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Dendron Rodcoils: Synthesis of Novel Organic Hybrid Structures

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Abstract: Convergent and divergent syntheses of novel organic hybrid structures termed dendron rodcoils (DRC) containing dendritic, rodlike, and coillike segments are described. The aryl ester dendron masked with 32 trifluoromethyl groups is prepared via a convergent approach using 5-(*tert*-butyldimethylsiloxy)-isophthalic acid as the monomer unit. The activation of the focal point of the dendron allows for successful coupling between the dendron and the diblock rodcoil molecules synthesized separately. In another example, the dendritic block is grown via divergent strategy from the terminus of rodcoil using 3,5-bis(*tert*-butyldimethylsiloxy)benzoic acid as an AB_2 monomer. A combination of catalyzed esterification reactions and silyl deprotection chemistry proved to be a very efficient method for construction of these nanosized structures with unusual molecular architecture. Both synthetic strategies allowed for the preparation of DRCs with nearly monodisperse dendritic blocks as demonstrated by NMR, MALDI-TOF, and GPC measurements.

Introduction

Well-defined molecular architecture, specific conformation, and shape persistence are known to be key structural elements which define properties and biological function of natural macromolecules. Their synthetic counterparts, on the other hand, generally lack these particular features, and most conventional polymers exist in random coil conformations. Therefore, synthesis of functional well-defined macromolecular structures represents a challenge for organic chemists. Some dendrimers[1a] are believed to be one of the few examples of shape-persistent nanostructures which differ drastically from linear analogues.[1] Because of their compact spherical shape and the presence of multiple functional groups on the periphery, dendrimers exhibit unusual rheological behavior,[2] enhanced catalytic activity,[3] and can be used for encapsulation of small molecules[4] and delivery of drugs.[5]

Recent advances in the area of dendrimer chemistry have demonstrated that properties can be significantly improved if dendritic segments are covalently linked to a structurally different block to create a hybrid organic structure. Examples include self-assembling dendrimers,[6] dendronized polymers,[7] dendritic-linear diblock structures,[8] and triblock hybrid dendrimers.[9] However, all diblock hybrid structures described in the literature contain flexible linear chain segments such as poly(ethylene oxide) or polystyrene and, therefore, cannot easily retain shape in solution or in the solid state. From a molecular design standpoint, the incorporation of rigid aromatic spacers between a dendritic block and a flexible coil can be interesting for several reasons. First of all, these molecules would generally have lower symmetry than would ordinary dendrimers and could, therefore, be polar nanostructures. In molecules having only dendritic and flexible coil segments, this low symmetry is easily lost. Second, rigid aromatic segments as the middle block could, depending on sterics, be useful in promoting aggregation into larger nanostructures through $\pi-\pi$ stacking.[10] Dendron rodcoil molecules could also improve the ability of dendrimers to modify the surface properties of conventional polymers.

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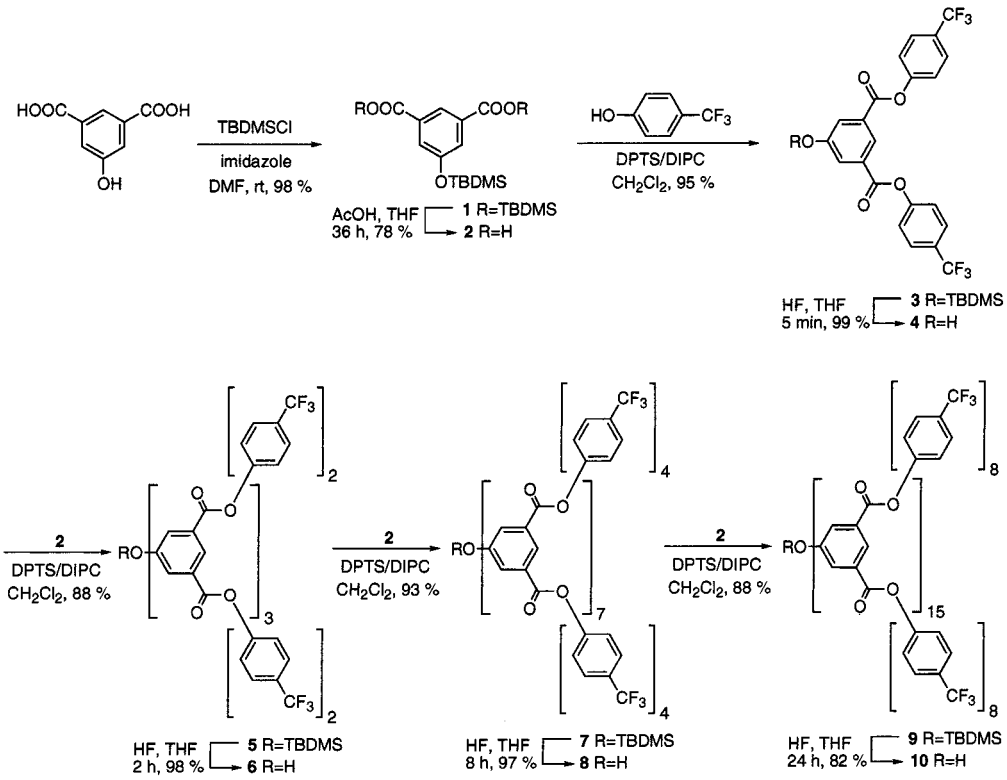
Scheme 1



According to theoretical and experimental studies carried out by A. M. Mayes and co-workers,[11] highly branched structures should undergo spontaneous migration to surfaces when mixed with linear polymers. The presence of rod segments would spatially separate the dendron and the coil, thus preventing the latter from being buried inside the high generation dendron as may be the case in diblock dendritic-linear hybrid structures described in the literature. This way, flexible coil segments could promote grafting and/or mixing of DRC molecules with linear polymer matrixes (polybutadiene or polyisoprene in the case of molecules described in this paper). Surface modification of materials would occur by covalent capture of DRC molecules through the coil segment's reaction with the matrix following their spontaneous migration to surface regions.

Results and Discussion

Convergent Synthesis. Over the past several years, we synthesized a broad variety of novel hybrid structures called dendron rodcoils (DRCs) which are composed of three major blocks, a dendritic aryl ester block, a rigid biphenyl ester segment, and a flexible oligoisoprene coil. We explored two major strategies which can be used for design and preparation of triblock DRC molecules. The first one involves convergent growth of functionalized dendrons followed by a coupling reaction with rodcoil molecules. This approach requires preparation of the dendron with a functional group at the focal point that can be coupled to the terminus of a rodcoil synthesized separately. Scheme 1 illustrates the synthesis of trifluoromethyl-terminated aryl ester dendron (G4) via the convergent approach. Unlike other groups, which previously reported the synthesis of aryl ester demdrimers,[12] we used the TBDMS-protected derivative of 5-hydroxy-isophthalic acid (compound **2**) as an AB_2 monomer for the preparation of dendron. The reaction between 5-hydroxy-isophthalic acid (HIA) and 3 equiv of TBDMSCl afforded triprotected compound **1** and was followed by selective cleavage of silyl groups from two carboxyls under mild acidic conditions. The esterification coupling reactions involved in this synthesis were carried out under conditions developed in our laboratory for the preparation of aryl ester linear polymers.[13] Diisopropyl carbodiimide (DIPC) and 4-(*N*,*N*-

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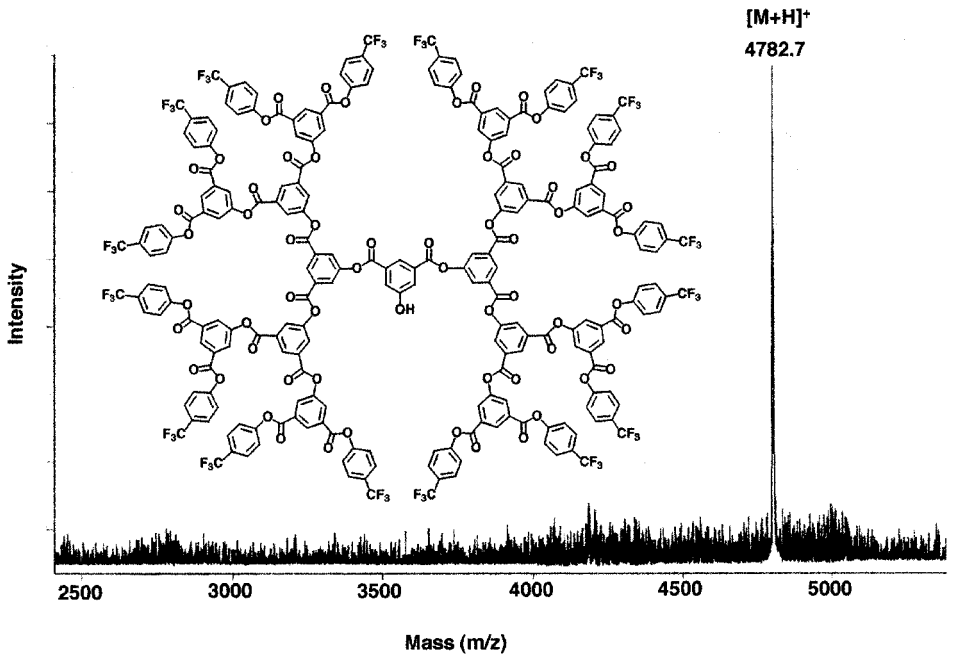

Figure 1. MALDI-TOF trace of the fourth generation dendron **10**.

dimethylamino)pyridinium-4-toluenesulfonic acid (DPTS) lead to very high yield for the esterification reactions between aromatic acids and phenols at room temperature as described previously.[10] We decided to use the advantages of this catalytic system for the synthesis of high generation dendritic structures, which requires high yield and purity at intermediate stages. These coupling conditions turned out to be very fast and versatile for the preparation of aryl ester dendrons. The successful esterification always proceeds with yields of greater than 80% which suggests that these coupling conditions are activated enough to overcome any steric hindrance through the fourth generation. The convergent approach allows for incorporation of the peripheral functional groups at the very beginning of the synthesis.[14] However, these groups have to be unreactive under synthetic conditions. We have chosen trifluoromethyl groups which are inert to DPTS and DIPC and can impart highly hydrophobic properties to the final product. Coupling between α,α,α-trifluoro-*p*-cresol and compound **2** afforded the first generation of a fluorinated dendron **3**. For activation of the focal point, we used hydrofluoric acid which can cleave TBDMS groups at room temperature. Surprisingly, we found that tetrabutylammonium fluoride (TBAF) can only be used for TBDMS deprotection when the generation of dendron does not exceed 2. Reaction between TBAF and G3 dendron **7** even at −78 °C results in nearly complete decomposition due to destruction of ester bonds via nucleophilic attack by fluoride anions. This instability of aromatic ester bonds toward even mild base like TBAF is most likely due to a high local concentration of esters in the interior of dendron. Hydrofluoric acid, on the other hand, appears to be the best deprotecting agent, because unlike TBAF or HCl it does not destroy ester linkages regardless of size and generation of aryl ester dendritic molecules. Successive coupling and deprotection reactions shown in Scheme 1 afford the fourth generation dendron **10** with the hydroxyl group at the focal point. Solubility was found to decrease rapidly and to pass through a minimum at generation 3. Compound **8** is only soluble in hot DMF, but the coupling to monomer **2** can be carried out successfully even in dichloromethane because the solubility of G4 dendron **9** is much higher. Even the deprotected compound **10** is soluble in nonpolar solvents such as dichloromethane or chloroform. Figure 1 shows a MALDI-TOF spectrum of this compound which demonstrates that G4 dendron is a defect-free molecule with a molecular weight of 4782 daltons.

Although the solubility problem can be easily overcome in this multistep synthesis once the generation of the dendron is higher than 3, the rate of the deprotection reactions decreases dramatically. As shown in Scheme 1, the cleavage of the TBDMS group takes only 5 min for a G1 dendron and 24 h for G4 molecules. Also, the yield becomes significantly lower for G4 versus G2 dendrons (82 versus 99%). This is possibly due to a combination of steric hindrance as well as the decreasing relative concentration of TBDMS groups. As the size of the dendron increases, accessibility of the TBDMS group to hydrophilic HF becomes quite limited. To minimize this problem, we prepared another derivative of HIA bearing one biphenyl unit which would bring the focal point closer to the periphery of the resultant G5 dendron, thus reducing its hindrance. Scheme 2 illustrates the synthesis of this AB_2 monomer (compound **15**) and its successive coupling to afford a G5 dendron. 4-Hydroxy-biphenylcarboxylic acid was first protected on both sides with TBDMS group to give compound **11** which was then reacted with HF for 5 min to cleave the silyl group only from the carboxyl group. On the other hand, reaction of HIA with 2 equiv of TBDMSCl using morpholine as a base allows for selective protection of carboxylic groups leaving the hydroxyl terminus open (compound **13**). Esterification of **13** with **12** under standard conditions (DPTS/DIPS) gives molecule **14** which is then reacted with acetic acid to cleave the silyl groups from two carboxyls (compound **15**). G4 dendron **10** was successfully coupled with **15**, and the deprotection of the focal point with HF was found to proceed rapidly

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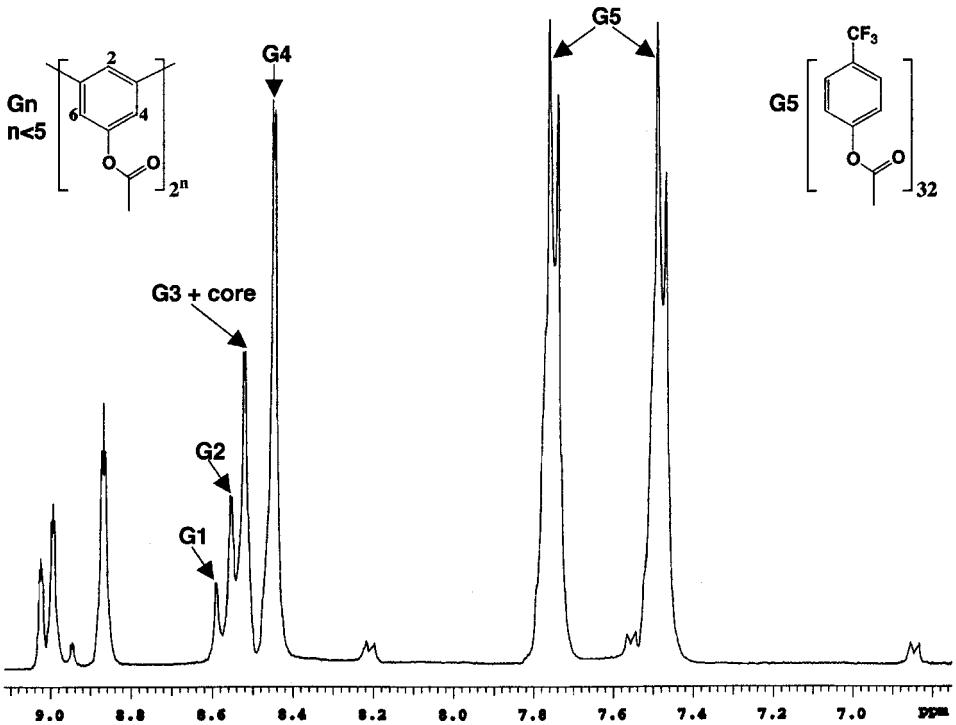
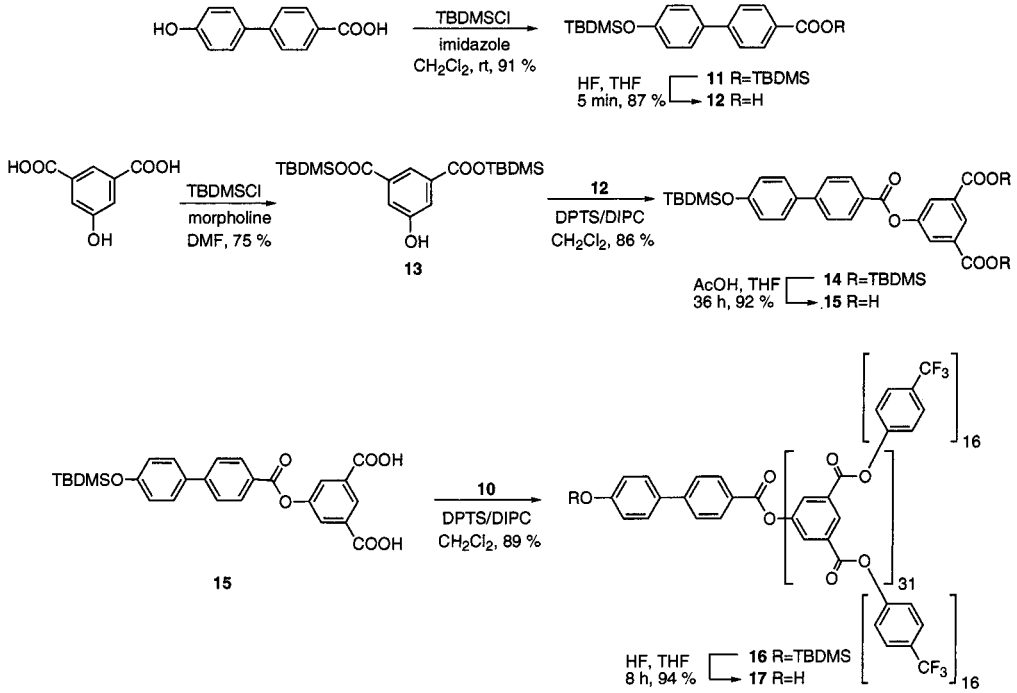


Figure 2. ^{1}H NMR spectrum of compound **17**. Arrows indicate resonances of protons located in different generational layers of the molecule.

Scheme 2

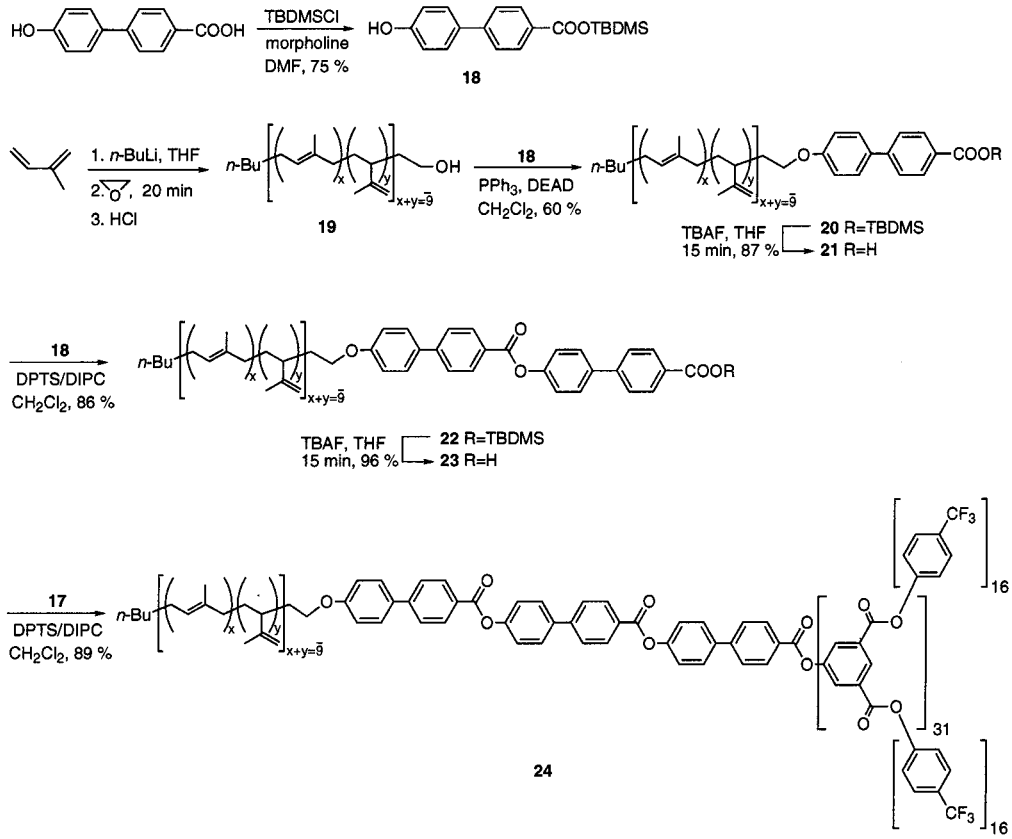


to give **17** in very high yield (94% within 8 h). These findings clearly demonstrate that incorporation of one biphenyl ester fragment between the center of the dendron and the focal point can significantly reduce steric barriers in the deprotection reaction.

Interestingly, ^{1}H NMR spectroscopy turned out to be a very informative method for identification of the outer and inner shells (generational layers) in these dendritic molecules. Figure 2 shows the ^{1}H NMR spectrum of compound **17** (G5-biphenyl-OH). Two doublets at 7.48 and 7.75 ppm represent two pairs of protons in the ortho- and meta-position with respect to CF_3 group in the peripheral G5 layer[15] of the molecule (64H in each doublet). As expected, the signals of protons from substituted HIA units are shifted downfield. Protons at position 4 and 6 in a given HIA monomeric unit generate a doublet, whereas the proton at position 2 gives a triplet with a very small coupling constant J (1.4−1.7 Hz). Most importantly, all the doublets and triplets can be resolved which allows one to identify five generational layers and even the core. For example, the doublet

(15) The outer layer (G5) is composed of trifluorocresol substituents, which are slightly different from HIA fragments in the four inner layers of the molecule.

Scheme 3



at 8.44 ppm integrates as 32 protons, and the triplet at 8.87 shows 16 protons. These are two fully isolated signals coming from the G4 layer. The next doublet integrates as 18 protons (16H from G3 layer and 2H from the core), and the other two doublets shifted downfield correspond to eight and four protons from G2 and G1 layers, respectively. On the other hand, the triplet from the core and that from the G3 layer are also isolated and located at 8.95 ppm (1H) and 8.99 ppm (8H). The signal at 9.02 ppm integrates as six protons and represents the overlapped resonances of protons from the G2 and G1 layers. Finally, three doublets with $J = 8.4$ Hz at 6.85, 7.57, and 8.21 ppm are also visible in the spectrum which correspond to biphenyl protons (the signal from two additional biphenyl protons is buried under the doublet at 7.75 ppm). This compound and all the intermediate precursors were also characterized by ^{13}C NMR, mass spectrometry, elemental analysis, and gel permeation chromatography (GPC).

The next part of the overall synthesis of DRC involves the separate preparation of functionalized rodcoil molecules which can be coupled to compound **17**. We previously synthesized and studied molecules that contain flexible oligoisoprene or oligobutadiene blocks and three biphenyl ester units.[16] Because compound **17** already has one biphenyl with a hydroxyl group, we prepared a carboxyl-terminated rodcoil with two biphenyl esters. Scheme 3 shows the synthesis of the rodcoil and its coupling to the G5 dendron. Compound **18**, which is a building block for the construction of the rod segment, was synthesized in one step via the reaction of 4-hydroxy-biphenylcarboxylic acid and TBDMSCl using morpholine as a base. Living anionic polymerization of isoprene was used to grow oligoisoprene coil with a low polydispersity index of 1.07, which contains on average nine monomeric units (mostly 1,4- and 3,4-addition according to NMR). Functionalization of the coil with a hydroxyl group was achieved by reaction between the living chains and ethylene oxide at room temperature. The Mitsunobu reaction between **18** and the coil afforded intermediate precursor **20** which was deprotected with TBAF to give carboxyl-terminated molecule **21**. The second biphenyl was then coupled under standard DPTS/DIPC conditions, and the following deprotection of the silyl group yielded rodcoil **23** which was isolated in a pure state simply by pouring the reaction mixture into excess methanol. This is a particularly convenient way to purify the product because the resultant rodcoil is not soluble in methanol, unlike all the starting materials and byproducts of the reaction. Finally, the esterification reaction between rodcoil **23** and compound **17** gave the first example of high generation DRC **24** containing 32 CF_3 groups on its periphery. The number average molecular weight (M_n) of this structure is about 11 000 measured by MALDI-TOF. The polydispersity index determined by GPC is similar to that of the starting rodcoil (1.08) prepared via living anionic polymerization which inevitably generates a small degree of structural diversity in the system. Figure 3 shows the chemical structure and the corresponding molecular graphics representation of DRC molecule **24**. This nanosized molecule measures 9 nm in length and 3.8 nm in diameter (dendritic block). This material was fully characterized by various techniques, and its properties will be reported elsewhere.

Divergent Synthesis. Analogous aryl ester dendron rodcoils were also synthesized via a divergent approach outlined in Scheme 4. We previously reported the synthesis of hydroxyl-

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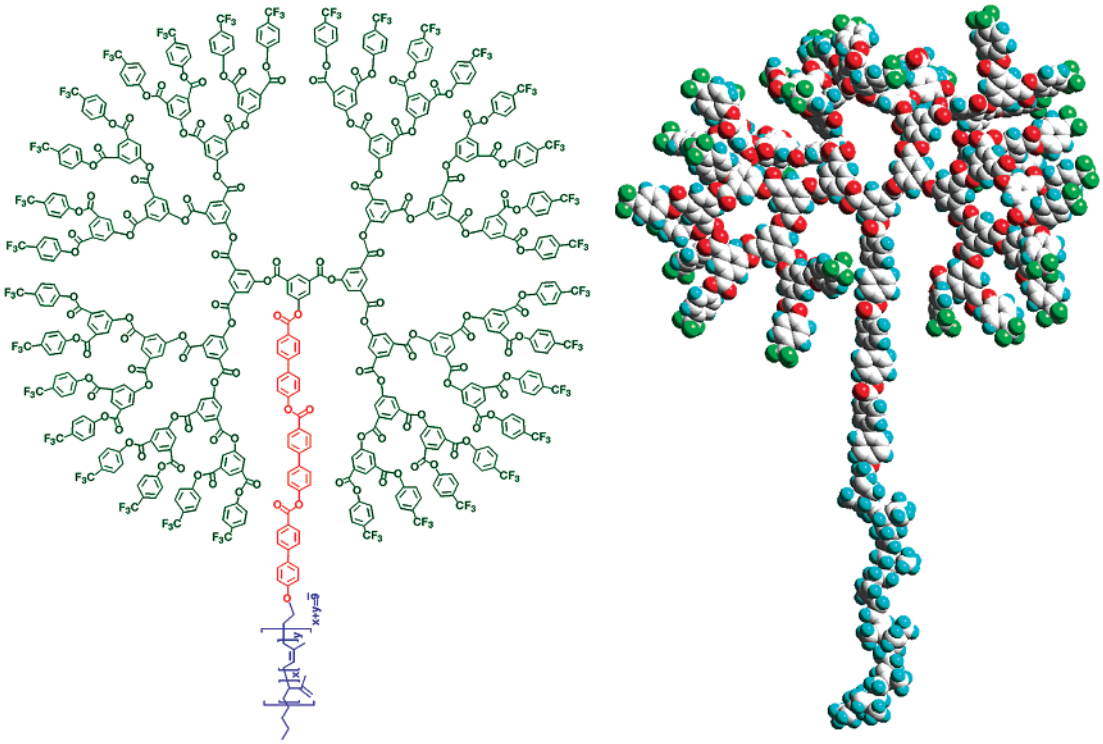

Figure 3. Chemical structure (right) and the corresponding molecular graphics representation of dendron rodcoil molecule **24**.

terminated G1 DRC **27** which has four OH groups on its periphery.[10] To convert **27** to high generation analogues, we prepared a slightly different AB_2 monomer (compound **26**) based on 3,5-dihydroxybenzoic acid (DHA) which can be used for divergent growth of the dendritic block. Reaction between DHA and 3 equiv of TBDMSCl gave the fully protected compound **25** which was converted to **26** via selective deprotection of the carboxylic group under acidic conditions. Esterification reactions and successive deprotection of TBDMS groups were carried out under conditions similar to those used for convergent synthesis. Repetition of these two types of reactions resulted in formation of a hydrophobic silyl-terminated DRC series (from G1 to G5) and a hydrophilic series of OH-terminated molecules. For example, molecule **34** contains 64 TBDMS groups and has a number average molecular weight (M_n) of 17 200 measured by MALDI, whereas molecule **33** can be considered as a dendritic amphiphile because it has 32 hydroxyl groups located in the outer layer. Completion of the deprotection reactions was monitored by NMR, GPC, and MALDI measurements for each intermediate generation. The advantage of this approach lies in the fact that TBDMS groups as well as hydroxyl groups are located on the periphery of the dendritic shell, which makes them easily accessible for deprotection reagents. As a result, all the reactions in Scheme 4 proceeded fairly rapidly and with nearly quantitative yields. Also, there was no solubility problem, and molecules **28**−**34** were found to be highly soluble in organic solvents.

It is well known that formation of structural defects during divergent synthesis can become a serious problem especially for high generation molecules.[17] We used different characterization techniques to estimate the number of defects and to find out if this depends on the generation of the dendron. NMR spectroscopy was very useful to monitor the completion of both deprotection and esterification reactions (disappearance of TBDMS and OH peaks, respectively). However, identification of generational layers as described previously for the CF_3-terminated molecules was only possible for G2 and G3 products, whereas high generation DRCs generate in this case rather broad signals which partially overlap with those of protons from the rod block. Therefore, measurements of absolute molecular weight by mass spectrometry were necessary to confirm the structure of high generation DRCs. Figure 4 shows MALDI-TOF spectra of all five TBDMS-terminated molecules (G1 through G5). The average molecular weights of these structures were found to be very close to theoretical values, and the polydispersity indices calculated from MALDI spectra were within the range from 1.004 to 1.01. As we mentioned previously, DRC molecules are structurally diverse due to the presence of the oligoisoprene coil segment synthesized by living anionic polymerization. However, the polydispersity remains nearly constant and does not depend on generation number. This suggests that divergent growth of the dendritic block does not result in the formation of a considerable amount of structural defects. Similar MALDI spectra were obtained for a series of hydrophilic DRC molecules terminated with hydroxyl groups. These data gave us a rare opportunity to make a comparison between molecular weights measured by two independent methods such as MALDI and GPC. Figure 5 shows molecular weight of silyl-terminated DRCs as a function of generation number. The difference between GPC and MALDI data is positive at low generation but decreases rapidly as the generation number increases. At G4 both numbers practically coincide, and for G5 molecules GPC molecular weight becomes even lower than the absolute molecular weight measured by MALDI. It is

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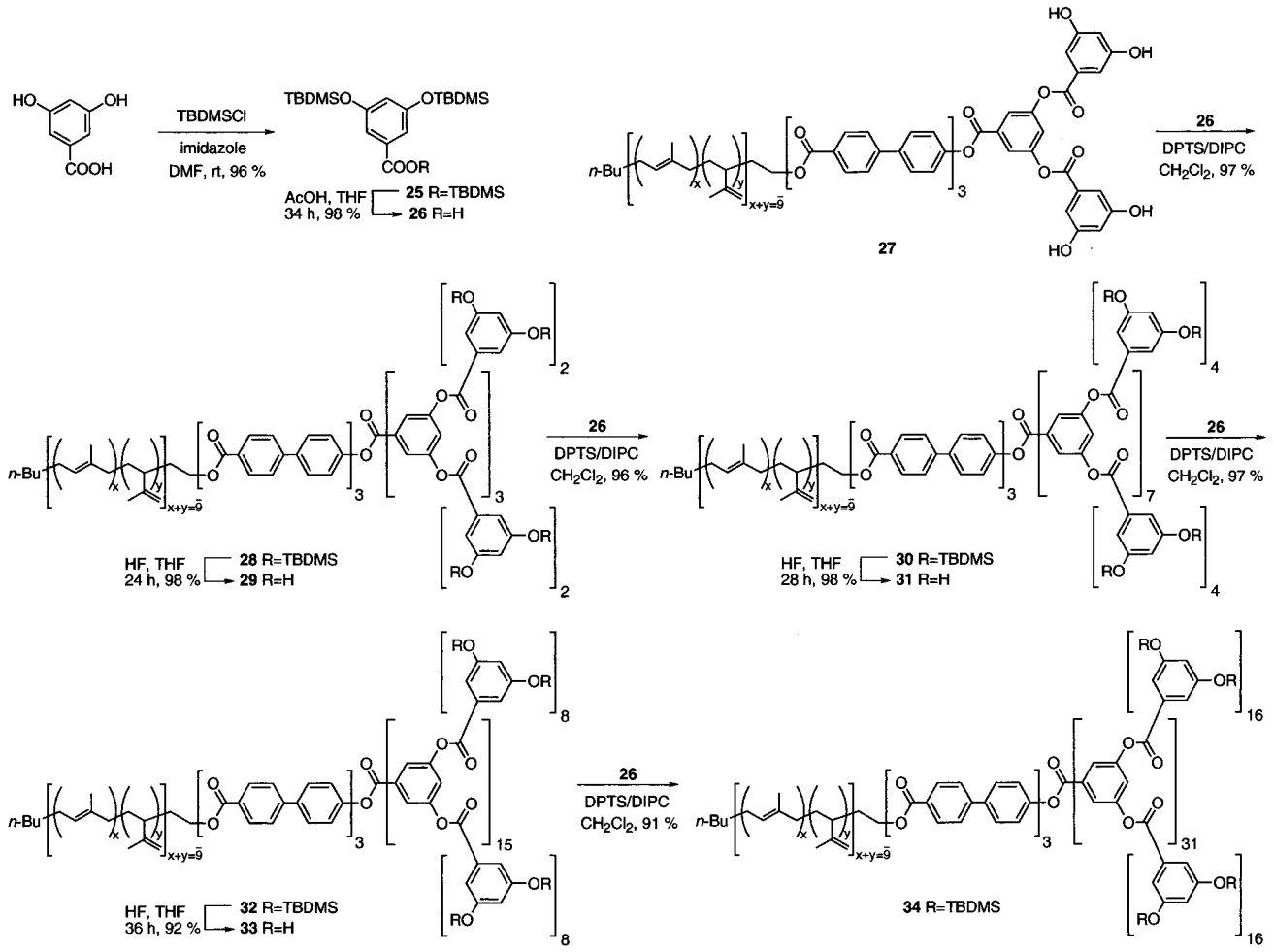
Scheme 4



well known that molecular weight estimated by GPC relative to polystyrene standards strongly depends on the shape and flexibility of molecules. For example, rigid rods have greater radii of gyration relative to polystyrene chains of the same molecular weight. As a result, they can only pass through much bigger pores of styrogel used in GPC columns, and that is why the measured molecular weight of rigid molecules is always overestimated by GPC. Low generation DRCs have fairly small dendritic blocks, and their overall rigidity and anisometric shape are still very high due to the presence of a much larger rodcoil segment. As the generation increases, the contribution of the dendron grows, and the difference between the GPC and MALDI data becomes less significant. On the other hand, all high generation dendrimers exhibit a significantly more compact globular shape than do their linear counterparts.[18] Therefore, the density of high generation dendrimers is much greater than that of linear polystyrene chains of the same molecular weight. As a result, GPC measures a considerably lower molecular weight as was previously described for various dendrimers.[18,19] An underestimated molecular weight by GPC was observed here only for G5 DRC molecules (Figure 5), indicating that the contribution of the compact dendritic block becomes greater in these molecules relative to that of the rigid biphenyl ester rod segments.

Conclusions

A series of novel block structures containing dendritic, rodlike, and coillike molecular segments termed dendron rodcoils were successfully synthesized using either a convergent or a divergent strategy. A combination of catalyzed esterification reactions and silyl protection/deprotection chemistry proved to be a very efficient and versatile method for construction of these nanosized molecules with unusual molecular architecture. Both synthetic strategies allowed for the preparation of nearly monodisperse dendritic molecules as demonstrated by NMR, MALDI-TOF, and GPC measurements. Properties of the highly hydrophobic and amphiphilic DRC structures will be described in an upcoming paper.

Experimental Section

General Procedures. Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and benzene were redistilled from Na^+/benzophenone ketyl, and 4-(*N*,*N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared as described elsewhere.[13] Isoprene was redistilled under nitrogen and dried over calcium hydride before use. The ^{1}H NMR and spectra were recorded in THF-d_8 or DMSO-d_6 solutions using a Varian Unity 500 (500 MHz) or Varian

(18) Xu, Z. F.; Moore J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354−1357.
(19) (a) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401. (b) Xu, Z. F.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537−4550. (c) Murer, P.; Seebach, D. *Helv. Chim. Acta* **1998**, *81*, 603.

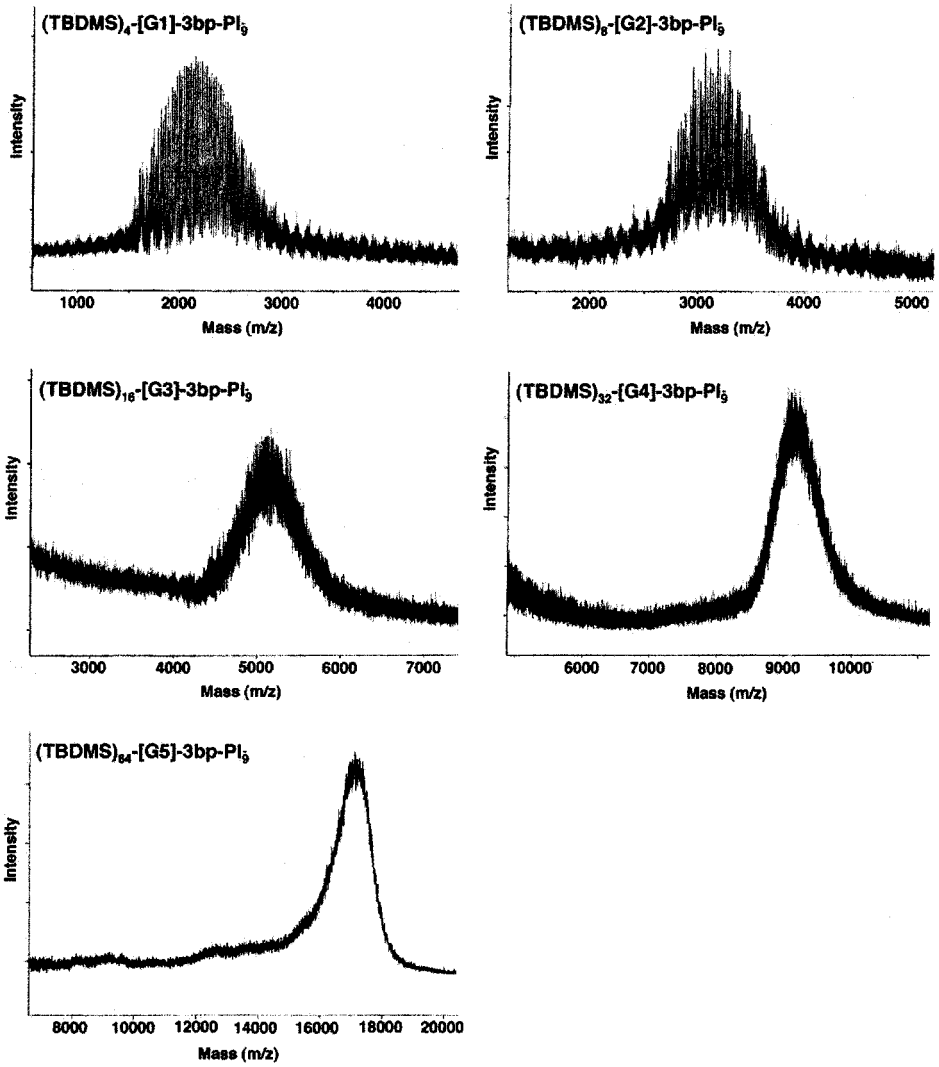


Figure 4. MALDI-TOF traces of the TBDMS-terminated DRC molecules (G1 through G5) synthesized via divergent approach. The generation number of the dendritic block is indicated in the upper left corner of each spectrum.

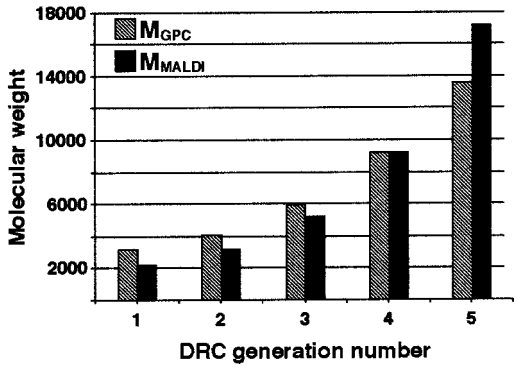


Figure 5. Molecular weight of the TBDMS-terminated DRC molecules as a function of the generation number of the dendritic segment measured by MALDI-TOF and GPC, respectively.

Unity 400 (400 MHz) spectrometer using the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 125 MHz on a Varian Unity 500 spectrometer using THF-d_8 or DMSO-d_6 as solvents. The following abbreviations are used: Ar refers to aromatic rings derived from 5-hydroxyisophthalic acid, Ph refers to aromatic rings derived from α,α,α-trifluoro-*p*-cresol, Ar′ refers to aromatic rings derived from biphenyl fragments, and Ar″ refers to aromatic rings derived from 3,5-dihydroxybenzoic acid. High-resolution field desorption mass spectra were collected on a Micromass 70-VSE spectrometer operating at 8 KV acceleration voltage and 4 KV extraction plate voltage. Matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained on a VG TofSpec spectrometer using dithranol and silver trifluoroacetate as a matrix for DRC molecules **28**−**34**. Molecular weights of compounds **9** and **10** were determined by MALDI using *trans*-3-indoleacrylic acid (IAA) as a matrix. Elemental analysis was performed using a Perkin-Elmer Model P2000 analyzer. Gel permeation chromatography (GPC) was carried out on a Waters 486 chromatograph in THF using styragel HMW 2 and styragel HMW 6E columns, 510 pumps, 486 UV-detector, and 410 RI detector.

General Procedure for Esterification Reactions (Convergent Synthesis of Dendrons). These preparations were carried out on a scale of 0.5−10 g depending on generation number. 5-*tert*-Butyldimethylsilyloxyisophthalic acid **2** (1 equiv), phenol (2.1 equiv), DPTS (2.2 equiv), and CH_2Cl_2 were all combined in an oven-dried flask with stirring bar under N_2. DIPC (2.2 equiv) was added via syringe, and the reaction was allowed to stir for 5 h. Urea impurities were then removed by precipitating the concentrated reaction mixture into methanol (three times). The precipitate was dissolved in CH_2Cl_2, and the crude product was purified by flash chromatography (silica gel).

General Procedure for Silyl Deprotection (Convergent Synthesis of Dendrons). These preparations were carried out on a scale of 0.5−10 g depending on generation number. Silyl protected dendron (1 equiv) was dissolved in THF in a plastic vessel. Hydrofluoric acid (49%

aqueous solution) was added via syringe (20 equiv). Depending on generation number, the reaction mixture was allowed to stir for several hours (1, 3, 8, 24, and 8 h for G1, G2, G3, G4, and G5 dendrons, respectively). The reaction was diluted by CH_2Cl_2 and quenched by a saturated solution of sodium bicarbonate. The resultant mixture was washed several times with water, and the crude product was purified by flash chromatography as outlined in the following text.

General Procedure for Esterification Reactions of Biphenyl Derivatives. The acid (1 equiv), phenol (1 equiv), DPTS (1.2 equiv), and CH_2Cl_2 were combined in a flask with stirring bar under nitrogen atmosphere. DIPC (1.5 equiv) was added via syringe, and the reaction was allowed to stir for 2 h. Urea impurities were then removed by precipitating the concentrated reaction mixture into methanol (three times). The precipitate was dissolved in CH_2Cl_2, and the crude product was purified by flash chromatography as outlined in the following text.

General Procedure for Silyl Deprotection of Biphenyl Derivatives. The protected phenol (or arylacid) (1 equiv) was dissolved in THF and cooled to −78 °C. TBAF (1.0 M solution in THF, 1.2 equiv) was added via syringe, and the reaction was stirred for 15 min at −78 °C. The reaction was quenched with 10% AcOH/THF. The reaction was diluted with CH_2Cl_2 and washed with H_2O. The organic layer was collected, dried, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography as outlined in the following text.

Compound 1. 5-Hydroxyisophthalic acid (1 equiv) and imidazole (3.8 equiv) were dissolved in *N*,*N*-dimethylformamide under N_2. *tert*-Butyldimethylsilyl chloride (3.5 equiv) was added, and the solution was stirred overnight. The resulting mixture was diluted with CH_2Cl_2, washed with saturated aqueous sodium bicarbonate and water, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the product was purified by column chromatography (CH_2Cl_2) to give **1** as a colorless liquid. Yield: 98%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.25 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.48 (s, 12H, COOSi(CH_3)$_2$C-(CH$_3$)$_3$), 0.97 (br s, 27H, Si(CH$_3$)$_2$C(CH_3)$_3$), 7.63 (d, 2H, J = 1.2 Hz, Ar*H*), 8.21 (t, 1H, J = 1.3 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.33, 0.24, 18.26, 19.13, 26.18, 121.15, 124.91, 133.17, 156.90, 167.41. FD-MS *m*/*z* 524.5 (M^+), calcd M = 524.9. Anal. Calcd for $C_{26}H_{48}O_5Si_3$: C, 59.54; H, 9.16; Si, 16.03. Found: C, 59.83; H, 9.29; Si, 16.36.

5-*tert*-Butyldimethylsilyloxyisophthalic Acid (2). Compound **1** (20 g) was dissolved in 300 mL of THF/H_2O/AcOH mixture (50:10:40) and stirred for 24 h. The reaction mixture was concentrated under reduced pressure and precipitated into 500 mL of ethanol. The precipitate was washed several times with saturated aqueous solution of sodium bicarbonate and water and was then recrystallized from 30% hexanes/CH_2Cl_2 to give **2** as white needlelike crystals (mp 176 °C). Yield: 78%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.15 (s, 6H, OSi-(CH_3)$_2$C(CH$_3$)$_3$), 0.92 (s, 9H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 7.50 (d, 2H, J = 1.1 Hz, Ar*H*), 8.05 (t, 1H, J = 1.3 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.36, 18.24, 26.09, 120.49, 124.91, 133.12, 155.82, 166.83. FD-MS *m*/*z* 296.4 [M^+], calcd M = 296.4. Anal. Calcd for $C_{14}H_{20}O_5Si$: C, 56.76; H, 6.76; Si, 9.46. Found: C, 56.81; H, 6.79; Si, 9.38.

(CF$_3$)$_2$-[G-1]-OTBDMS (3). This compound was prepared from α,α,α-trifluoro-*p*-cresol and **2** and was purified by flash chromatography eluting with CH_2Cl_2 to give **3** as a white solid (mp 158 °C). Yield: 95%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.28 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.03 (s, 9H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 7.50 (A of ABq, d, 4H, J = 8.4 Hz, CF$_3$Ph*H*), 7.80 (B of ABq, d, 4H, J = 8.4 Hz, CF$_3$Ph*H*), 7.97 (d, 2H, J = 1.6 Hz, Ar*H*), 8.55 (t, 1H, J = 2.0 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.36, 18.92, 26.07, 122.53, 123.03, 123.47, 127.68, 128.62, 128.81, 132.24, 154.87, 158.60, 164.10. FD-MS *m*/*z* 584.4 [M^+], calcd M = 584.8. Anal. Calcd for $C_{28}H_{26}F_6O_5Si$: C, 57.53; H, 4.45; F, 19.52; Si, 4.79. Found: C, 57.68; H, 4.53; F, 19.87; Si, 4.77.

(CF$_3$)$_2$-[G-1]-OH (4). This compound was prepared from **3** and was purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 10% THF/CH_2Cl_2 to give **4** as white needlelike crystals (mp 263 °C). Yield: 99%. ^{1}H NMR (500 MHz, THF-d_8): δ 7.50 (A of ABq, d, 4H, J = 8.4 Hz, CF$_3$Ph*H*), 7.80 (B of ABq, d, 4H, J = 8.4 Hz, CF$_3$Ph*H*), 7.86 (d, 2H, J = 1.5 Hz, Ar*H*), 8.45 (t, 1H, J = 2.1 Hz, Ar*H*), 9.29 (s, 1H, ArO*H*). ^{13}C NMR (125 MHz, THF-d_8): δ 122.53, 122.98, 123.46, 127.68, 128.61, 128.84, 132.18, 154.87, 159.50, 164.07. FD-MS *m*/*z* 470.3 [M^+], calcd M = 470.3. Anal. Calcd for $C_{22}H_{12}F_6O_5$: C, 56.17; H, 2.55; F, 24.26. Found: C, 56.29; H, 2.49; F, 24.19.

(CF$_3$)$_4$-[G-2]-OTBDMS (5). This compound was prepared from **4** and **2** and was purified by flash chromatography eluting with CH_2Cl_2 to give **5** as a colorless glass. Yield: 88%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.30 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.03 (s, 9H, OSi(CH$_3$)$_2$C-(CH_3)$_3$), 7.53 (A of ABq, d, 8H, J = 8.6 Hz, CF$_3$Ph*H*), 7.81 (B of ABq, d, 8H, J = 8.6 Hz, CF$_3$Ph*H*), 8.03 (d, 2H, J = 1.7 Hz, Ar*H*), 8.46 (d, 4H, J = 1.7 Hz, Ar*H*), 8.67 (t, 1H, J = 1.7 Hz, Ar*H*), 8.89 (t, 2H, J = 1.6 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.4, 18.93, 25.68, 122.77, 123.41, 124.12, 126.28, 127.75, 128.82, 129.06, 129.52, 132.01, 132.60, 152.58, 154.73, 157.57, 163.41, 164.43. FD-MS *m*/*z* 1200.4 [M^+], calcd M = 1201.0. Anal. Calcd for $C_{58}H_{40}F_{12}O_{13}Si$: C, 58.00; H, 3.33; F, 19.00; Si, 2.33. Found: C, 58.21; H, 2.41; F, 19.09; Si, 2.31.

(CF$_3$)$_4$-[G-2]-OH (6). This compound was prepared from **5** and was purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 10% THF/CH_2Cl_2 to give **6** as a colorless glass. Yield: 98%. ^{1}H NMR (500 MHz, THF-d_8): δ 7.54 (A of ABq, d, 8H, J = 8.4 Hz, CF$_3$Ph*H*), 7.81 (B of ABq, d, 8H, J = 8.4 Hz, CF$_3$Ph*H*), 7.93 (d, 2H, J = 1.5 Hz, Ar*H*), 8.46 (d, 4H, J = 1.7 Hz, Ar*H*), 8.56 (t, 1H, J = 1.6 Hz, Ar*H*), 8.89 (t, 2H, J = 1.6 Hz, Ar*H*), 9.39 (s, 1H, ArO*H*). ^{13}C NMR (125 MHz, THF-d_8): δ 122.79, 123.44, 124.10, 126.26, 127.74, 128.81, 129.06, 129.51, 131.99, 132.60, 152.60, 154.72, 159.58, 163.40, 164.40. FD-MS *m*/*z* 1086.45 [M^+], calcd M = 1086.74. Anal. Calcd for $C_{52}H_{26}F_{12}O_{13}$: C, 57.46; H, 2.39; F, 20.99. Found: C, 57.71; H, 2.46; F, 20.79.

(CF$_3$)$_8$-[G-3]-OTBDMS (7). This compound was prepared from **6** and **2** and was purified by flash chromatography eluting with 5% THF/CH_2Cl_2 to give **7** as a colorless glass. Yield: 93%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.32 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.03 (s, 9H, OSi(CH$_3$)$_2$C-(CH_3)$_3$), 7.53 (A of ABq, d, 16H, J = 8.5 Hz, CF$_3$Ph*H*), 7.81 (B of ABq, d, 16H, J = 8.5 Hz, CF$_3$Ph*H*), 8.04 (d, 2H, J = 1.8 Hz, Ar*H*), 8.50 (d, 8H, J = 1.6 Hz, Ar*H*), 8.53 (d, 4H, J = 1.7 Hz, Ar*H*), 8.68 (t, 1H, J = 1.7 Hz, Ar*H*), 8.91 (t, 4H, J = 2.1 Hz, Ar*H*), 9.01 (t, 2H, J = 2.1 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.1, 19.01, 25.61, 121.87, 123.39, 124.06, 126.23, 127.71, 128.37, 128.58, 128.84, 129.11, 129.40, 129.55, 132.29, 132.56, 152.30, 152.52, 154.63, 157.73, 163.33, 163.64, 164.34. FD-MS *m*/*z* 2432.4 [M^+], calcd M = 2433.83. Anal. Calcd for $C_{118}H_{68}F_{24}O_{29}Si$: C, 58.22; H, 2.80; F, 18.75; Si, 1.15. Found: C, 58.23; H, 2.96; F, 18.86; Si, 1.23.

(CF$_3$)$_8$-[G-3]-OH (8). This compound was prepared from **7** and was purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 30% THF/CH_2Cl_2 to give **8** as a colorless glass. Yield: 97%. ^{1}H NMR (500 MHz, THF-d_8): δ 7.53 (A of ABq, d, 16H, J = 8.4 Hz, CF$_3$Ph*H*), 7.80 (B of ABq, d, 16H, J = 8.4 Hz, CF$_3$Ph*H*), 7.95 (d, 2H, J = 1.5 Hz, Ar*H*), 8.50 (d, 8H, J = 1.5 Hz, Ar*H*), 8.53 (d, 4H, J = 1.7 Hz, Ar*H*), 8.57 (t, 1H, J = 1.6 Hz, Ar*H*), 8.91 (t, 4H, J = 2.1 Hz, Ar*H*), 9.01 (t, 2H, J = 2.1 Hz, Ar*H*), 9.40 (s, 1H, ArO*H*). ^{13}C NMR (125 MHz, THF-d_8): δ 121.88, 123.40, 124.04, 126.20, 127.73, 128.37, 128.57, 128.84, 129.09, 129.39, 129.56, 129.71, 132.28, 132.54, 152.30, 154.60, 159.71, 163.35, 163.64, 164.39. FD-MS *m*/*z* 2318.9 [M^+], calcd M = 2319.3. Anal. Calcd for $C_{112}H_{54}F_{24}O_{29}$: C, 57.98; H, 2.33; F, 19.67. Found: C, 58.11; H, 2.46; F, 19.79.

(CF$_3$)$_{16}$-[G-4]-OTBDMS (9). This compound was prepared from **8** and **2** and was purified by flash chromatography eluting with CH_2Cl_2 to give **9** as a colorless glass. Yield: 88%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.32 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.04 (s, 9H, OSi(CH$_3$)$_2$C-(CH_3)$_3$), 7.52 (A of ABq, d, 32H, J = 8.6 Hz, CF$_3$Ph*H*), 7.79 (B of ABq, d, 32H, J = 8.6 Hz, CF$_3$Ph*H*), 8.03 (d, 2H, J = 1.8 Hz, Ar*H*),

8.48 (d, 16H, J = 1.5 Hz, Ar*H*), 8.54 (d, 4H, J = 1.7 Hz, Ar*H*), 8.56 (d, 8H, J = 1.6 Hz, Ar*H*), 8.69 (t, 1H, J = 1.7 Hz, Ar*H*), 8.90 (t, 8H, J = 2.1 Hz, Ar*H*), 9.02 (t, 6H, J = 2.1 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.4, 18.92, 25.72, 121.89, 123.40, 124.05, 125.30, 126.21, 127.75, 128.38, 128.60, 128.86, 129.12, 129.44, 129.61, 129.71, 132.24, 132.52, 132.65, 152.40, 152.47, 152.59, 154.65, 157.55, 163.36, 163.66, 163.75, 164.17. MALDI-MS m/z 4896.7 [M+H]$^+$, calcd M = 4896.1. Anal. Calcd for $C_{238}H_{124}F_{48}O_{61}Si$: C, 58.33; H, 2.53; F, 18.63; Si, 0.57. Found: C, 58.42; H, 2.56; F, 18.79; Si, 0.63.

$(CF_3)_{16}$-[G-4]-OH (10). This compound was prepared from **9** and was purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 10% THF/CH_2Cl_2 to give **10** as a colorless glass. Yield: 82%. ^{1}H NMR (500 MHz, THF-d_8): δ 7.51 (A of ABq, d, 32H, J = 8.4 Hz, CF_3Ph*H*), 7.78 (B of ABq, d, 32H, J = 8.4 Hz, CF_3Ph*H*), 7.94 (d, 2H, J = 1.5 Hz, Ar*H*), 8.48 (d, 16H, J = 1.3 Hz, Ar*H*), 8.54 (d, 4H, J = 1.7 Hz, Ar*H*), 8.56 (d, 8H, J = 1.6 Hz, Ar*H*), 8.58 (t, 1H, J = 1.6 Hz, Ar*H*), 8.90 (t, 8H, J = 2.1 Hz, Ar*H*), 9.02 (t, 6H, J = 2.1 Hz, Ar*H*), 9.40 (s, 1H, ArO*H*). ^{13}C NMR (125 MHz, THF-d_8): δ 121.91, 123.38, 124.08, 126.23, 127.75, 128.37, 128.61, 128.86, 129.10, 129.44, 129.61, 129.74, 132.02, 132.20, 132.51, 132.65, 152.40, 152.47, 152.61, 154.67, 159.52, 163.37, 163.64, 163.75, 164.23. MALDI-MS m/z 4782.7 [M + H]$^+$, calcd M = 4782.2. Anal. Calcd for $C_{232}H_{110}F_{48}O_{61}$: C, 58.22; H, 2.30; F, 19.07. Found: C, 58.29; H, 2.45; F, 19.03.

Compound 11. A dry flask was charged with 4′-hydroxy-4-biphenylcarboxylic acid (1 equiv), imidazole (2.2 equiv), and dichloromethane. After stirring for 10 min, *tert*-butyldimethylsilyl chloride (2.6 equiv) was added. The solution was stirred overnight at room temperature, then diluted with dichloromethane and washed several times with saturated aqueous sodium bicarbonate and water. The organic layers were then dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The product was purified by flash chromatography eluting with CH_2Cl_2 to give **11** as a colorless liquid. Yield: 91%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (br s, 12H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.04 (br s, 18H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 6.96 (d, 2H, J = 8.5 Hz, Ar′*H*), 7.60 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.69 (d, 2H, J = 8.6 Hz, Ar′*H*), 8.16 (d, 2H, J = 8.4 Hz, Ar′*H*). FD-MS m/z 442.4 [M$^+$], calcd M = 442.7. Anal. Calcd for $C_{25}H_{38}O_3Si_2$: C, 67.87; H, 8.60; Si, 12.67. Found: C, 67.72; H, 8.71; Si, 12.35.

4′-*tert*-Butyldimethylsilyloxy-4-biphenylcarboxylic Acid (12). This compound was prepared from **11** and was purified by flash chromatography eluting with 30% THF/CH_2Cl_2 and recrystallization from 70% hexane/CH_2Cl_2 to give **12** as white crystals (mp 245 °C). Yield: 87%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.24 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.02 (s, 9H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 6.94 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.58 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.66 (d, 2H, J = 8.4 Hz, Ar′*H*), 8.06 (d, 2H, J = 8.4 Hz, Ar′*H*). FD-MS m/z 328.4 [M$^+$], calcd M = 328.5. Anal. Calcd for $C_{19}H_{24}O_3Si$: C, 69.51; H, 7.32; Si, 8.54. Found: C, 70.12; H, 7.55; Si, 8.39.

Compound 13. Morpholine (2 equiv), 5-hydroxy-isophthalic acid (1 equiv), and *N*,*N*-dimethylformamide were placed in a flask and stirred. *tert*-Butyldimethylsilyl chloride (2 equiv) was added, and the solution was stirred at room temperature for 3 min. The resulting mixture was diluted with dichloromethane, washed three times with water, and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the product was purified by flash chromatography eluting with 5% THF/CH_2Cl_2 to give **13** as a colorless liquid. Yield: 75%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.42 (s, 12H, Si(CH_3)$_2$C(CH$_3$)$_3$), 1.05 (s, 18H, Si(CH$_3$)$_2$C(CH_3)$_3$), 7.41 (d, 2H, J = 1.2 Hz, Ar*H*), 8.12 (t, 1H, J = 1.3 Hz, Ar*H*), 9.12 (s, 1H, ArO*H*). ^{13}C NMR (125 MHz, THF-d_8): δ 0.21, 19.08, 26.08, 121.12, 124.87, 133.15, 156.85, 167.35. FD-MS m/z 410.6 [M$^+$], calcd M = 410.6. Anal. Calcd for $C_{20}H_{34}O_5Si_2$: C, 58.54; H, 8.29; Si, 13.66. Found: C, 58.78; H, 8.41; Si, 13.38.

Compound 14. This compound was prepared from **13** and **12** and was purified by flash chromatography eluting with CH_2Cl_2 to give **14** as a white solid. Yield: 86%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.46 (s, 12H, COOSi(CH_3)$_2$C(CH$_3$)$_3$), 1.01 (br s, 27H, Si(CH$_3$)$_2$C(CH_3)$_3$), 7.04 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.67 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.81 (d, 2H, J = 8.5 Hz, Ar′*H*), 8.15 (d, 2H, J = 1.5 Hz, Ar*H*), 8.26 (d, 2H, J = 8.6 Hz, Ar′*H*), 8.65 (t, 1H, J = 1.5 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.36, 0.24, 18.91, 19.03, 26.09, 121.43, 127.39, 127.92, 128.31, 128.80, 129.25, 131.49, 133.73, 146.91, 152.29, 157.16, 157.47, 164.98, 166.33. FD-MS m/z 720.4 [M$^+$], calcd M = 721.1. Anal. Calcd for $C_{39}H_{56}O_7Si_3$: C, 65.00; H, 7.78; Si, 11.67. Found: C, 65.17; H, 7.89; Si, 11.71.

Compound 15. Compound **14** (5 g) was dissolved in 100 mL of THF/H_2O/AcOH mixture (50:10:40) and stirred for 36 h. The reaction mixture was concentrated under reduced pressure and precipitated into 500 mL of ethanol. The precipitate was washed several times with saturated aqueous solution of sodium bicarbonate and water and was then recrystallized from 30% hexanes/CH_2Cl_2 to give **15** as a white solid. Yield: 92%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.03 (s, 9H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 6.98 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.66 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.81 (d, 2H, J = 8.4 Hz, Ar′*H*), 8.11 (d, 2H, J = 1.5 Hz, Ar*H*), 8.24 (d, 2H, J = 8.6 Hz, Ar′*H*), 8.58 (t, 1H, J = 1.4 Hz, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.36, 18.91, 26.06, 121.41, 127.36, 127.92, 128.29, 128.80, 129.22, 131.48, 133.70, 146.92, 152.27, 157.16, 157.31, 164.94, 166.27. FD-MS m/z 492.5 [M$^+$], calcd M = 492.6. Anal. Calcd for $C_{27}H_{28}O_7Si$: C, 65.85; H, 5.69; Si, 5.69. Found: C, 65.43; H, 5.87; Si, 5.73.

$(CF_3)_{32}$-[G-5]-1bp-OTBDMS (16). This compound was prepared from **15** and **10** and was purified by flash chromatography eluting with CH_2Cl_2 to give **16** as a colorless glass. Yield: 89%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.28 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.04 (s, 9H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 6.99 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.50 (A of ABq, d, 64H, J = 10.2 Hz, CF_3Ph*H*), 7.68 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.77 (B of ABq, d, 64H, J = 10.2 Hz, CF_3Ph*H*), 7.83 (d, 2H, J = 8.6 Hz, Ar′*H*), 8.27 (d, 2H, J = 8.6 Hz, Ar′*H*), 8.44 (d, 32H, J = 1.5 Hz, Ar*H*), 8.52 (d, 18H, J = 1.7 Hz, Ar*H*), 8.55 (d, 8H, J = 1.7 Hz, Ar*H*), 8.59 (d, 4H, J = 1.8 Hz, Ar*H*), 8.88 (m, 16H, Ar*H*), 8.96 (t, 1H, J = 1.6 Hz, Ar*H*), 8.99 (m, 8H, Ar*H*), 9.03 (m, 6H, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ −4.46, 19.03, 26.09, 121.72, 123.27, 123.43, 123.68, 123.87, 124.10, 126.02, 126.26, 127.62, 128.20, 129.09, 129.49, 129.61, 131.52, 132.03, 132.21, 132.59, 132.66, 147.21, 151.26, 151.41, 151.77, 152.42, 152.58, 152.83, 153.82, 154.26, 154.68, 157.58, 160.71, 162.24, 162.39, 162.72, 163.40, 164.17. Anal. Calcd for $C_{491}H_{244}F_{96}O_{127}Si$: C, 58.80; H, 2.44; F, 18.20; Si, 0.28. Found: C, 58.69; H, 2.49; F, 18.14; Si, 0.33.

$(CF_3)_{32}$-[G-5]-1bp-OH (17). This compound was prepared from **16** and was purified by flash chromatography eluting with 10% THF/CH_2Cl_2 to give **17** as a colorless glass. Yield: 94%. ^{1}H NMR (500 MHz, THF-d_8): δ 6.85 (d, 2H, J = 8.6 Hz, Ar′*H*), 7.48 (A of ABq, d, 64H, J = 10.2 Hz, CF_3Ph*H*), 7.57 (d, 2H, J = 8.4 Hz, Ar′*H*), 7.75 (d, 66H, B of ABq, CF_3Ph*H* (64), J = 10.2 Hz and Ar′*H* (2)), 8.21 (d, 2H, J = 8.6 Hz, Ar′*H*), 8.44 (d, 32H, J = 1.5 Hz, Ar*H*), 8.52 (d, 19H, J = 1.7 Hz, Ar*H*(18) and Ar′O*H* (1)), 8.55 (d, 8H, J = 1.7 Hz, Ar*H*), 8.59 (d, 4H, J = 1.8 Hz, Ar*H*), 8.87 (t, 16H, Ar*H*), 8.95 (t, 1H, J = 1.6 Hz, Ar*H*), 8.99 (t, 8H, Ar*H*), 9.02 (t, 6H, Ar*H*). ^{13}C NMR (125 MHz, THF-d_8): δ 121.69, 123.28, 123.42, 123.70, 123.86, 124.08, 126.02, 126.24, 127.62, 128.21, 129.10, 129.47, 129.63, 131.52, 132.01, 132.19, 132.59, 132.66, 147.23, 151.25, 151.41, 151.75, 152.42, 152.56, 152.85, 153.82, 154.22, 154.65, 159.52, 160.71, 162.21, 162.39, 162.71, 163.40, 164.18. GPC (254 nm, THF) PDI = 1.03, M_n = 12 121. Anal. Calcd for $C_{485}H_{230}F_{96}O_{127}$: C, 58.75; H, 2.32; F, 18.41. Found: C, 58.59; H, 2.42; F, 18.13.

Compound 18. Morpholine (1 equiv), 4′-hydro-4-biphenylcarboxylic acid (1 equiv), and *N*,*N*-dimethylformamide were placed in a flask and stirred. *tert*-Butyldimethylsilyl chloride (1 equiv) was added, and the solution was stirred at room temperature for 3 min. The resulting mixture was diluted with CH_2Cl_2 and washed three times with water. The solvent was removed by rotary evaporation, and the crude product was purified by flash chromatography eluting with 5% THF/CH_2Cl_2

to give **18** as a white solid. Yield: 75%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.44 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.98 (s, 9H, OSi(CH$_3$)$_2$C(CH_3)$_3$), 6.98 (d, 2H, J = 8.6 Hz, Ar′H), 7.52 (d, 2H, J = 8.6 Hz, Ar′H), 7.63 (d, 2H, J = 8.6 Hz, Ar′H), 8.23 (d, 2H, J = 8.5 Hz, Ar′H), 8.44 (s, 1H, Ar′OH). FD-MS m/z 328.3 [M$^+$], calcd M = 328.5. Anal. Calcd for $C_{19}H_{24}O_3Si$: C, 69.51; H, 7.32; Si, 8.54. Found: C, 69.27; H, 7.61; Si, 8.08.

PI$_{\bar{9}}$-OH (19). THF (100 mL) was placed in a flask under nitrogen atmosphere, and *n*-BuLi (1 equiv) was added followed by the addition of isoprene (9 equiv). The reaction was stirred for 30 min, then quenched by bubbling ethylene oxide through the solution for 15 min followed by addition of 10 mL of 3 N HCl/THF ($^1/_2$). The solvent was removed by rotary evaporation. The crude material was purified by flash chromatography eluting with 50% CH_2Cl_2/hexane gradually increasing to CH_2Cl_2 to give **19** as a colorless liquid. Yield: 73%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.5−2.8 (br m, 70H aliphatic), 3.61 (br m, 2H, CH_2OH), 4.5−5.2 (br m, 14H vinyl). FD-MS m/z 730, 663, 596, 797, 864. Anal. Calcd for $C_{51}H_{86}O_2$: C, 83.83; H, 11.78. Found: C, 85.57; H, 12.42.

PI$_{\bar{9}}$-1bp-COOTBDMS (20). Compound **18** (1.3 equiv), oligoisoprene coil **19** (1 equiv), and triphenyl phosphine (1.5 equiv) were dissolved in CH_2Cl_2. After stirring for 5 min, diethyl azodicarboxylate (1.5 equiv) was added dropwise, and the reaction mixture was allowed to stir for 2 h. The resulting mixture was diluted with CH_2Cl_2 and washed three times with water. The solvent was removed by rotary evaporation, and the crude product was purified by flash chromatography eluting with CH_2Cl_2 to give **20** as a colorless liquid. Yield: 60%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.46 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.5−2.8 (br m, 80H aliphatic), 4.03 (br m, 2H, CH_2OAr′), 4.5−5.2 (br m, 14H vinyl), 7.01 (d, 2H, J = 8.7 Hz, Ar′H), 7.58 (d, 2H, J = 8.6 Hz, Ar′H), 7.67 (d, 2H, J = 8.6 Hz, Ar′H), 8.21 (d, 2H, J = 8.5 Hz, Ar′H). GPC (254 nm, THF) PDI = 1.09, M_n = 1260.

PI$_{\bar{9}}$-1bp-COOH (21). This was prepared from **20** and purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 30% THF/CH_2Cl_2 to give 2**1** as a colorless liquid. Yield: 87%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.5−2.8 (br m, 70H aliphatic), 4.01 (br m, 2H, CH_2OAr′), 4.5−5.2 (br m, 14H vinyl), 7.01 (d, 2H, J = 8.6 Hz, Ar′H), 7.55 (d, 2H, J = 8.6 Hz, Ar′H), 7.65 (d, 2H, J = 8.6 Hz, Ar′H), 8.14 (d, 2H, J = 8.5 Hz, Ar′H). GPC (254 nm, THF) PDI = 1.08, M_n = 1109.

PI$_{\bar{9}}$-2bp-COOTBDMS (22). This was prepared from compounds **21** and **18** and purified by flash chromatography eluting with CH_2Cl_2 to give **22** as a tacky solid. Yield: 86%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.46 (s, 6H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.5−2.9 (br m, 80H aliphatic), 4.04 (br m, 2H, CH_2OAr′), 4.5−5.2 (br m, 14H vinyl), 7.04 (d, 2H, J = 8.6 Hz, Ar′H), 7.42 (d, 2H, J = 8.4 Hz, Ar′H), 7.70 (d, 2H, J = 8.5 Hz, Ar′H), 7.82 (m, 6H, Ar′H), 8.21 (d, 2H, J = 8.6 Hz, Ar′H), 8.25 (d, 2H, J = 8.7 Hz, Ar′H). GPC (254 nm, THF) PDI = 1.07, M_n = 1670.

PI$_{\bar{9}}$-2bp-COOH (23). This was prepared from **22** and purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 30% THF/CH_2Cl_2 to give **23** as a white solid. Yield: 96%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.5−2.9 (br m, 70H aliphatic), 4.04 (br m, 2H, CH_2-OAr′), 4.5−5.2 (br m, 14H vinyl), 7.03 (d, 2H, J = 8.6 Hz, Ar′H), 7.41 (d, 2H, J = 8.4 Hz, Ar′H), 7.68 (d, 2H, J = 8.6 Hz, Ar′H), 7.81 (m, 6H, Ar′H), 8.16 (d, 2H, J = 8.6 Hz, Ar′H), 8.24 (d, 2H, J = 8.5 Hz, Ar′H). GPC (254 nm, THF) PDI = 1.07, M_n = 1410.

(CF$_3$)$_{32}$-[G-5]-3bp-PI$_{\bar{9}}$ (24). This was prepared from compound **17** and **23** and purified by flash chromatography eluting with CH_2Cl_2 to give **24** as a colorless glass. Yield: 89%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.5−2.8 (br m, 70H aliphatic), 4.04 (br m, 2H, CH_2OAr′), 4.5−5.2 (br m, 14H vinyl), 7.42 (d, 6H, J = 8.6 Hz, Ar′H), 7.48 (A of ABq, d, 64H, J = 9.1 Hz, CF$_3$PhH), 7.75 (d, 66H, B of ABq, CF$_3$PhH (64) and Ar′H (2)), 7.83 (m, 6H, Ar′H), 7.90 (d, 4H, J = 7.8 Hz, Ar′H), 8.27 (m, 6H, Ar′H), 8.44 (d, 32H, J = 1.5 Hz, ArH), 8.52 (d, 18H, J = 1.6 Hz, ArH), 8.55 (d, 8H, J = 1.6 Hz, ArH), 8.60 (d, 4H, J = 1.4 Hz, ArH), 8.87 (t, 16H, ArH), 8.97 (t, 1H, J = 1.6 Hz, ArH), 9.00 (t, 8H, ArH), 9.03 (t, 6H, ArH). ^{13}C NMR (125 MHz, THF-d_8): δ 14.43, 19.23, 23.52, 24.98, 28.10, 30.01, 32.79, 40.21, 43.05, 45.82, 63.42, 65.23, 67.93, 108.91, 108.96, 109.03, 121.56, 121.72, 123.27, 123.40, 123.68, 123.76, 124.10, 126.02, 126.13, 127.67, 128.05, 128.24, 129.10, 129.43, 129.67, 130.24, 131.52, 131.98, 132.03, 132.19, 132.59, 132.63, 147.26, 150.79, 151.25, 151.41, 151.75, 152.42, 152.56, 152.85, 153.82, 154.22, 154.65, 157.58, 160.71, 162.34, 162.39, 162.77, 163.42, 164.18. Calcd M = 11 032. Found MALDI-TOF: M_n = 11 000. GPC (254 nm, THF) PDI = 1.08, M_n = 13 450.

General Procedure for Esterification Reactions (Divergent Synthesis of the Dendritic Part of Dendron Rodcoils). These preparations were carried out on a scale of 4−12 g depending on generation number. A mixture of the appropriate dendron rodcoil (HO)$_m$-[G-*n*]-3bp-PI$_{\bar{9}}$ (1 equiv), 3,5-bis(*tert*-butyldimethylsilyloxy)benzoic acid **26** ((*m* + 1) equiv), and DPTS ((*m* + 1) equiv) was dissolved in CH_2Cl_2 and stirred under nitrogen. DIPC ((*m* + 1) equiv) was added via syringe, and the reaction was allowed to stir for 3 h. Urea impurities were then removed by precipitating the concentrated reaction mixture into methanol (three times). The precipitate was dissolved in CH_2Cl_2, and the crude product was purified by flash chromatography as outlined in the following text.

General Procedure for Silyl Deprotection (Divergent Synthesis of the Dendritic Part of Dendron Rodcoils). These preparations were carried out on a scale of 4−12 g depending on generation number. Silyl protected dendron rodcoil (TBDMSO)$_m$-[G-*n*]-3bp-PI$_{\bar{9}}$ (1 equiv) was dissolved in THF in a plastic vessel. Hydrofluoric acid (49% aqueous solution) was added via syringe ((*m* + 10) equiv). Depending on generation number, the reaction mixture was allowed to stir for several hours (from 24 to 36 h). The reaction was diluted by CH_2Cl_2 and quenched by a saturated solution of sodium bicarbonate. The resultant mixture was washed several times with water, and the crude product was purified by flash chromatography as outlined in the following text.

Compound 25. 3,5-Dihydroxybenzoic acid (1 equiv) and imidazole (3.5 equiv) were dissolved in *N*,*N*-dimethylformamide under nitrogen atmosphere. *tert*-Butyldimethylsilyl chloride (3.5 equiv) was added, and the solution was stirred overnight. The resulting mixture was diluted with CH_2Cl_2, washed with water, and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the product was purified by flash chromatography (CH_2Cl_2) to give **25** as a colorless liquid. Yield: 96%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.23 (s, 12H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.47 (s, 6H, COOSi(CH_3)$_2$C(CH$_3$)$_3$), 1.01 (br s, 27H, Si(CH$_3$)$_2$C(CH_3)$_3$), 6.60 (t, 1H, J = 2.2 Hz, Ar″H), 7.22 (d, 2H, J = 2.4 Hz, Ar″H). ^{13}C NMR (125 MHz, THF-d_8): δ −4.31, 0.17, 18.98, 19.19, 26.17, 115.65, 117.31, 133.97, 157.96, 167.40. FD-MS m/z 496.5 [M$^+$], calcd M = 496.9. Anal. Calcd for $C_{25}H_{48}O_4Si_3$: C, 60.48; H, 9.68; Si, 16.94. Found: C, 60.63; H, 9.74; Si, 16.69.

Compound 26. Compound **25** (18 g) was dissolved in 300 mL of THF/H_2O/AcOH mixture (50:10:40) and stirred for 24 h. The reaction mixture was concentrated under reduced pressure and precipitated into 500 mL of ethanol. The precipitate was washed several times with saturated aqueous solution of sodium bicarbonate and water and then was purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 40% THF/CH_2Cl_2 and recrystallization from 40% hexanes/CH_2Cl_2 to give **26** as a white solid. Yield: 98%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.22 (s, 12H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 1.00 (s, 18H, Si(CH$_3$)$_2$C(CH_3)$_3$), 6.54 (t, 1H, J = 2.2 Hz, Ar″H), 7.14 (d, 2H, J = 2.4 Hz, Ar″H). ^{13}C NMR (125 MHz, THF-d_8): δ −4.29, 18.88, 26.10, 115.47, 117.09, 133.80, 157.41, 167.21. FD-MS m/z 382.4 [M$^+$], calcd M = 382.6. Anal. Calcd for $C_{19}H_{34}O_4Si_2$: C, 59.69; H, 8.90; Si, 14.65. Found: C, 59.73; H, 8.99; Si, 14.61.

(TBDMSO)$_8$-[G-2]-3bp-PI$_{\bar{9}}$ (28). This was prepared from compounds **27** and **26** and was purified by flash chromatography eluting with CH_2Cl_2 to give **28** as a white solid. Yield: 97%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (s, 48H, OSi(CH_3)$_2$C(CH$_3$)$_3$), 0.5−2.8 (br m,

142H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.67 (t, 4H, J = 2.3 Hz, Ar″*H*), 7.32 (d, 8H, J = 2.4 Hz, Ar″*H*), 7.43 (m, 6H, Ar′*H*), 7.61 (t, 2H, J = 2.1 Hz, Ar″*H*), 7.78 (m, 5H, Ar′*H*(4) and Ar″*H*(1)), 7.85 (d, 4H, J = 8.6 Hz, Ar′*H*), 7.89 (d, 4H, J = 8.4 Hz, Ar′*H*), 8.07 (d, 4H, J = 2.2 Hz, Ar″*H*), 8.09 (m, 2H, Ar′*H*), 8.13 (d, 2H, J = 2.2 Hz, Ar″*H*), 8.29 (d, 4H, J = 8.2 Hz, Ar′*H*). Calcd M = 3166. Found MALDI-TOF: M_n = 3200. GPC (254 nm, THF) PDI = 1.06, M_n = 3890.

(HO)$_8$-[G-2]-3bp-PI$_{\bar{9}}$ (29). This was prepared from **28** and was purified by flash chromatography eluting with 30% THF/CH_2Cl_2 to give **29** as a white solid. Yield: 98%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.5−2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.50 (t, 4H, J = 2.2 Hz, Ar″*H*), 7.09 (d, 8H, J = 2.3 Hz, Ar″*H*), 7.42 (m, 6H, Ar′*H*), 7.59 (t, 2H, J = 2.2 Hz, Ar″*H*), 7.78 (m, 5H, Ar′*H*(4) and Ar″*H*(1)), 7.84 (d, 4H, J = 8.4 Hz, Ar′*H*), 7.88 (d, 4H, J = 8.3 Hz, Ar′*H*), 8.02 (d, 4H, J = 2.2 Hz, Ar″*H*), 8.09 (m, 2H, Ar′*H*), 8.12 (d, 2H, J = 2.2 Hz, Ar″*H*), 8.29 (d, 4H, J = 8.0 Hz, Ar′*H*), 8.56 (s, 8H, Ar″O*H*). Calcd M = 2254. Found MALDI-TOF: M_n = 2265. GPC (254 nm, THF) PDI = 1.07, M_n = 3040.

(TBDMSO)$_{16}$-[G-3]-3bp-PI$_{\bar{9}}$ (30). This was prepared from **29** and was purified by flash chromatography eluting with CH_2Cl_2 to give **30** as a white solid. Yield: 96%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (s, 96H, OSi(CH_3)$_2$C(CH_3)$_3$), 0.5−2.8 (br m, 214H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.68 (t, 8H, J = 2.3 Hz, Ar″*H*), 7.33 (d, 16H, J = 2.2 Hz, Ar″*H*), 7.44 (m, 6H, Ar′*H*), 7.61 (t, 4H, J = 2.2 Hz, Ar″*H*), 7.79 (m, 7H, Ar′*H*(4) and Ar″*H*(3)), 7.86 (m, 4H, Ar′*H*), 7.90 (m, 4H, Ar′*H*), 8.08 (d, 8H, J = 2.2 Hz, Ar″*H*), 8.12 (m, 4H, Ar′*H*(2) and Ar″*H*(2)), 8.17 (d, 4H, J = 2.2 Hz, Ar″*H*), 8.30 (d, 4H, J = 8.0 Hz, Ar′*H*). Calcd M = 5167. Found MALDI-TOF: M_n = 5181. GPC (254 nm, THF) PDI = 1.06, M_n = 6280.

(HO)$_{16}$-[G-3]-3bp-PI$_{\bar{9}}$ (31). This was prepared from **30** and was purified by flash chromatography eluting with 50% THF/CH_2Cl_2 to give **31** as a white solid. Yield: 98%. ^{1}H NMR (400 MHz, THF-d_8): δ 0.5−2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.50 (t, 8H, J = 2.2 Hz, Ar″*H*), 7.09 (d, 16H, J = 2.2 Hz, Ar″*H*), 7.43 (m, 6H, Ar′*H*), 7.59 (t, 4H, J = 2.2 Hz, Ar″*H*), 7.79 (m, 7H, Ar′*H*(4) and Ar″*H*(3)), 7.85 (m, 4H, Ar′*H*), 7.90 (d, 4H, J = 8.0 Hz, Ar′*H*), 8.03 (d, 8H, J = 2.2 Hz, Ar″*H*), 8.10 (m, 2H, Ar′*H*), 8.13 (d, 2H, J = 2.2 Hz, Ar″*H*), 8.17 (d, 4H, J = 2.2 Hz, Ar″*H*), 8.30 (d, 4H, J = 8.1 Hz, Ar′*H*), 8.58 (s, 16H, Ar″O*H*). Calcd M = 3343. Found MALDI-TOF: M_n = 3362. GPC (254 nm, THF) PDI = 1.06, M_n = 3950.

(TBDMSO)$_{32}$-[G-4]-3bp-PI$_{\bar{9}}$ (32). This was prepared from **31** and was purified by flash chromatography eluting with CH_2Cl_2 to give **32** as a white solid. Yield: 97%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (s, 192H, OSi(CH_3)$_2$C(CH_3)$_3$), 0.5−2.8 (br m, 358H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.67 (t, 16H, J = 2.3 Hz, Ar″*H*), 7.32 (d, 32H, J = 2.2 Hz, Ar″*H*), 7.43 (m, 6H, Ar′*H*), 7.60 (t, 8H, J = 2.1 Hz, Ar″*H*), 7.78 (t, 6H, J = 2.1 Hz, Ar″*H*), 7.80 (m, 5H, Ar′*H*(4) and Ar″*H*(1)), 7.86 (m, 4H, Ar′*H*), 7.90 (m, 4H, Ar′*H*), 8.07 (d, 16H, J = 2.2 Hz, Ar″*H*), 8.09 (d, 2H, J = 2.2 Hz, Ar″*H*), 8.11 (m, 2H, Ar′*H*), 8.16 (m, 12H, Ar″*H*), 8.30 (d, 4H, J = 8.0 Hz, Ar′*H*). Calcd M = 9167. Found MALDI-TOF: M_n = 9200. GPC (254 nm, THF) PDI = 1.06, M_n = 9190.

(HO)$_{32}$-[G-4]-3bp-PI$_{\bar{9}}$ (33). This was prepared from **32** and was purified by flash chromatography eluting with 50% THF/CH_2Cl_2 to give **33** as a white solid. Yield: 92%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.5−2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.48 (t, 16H, J = 2.2 Hz, Ar″*H*), 7.07 (d, 32H, J = 2.2 Hz, Ar″*H*), 7.42 (m, 6H, Ar′*H*), 7.58 (t, 8H, J = 2.2 Hz, Ar″*H*), 7.77 (m, 7H, Ar″*H*), 7.92−7.79 (m, 12H, Ar′*H*), 8.02 (d, 16H, J = 2.2 Hz, Ar″*H*), 8.08 (d, 2H, J = 2.2 Hz, Ar″*H*), 8.11 (m, 2H, Ar′*H*), 8.15 (d, 12H, J = 2.2 Hz, Ar″*H*), 8.29 (m, 4H, Ar′*H*), 8.56 (s, 32H, Ar″O*H*). Calcd M = 5519. Found MALDI-TOF: M_n = 5528. GPC (254 nm, THF) PDI = 1.08, M_n = 6230.

(TBDMSO)$_{64}$-[G-5]-3bp-PI$_{\bar{9}}$ (34). This was prepared from compounds **33** and **26** and was purified by flash chromatography eluting with CH_2Cl_2 to give **34** as a white solid. Yield: 91%. ^{1}H NMR (500 MHz, THF-d_8): δ 0.26 (s, 384H, OSi(CH_3)$_2$C(CH_3)$_3$), 0.5−2.8 (br m, 646H aliphatic), 4.30 (br m, 2H, CH_2OCOAr′), 4.5−5.2 (br m, 14H vinyl), 6.64 (t, 32H, J = 2.2 Hz, Ar″*H*), 7.30 (d, 64H, J = 2.4 Hz, Ar″*H*), 7.41 (m, 6H, Ar′*H*), 7.58 (t, 16H, J = 2.1 Hz, Ar″*H*), 7.76 (t, 15H, J = 2.0 Hz, Ar″*H*), 7.80 (m, 8H, Ar′*H*), 7.89 (m, 4H, Ar′*H*), 8.05 (d, 32H, J = 2.1 Hz, Ar″*H*), 8.10 (m, 2H, Ar′*H*), 8.14 (m, 30H, Ar″*H*), 8.29 (d, 4H, J = 8.0 Hz, Ar′*H*). Calcd M = 17 168. Found MALDI-TOF: M_n = 17 195. GPC (254 nm, THF) PDI = 1.06, M_n = 13 570.

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