscale.[33] Various types of arrangements such as isotropic globular aggregates, percolated networks of nanometer size anisotropic objects with a ribbon-

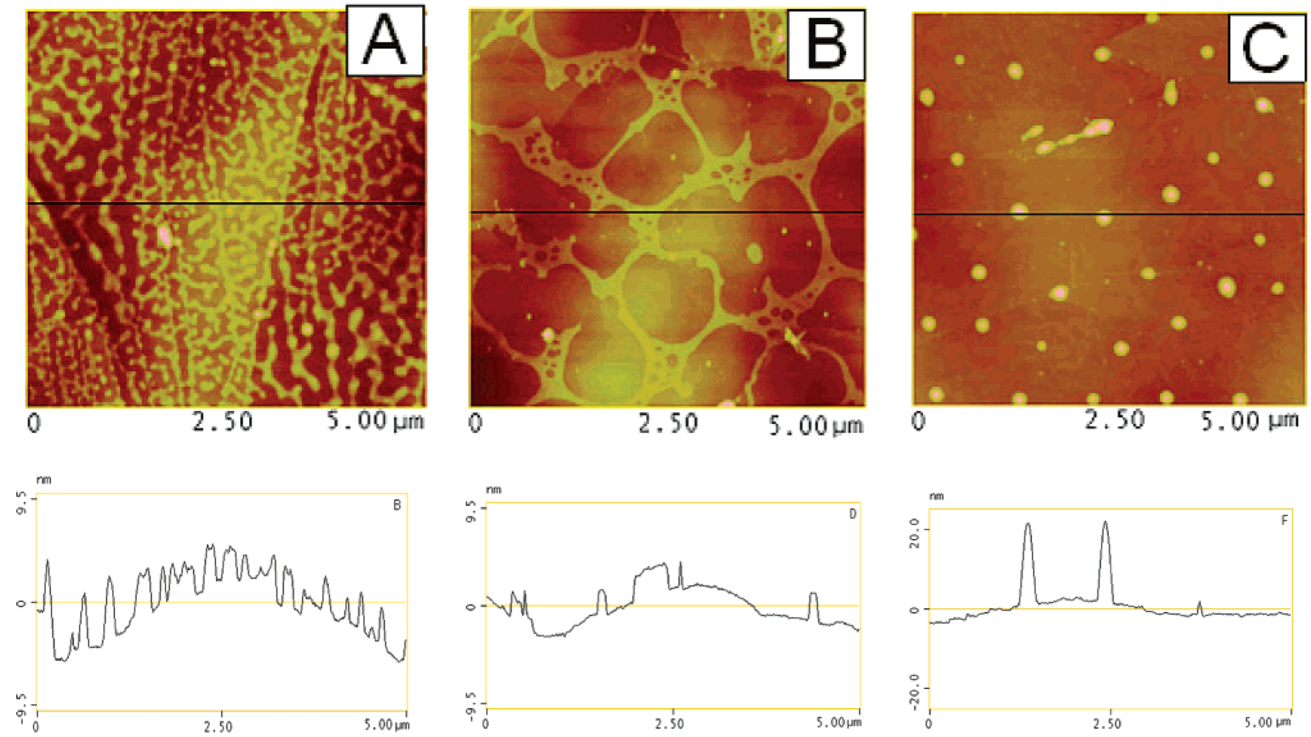


Figure 1. AFM topography images after dropcasting a THF solution of 1 × 10^{-6} M of **TdG_2C_3F** (A), **$TdG_2C_2F_2$** (B), and **TdG_2CF_3** (C) on a HOPG substrate and the according topography profiles along the lines indicated in the images.

like shape, as well as quite uniform nanofibers have thereby been visualized.

The formation of a given structure depends on a subtle interplay of a number of parameters including the method of the deposition process, the choice of the solvent, the concentration as well as the temperature of the solution and the substrate. To observe the direct influence of the pentafluorophenyl functionalization upon the self-assembly process these conditions were kept constant. Varying the pentafluorophenyl content in the drop-cast systems, by the desymmetrized dendrimers **TdG_2CF_3**, **$TdG_2C_2F_2$**, and **TdG_2C_3F,** by progressive blending of the unfunctionalized PD **TdG_2** (Figure 2.) with increasing amounts of **TdG_2F,** or by depositing **TdG_2** in the presence of hexafluorobenzene (C_6F_6), the control of the self-assembly process toward different architectures became possible.

1. Self-Assembly of TdG_2CF_3, $TdG_2C_2F_2$, and TdG_2C_3F. Figure 1 shows AFM topography images of the drop cast products of the desymmetrized dendrimers **TdG_2C_3F**, **$TdG_2C_2F_2$**, and **TdG_2CF_3**, respectively. **TdG_2C_3F** forms worm-like aggregates as shown in Figure 1A. The height of these differently shaped aggregates ranges from 2.6 to 5.3 nm. Under the same conditions, deposition of **$TdG_2C_2F_2$** leads to the formation of a network consisting of "cells" whereby within the narrow strips smaller holes can be observed. The cross-section profile of the film along the line indicated in Figure 1B displays a uniform film height of 2.3−3.0 nm. In contrast, **TdG_2CF_3**, the polyphenylene dendrimer with the highest pentafluorophenyl content forms round particles with heights of about 18−23 nm.

2. Self-Assembly of TdG_2C and TdG_2F Blends. Figure 2 compares surface morphologies of a series of samples obtained by drop casting a 10^{-6} THF solution of pure **TdG_2C** (A) and its blends of 25 (B), 50 (C), and 75 mol % (D) with **TdG_2F**. **TdG_2C** exclusively self-assembles into nanofibers which are in general randomly dispersed on the HOPG substrate as shown in Figure 2A. The length (up to 100 μm), the height (8 ± 2 nm) and the lateral dimensions (85 ± 5 nm) of these remarkable self-assembled architectures agree with our previous observations.[5,34] Starting from this finding blending of **TdG_2C** with increasing amounts of **TdG_2F** reveals a noteworthy trend in the morphology of the self-assembled systems: Increasing the amounts of **TdG_2F** from 25 to 75 mol % leads first to a shortening of the length of the formed nanofibers to end up in their total disappearance for the highest concentration of **TdG_2F.** Interestingly, the height and the width of the nanofibers remain fairly unchanged as compared to fibers of **TdG_2C**. Increasing the amount of **TdG_2F** to 75 mol % yields the formation of randomly dispersed unstructured aggregates similar to those observed in the case of **TdG_2CF_3**

3. Self-Assembly in the Presence of C_6F_6. Another approach to introduce perfluorophenyl groups into the drop-cast systems is the deposition of **TdG_2C** in the presence of varying amounts of hexafluorobenzene (C_6F_6). Figure 3 shows a set of AFM topography images obtained upon gradually increasing the relative amount of C_6F_6 in the mixed solvent. Otherwise, the sample preparation was identical to the experiments presented before. At low (5%) and intermediate (20%) concentrations of C_6F_6, fibers can still clearly be observed. However, at concentrations above 40%, similar as in the blended two-component system, no nanofibers are formed. In contrast to the experiments with blends of two dendrimers (**TdG_2C** and **TdG_2F**) the transition toward unstructured topologies occurs via the appearance of increasing amounts of clusters, rather than by the shortening of the dendrimer nanofibers. These clusters become larger as the relative amount of C_6F_6 in the mixed solvent increases and are exclusively observed at concentrations of 40% or above of C_6F_6.

During self-assembly the substrate is initially coated with a uniform layer of solution, and assuming a nonuniform evaporation of the solvent, areas of uncovered dry surface are obtained.[35] The unstable film evolves via nucleation and growth of the formed dry patches. At the end, the dry uncoated areas coalesce, the solvent evaporates completely and ultimately the molecules

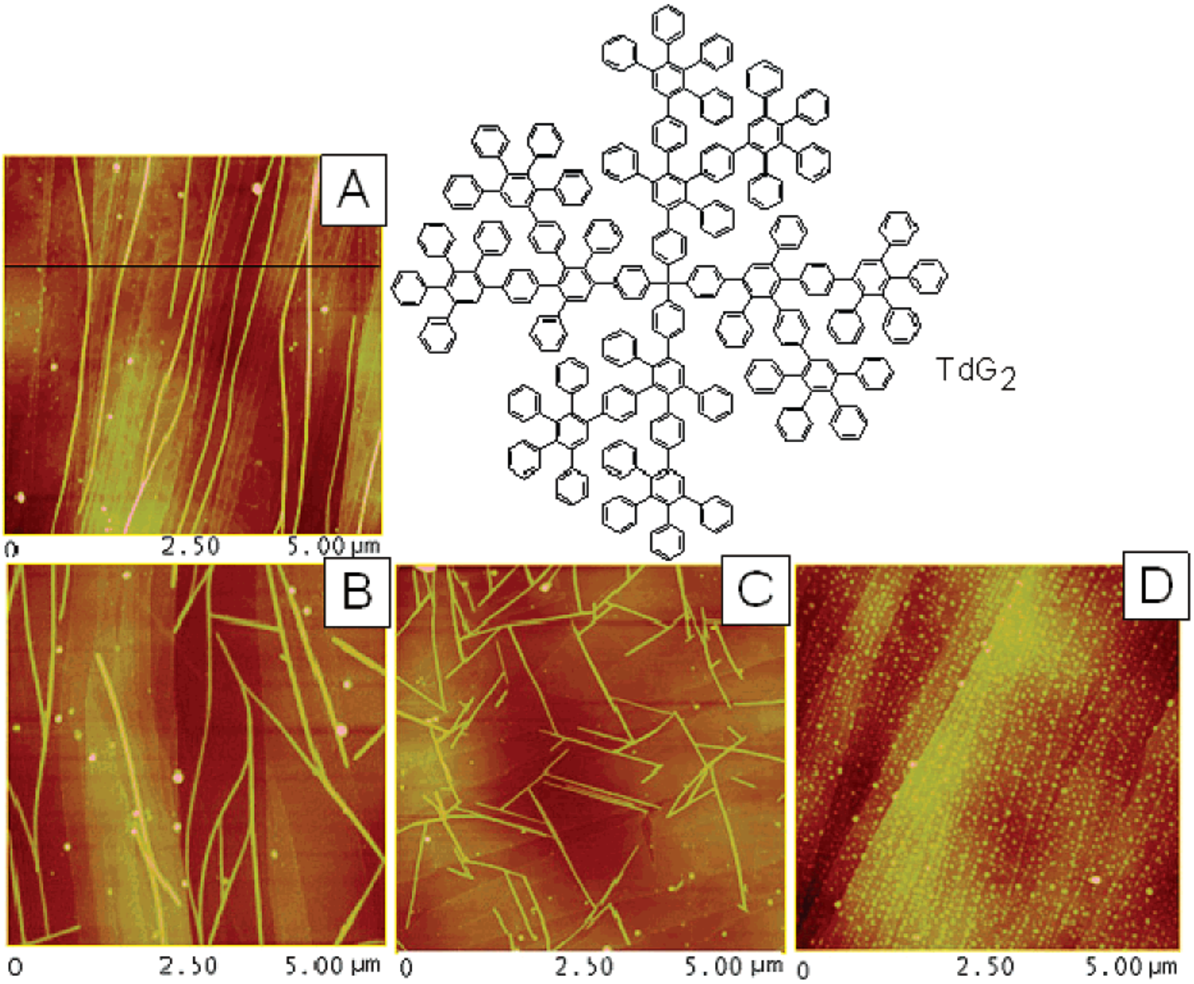


Figure 2. AFM topography images after drop casting a THF solution of 1 × 10^{-6} M **TdG$_2$C** (A) and **TdG$_2$C** blended with 25 (B), 50 (C), and 75 mol % (D) **TdG$_2$F**.

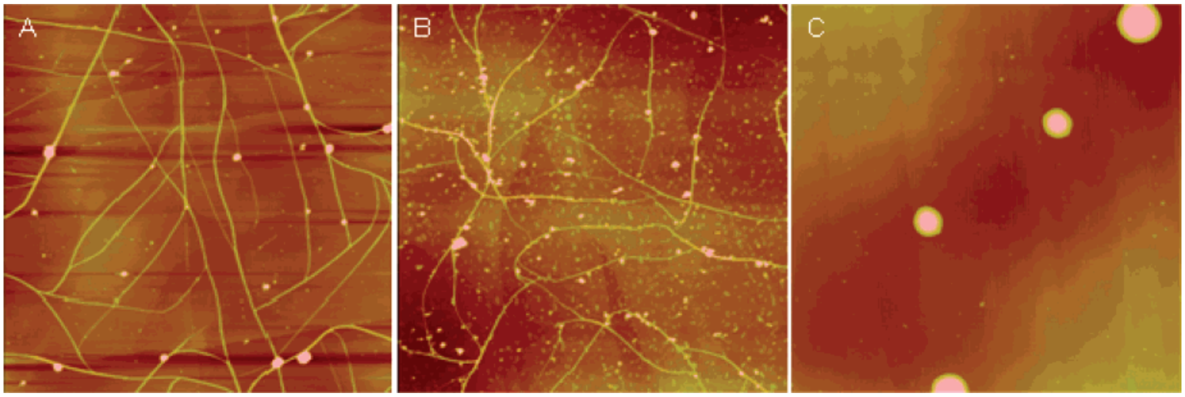


Figure 3. AFM topography images (15 × 15 μm^2) after drop-casting a solution of ∼10^{-5} M TdG$_2$C dissolved in THF/C$_6$F$_6$ with 5% C$_6$F$_6$ (A), 20% C$_6$F$_6$ (B), and 40% C$_6$F$_6$ (C) on HOPG.

are frozen at the interface between the uncovered areas. How far the solute molecules migrate along these interfaces is mainly dependent upon solvent evaporation rate, the intermolecular interactions between the dendrimers and their surface affinity. It is assumed that by the variation of the pentafluorophenyl content primarily the intermolecular interactions of the solute and its surface affinity are influenced. The driving force for the formation of the fibers is attributed to the $\pi-\pi$ and van der Waals interactions among dendrimer branches.[5,34] The introduction of pentafluorophenyl groups at the periphery of PDs increases the intermolecular $\pi-\pi$ interactions. Consequently, one would expect that the self-assembly into nanofibers should be enhanced. The above presented experiments clearly demonstrate that this is not the case. In all the examples, the introduction of pentafluorophenyl decorated dendritic surfaces inhibited (as in the case of the desymmetrized dendrimers **TdG$_2$CF$_3$**, **TdG$_2$C$_2$F$_2$**, and **TdG$_2$C$_3$F)**, or led to a gradual suppression of (as in the case of the mixed systems) the nanofiber formation. The second factor which varies with the introduction of perfluoroaromatics is the affinity of the solute molecules toward the HOPG surface. A higher affinity slows down the migration of the PDs along the solvent/air intereface and the nucleation driven by intermolecular $\pi-\pi$ interactions becomes the determining factor, leading to the formation of the observed nanofibers. Obviously with increasing pentafluorophenyl substitution the interaction between the PDs and the HOPG surface decreases allowing a longer migration of the molecules. As such the species with the lowest perfluorophenyl content (**TdG_2C_3F**) assembles into the fine percolated network structure with the highest surface coverage shown in Figure 1A. Increasing the peripheral pentafluorophenyl substitution (**$TdG_2C_2F_2$**) yields a rougher network structure with large uncovered HOPG areas in between (Figure 1B). When most of the dendrimer periphery is covered by pentafluorophenyl units, (**TdG_2CF_3**) dewetting is the dominant force in the self-assembly process. This leads to the formation of the globular structures shown in Figure 1C.

A similar situation is found in the case of the blended dendrimer systems. Increasing the perfluoroaromatic component has a negative effect on the self-assembly of the polyphenylene nanoparticles into nanofibers though not to the same extent as for the pure components. Up to a concentration of 50 mol % of **TdG_2F** the self-assembled nanofibers can still be observed. This was not the case for **$TdG_2C_2F_2$** in which also 50% of the total dendritic surface present in the self-assembly process is covered by pentafluorophenyl groups. The difference between both systems is found in the distribution of the pentafluorophenyl components in the system. While in desymmetrized dendrimers each nanoparticle experiences the same influence of the perfluoroaromatic groups, this is not the case in the blended mixture. In this second example, the unfunctionalized component leads to the formation of more strongly interacting nucleation centers with the HOPG surface allowing the development of nanofibers.

The third set of experiments examining the self-assembly of **TdG_2C** in the presence of C_6F_6 deals with the influence of the perfluoroaromatic component upon the self-assembly of PDs from a fundamentally different view. This case presents the self-assembly of a PD−host−C_6F_6−guest system initially formed in solution. The uptake of polar aromatics into the nanoporous polyphenylenic scaffold of PDs is well established.[20,36] Most likely the polyphenylene dendrimers are gradually saturated with C_6F_6 prior to self-assembly on HOPG. However this saturation occurs randomly within the dendritic structure leading to host−guest assemblies with different intermolecular and surface affinity. This explains the observation of a larger number of unstructured aggregates already at lower concentrations of C_6F_6 coexisting with self-assembled dendrimer nanorods.

Conclusions

A new series of fully and partially pentafluorophenyl substituted PDs up to generation 3 has been synthesized and characterized. The self-assembly of the second-generation species from 10^{-6} M THF solution has been studied on freshly cleaved HOPG surfaces.

The presence of different amounts of perfluoroaromatic units either covalently attached to the dendrimer periphery or as free guest molecules produces complex changes in the self-assembled surface morphology which can be explained in terms of the changes in the intermolecular interactions and the surface affinity. In particular, micrometer long nanofibers have been obtained together with percolated networks and globular aggregates. The morphology of the self-assembled aggregates is dictated by complex nucleation and dewetting processes depending on the amount and distribution of the perfluoroaromatics within the system. The results obtained using **TdG_2C** and **TdG_2F** molecules are in good agreement with similar results obtained with solutions of polyphenylene dendrimers, which were corroborated by computer simulations.[5] Interestingly, the dimensions of the observed polyphenylene dendrimer nanofibers can be controlled by blending in components inhibiting the fiber formation. One of the challenges that remain to be solved is the stabilization of these fibers. A way to achieve this might be by introducing functionalities which could covalently link the dendrimers in the nanofibers after self-assembly.

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Supporting Information Available: Text giving a detailed experimental section and schmes showing the reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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