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# Triazole-linked dendro[60]fullerenes: modular synthesis via a 'click' reaction and acidity-dependent self-assembly on the surface

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# A R T I C L E I N F O

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# ABSTRACT

A series of Fréchet-type dendron functionalized [60]fullerene derivatives that bear a 1,2,3-triazole linkage group, referred to as triazole-linked dendro[60]fullerenes, were prepared via a modular synthetic protocol based on a Cu-catalyzed [3+2] cycloaddition ('click') reaction. Electronic properties of these dendro[60]fullerenes were investigated by UV-vis spectroscopy and cyclic voltammetry. Interfacial supramolecular self-assembly behavior of these dendro[60]fullerenes was studied using atomic force microscopy (AFM). The resulting self-assemblies showed different nanoscale packing geometries and morphologies on the surface, which are controllable by parameters such as the generation of dendron, the nature of peripheral functionalities, and the experimental conditions (e.g., acidity) applied. Correlations between molecular structure and self-assembling outcome were surveyed and discussed. The results of this study suggest a new avenue to gain better 'bottom-up' control over the self-assembly of dendrimer–fullerene hybrid materials in terms of shape and size.

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# 1. Introduction

Ever since its first discovery in the early 1980s. [60]fullerene  $(C_{60})$  has become one of the most intensively investigated carbon nanomaterials, in view of its aesthetic spherical molecular structure, extremely small size (ca. 0.7 nm in diameter), and rich electronic and photophysical properties resulting from its unique 3D electron delocalization.<sup>1,2</sup> So far, the applications of  $C_{60}$  and its various derivatives have encompassed a great number of areas, ranging from molecular devices (e.g., photovoltaics,<sup>3–9</sup> nonlinear optics<sup>10–13</sup>), molecular machinery,<sup>14,15</sup> supramolecular chemistry,<sup>16–21</sup> to biomedicine (photodynamic therapeutic agents),<sup>22</sup> and others. One of the design requirements for efficient use of  $C_{60}$ materials in various device applications is the capability of attaining micro- and nanoscopic ordering in the solid state or at the interface. In particular, spatially ordered C<sub>60</sub> acceptor domains on the length scale of the exciton diffusion are crucial to optimize the efficiency of  $C_{60}$  based bulk heterojunction photovoltaic cells.<sup>23–26</sup> To achieve ordering of C<sub>60</sub> at the molecular or supramolecular level in a controlled manner is, however, not a trivial task.<sup>17</sup> Significant challenges arise mainly from the fact that pristine  $C_{60}$  cages show a strong tendency to cluster via  $\pi$ - $\pi$  stacking,<sup>27,28</sup> totally lacking such directional interactions as can be found in metal-ligand

complexation or hydrogen bonding. To circumvent this hurdle, various approaches have been developed, including using templates<sup>29–31</sup> and attaching other molecular moieties that can impart attributes of directional bonding.<sup>32–35</sup>

Chemical functionalization of C<sub>60</sub> offers a facile way of modifying and tuning the properties of  $C_{60}$  based molecular materials. It is particularly advantageous in that control over molecular and supramolecular behaviors can be achievable through tailoring of molecular structures. One actively pursued research area in this regard is the preparation and characterization of supramolecular nano-assemblies of functionalized C<sub>60</sub> molecules. For instance, Nakamura and co-workers recently demonstrated that a type of 'shuttle-cock' shaped C<sub>60</sub> derivative with different molecular appendages was able to self-assemble into distinct nanometer-scale objects, such as columns<sup>36</sup> and lamellae.<sup>37</sup> Numerous amphiphilic C<sub>60</sub> derivatives<sup>17,35,38,16</sup> that contain ionic moieties or polar groups were reported to form nanostructures with defined shapes (spheres, vesicles, needles, tubules, etc.) in the solid state or on surfaces through self-assembly, while the morphology and size of these nano-assemblies were dependent on factors such as molecular structures and experimental conditions.

Apart from [60]fullerene, various dendrimers constitute another important class of molecular building blocks for structurally defined and controllable nanostructures. To take advantage of the unique and extraordinary molecular and supramolecular properties of both  $C_{60}$  and dendrimers, hybrid molecular systems of  $C_{60}$  and dendrimers, called dendro[60]fullerenes, <sup>39,40</sup> have been





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actively sought after in the recent literature. Representative studies include dendro[60]fullerenes consisting of Fréchet,  $^{41,42}$  New-kome,  $^{43,44}$  and depsipeptide types of dendrons.  $^{45}$ 

The use of dendro[60]fullerenes to assemble nanoscale architectures is an attractive and challenging direction in the supramolecular chemistry of  $C_{60}$ . On one hand, the  $C_{60}$  cage tends to show a strong penchant for aggregation driven by hydrophobicity and  $\pi$ - $\pi$  stacking forces.<sup>27</sup> On the other hand, numerous dendritic molecules have already demonstrated the ability to form ordered superstructures with (pre)determined geometries and hierarchical orders through the process of self-assembly.<sup>46,47</sup> As for self-assembly using dendro[60]fullerenes,<sup>48,49</sup> the control of shape and hierarchical morphology, however, has not yet reached the level achieved by some functional dendrimers<sup>50–52</sup> or other types of  $C_{60}$ derivatives.<sup>34,53–55,37</sup> There are two major hurdles, which have retarded progress towards precisely controlled dendro[60]fullerene self-assemblies, to overcome. First, the synthesis of dendro[60]fullerenes is not easy and usually requires multi-step synthesis and tedious purification procedures. Second, the selfassembly of C<sub>60</sub> derivatives is often complicated by the involvement of intricate intermolecular forces. Clear understanding of such forces is needed for the development of rational strategies for control and manipulation of self-assembling attributes. In this regard, synthesis and investigation of new dendro[60]fullerene varieties are crucially important.

This article is aimed at addressing the aforementioned challenging issues in dendro[60]fullerene supramolecular chemistry. We devised a modular synthetic strategy, on the basis of copiously documented accounts of 'click' chemistry,<sup>56–58</sup> to allow for facile and rapid access to various dendro[60]fullerenes with complex

molecular structures. A series of Fréchet-type dendron functionalized  $C_{60}$  derivatives were designed, in which the dendrons and  $C_{60}$ moieties are covalently linked by a 1,2.3-triazole unit that is assembled via a Cu(I)-catalyzed Huisgen [3+2] cycloaddition ('click') reaction. It is worth mentioning that a similar 'click' protocol has been recently demonstrated by Nierengarten's group, which shows excellent efficiency in making  $C_{60}$  hexakis-adducts.<sup>59</sup> The self-assembly behavior of these new 1,2,3-triazole-linked dendro[60]fullerenes on the surface of mica was then investigated, and the detailed results are discussed in the following context.

# 2. Results and discussion

# 2.1. Synthesis of triazole-linked dendro[60]fullerenes

Two groups of Fréchet-type dendrons, ranging from first to third generations (**2–5**), were synthesized following a convergent protocol as reported in the literature<sup>60</sup> with suitable modifications. In order to examine the appendage group effects, one series of dendrons was prepared with phenyl groups on the periphery, while another was grafted with *meta*-bis(*n*-decyloxy) groups on each of the peripheral phenyl groups. Synthetic details for these dendrons are outlined in Scheme 1. The dendrons with azido pendants could be readily linked to a  $C_{60}$  core via a highly efficient 'click' reaction that was first developed by Sharpless and co-workers.<sup>61</sup> For the 'click' reaction, an alkynyl functionalized  $C_{60}$  building block **8** was needed, and its synthesis was carried out via a Sonogashira coupling of *p*-bromobenzaldehyde with trimethylsilylacetylene (TMSA) followed by a 1,3-dipolar cycloaddition reaction as described in Scheme 2.<sup>62</sup> Compound **8** was then desilylated with



Scheme 1. Synthesis of azido-functionalized dendron building blocks G1-G3. (a) K2CO3, 18-crown-6, acetone; (b) LiAlH4, THF; (c) CBr4, PPh3; (d) NaN3, DMSO.



Scheme 2. Synthesis of 1,2,3-triazole-linked dendro[60]fullerenes 9a-e via a 'click' reaction.

tetrabutylammonium fluoride (TBAF) in a solvent mixture of THF/ MeOH to form a terminal alkyne in situ, to which a suitable azidoattached dendron precursor was subsequently added together with Et<sub>3</sub>N and a catalytic amount of Cul. The 'click' reaction generally went to completion within 12 h at ambient temperatures. The resulting 1,2,3-triazole-linked dendro[60]fullerene products showed satisfactory to good solubility in common organic solvents, and could be readily purified through a standard flash column chromatographic procedure. The yields of these 'click' reactions varied from 38 to 80% (see Scheme 2), in large part depending on the solubility of the dendro[60]fullerene products, for it was observed that the yields increased with increasing dendron generation as well as the number of solubilizing *n*-decyloxy chains attached.

The molecular structures of the dendro[60]fullerenes, 9a-e, were verified by IR, <sup>1</sup>H NMR, and MALDI-TOF mass spectrometric characterizations. All the MALDI-MS spectra of **9a-e** clearly showed molecular ion peaks, while the <sup>1</sup>H NMR spectra provided convincing evidence for the formation of the 1,2,3-triazole linkage group resulting from the 'click' reactions. <sup>13</sup>C NMR characterizations were, however, of limited use in structural elucidation, due to the low concentrations that these dendro[60]fullerenes (9a-e) could achieve in chloroform. Figure 1 depicts the <sup>1</sup>H NMR spectra of **9a–e** where key proton signals corresponding to the linkage groups between the  $C_{60}$  cores and the dendron units are briefly assigned. Notice that the chemical shifts ( $\delta$ ) of these protons are virtually unchanged as the generation of dendron increases. This observation implies that the linkage groups are experiencing very similar chemical environments created by different dendron moieties. To facilitate discussions of the properties of these dendro[60]fullerenes in the following context, compounds **9a-e** are henceforth generally referred to as  $C_{60}$ – $G_n$ –X, wherein  $G_n$  denotes the generation of dendron attached and X refers to the peripheral R' group designated in Scheme 1.

#### 2.2. Electronic and electrochemical properties

Electronic properties of the dendro[60]fullerenes were investigated by UV–vis spectroscopy. Figure 2 depicts the normalized UV–vis spectra for **9a–e**, all of which show very similar low-energy absorption spectral profiles. The appreciable absorption shoulder bands ranging from ca. 300 to 520 nm are ascribed to the characteristic  $\pi \rightarrow \pi^*$  electronic transitions on the C<sub>60</sub> core.<sup>63</sup> The spectral envelop in this region for **9a–e** varies slightly, which might be caused by the dendron effects, that is, the varying generation and functionality of the dendron moiety could have led to different

aggregation behaviors for **9a–e** in solution, resulting in subtly different absorption profiles.

Electrochemical properties for dendro[60]fullerenes **9a-d** were studied by cyclic voltammetry and the cyclic voltammograms obtained are given in Figure 3. In the positive potential region, 9a-d show no discernible redox currents. In the negative potential region, however, all four compounds display very rich redox characteristics attributable to the  $C_{60}$  core.<sup>64</sup> Compounds **9a** and **9b** that are functionalized with  $G_1$  dendrons clearly show three quasi-reversible redox waves in the reduction window of their cyclic voltammograms (see Fig. 3a and b). These redox features can be assigned to sequential reduction steps on the  $C_{60}$  cage. For the G<sub>2</sub>-functionalized compounds, **9c** and **9d** (see Fig. 3c and 3d), the cyclic voltammograms appear relatively complex and more difficult to assign. The three pairs of redox waves corresponding to the C<sub>60</sub> cage are vaguely identifiable and irreversible in nature. The loss of reversibility for these redox steps is likely due to the enhanced shielding effect on the electroactive C<sub>60</sub> core as the generation of dendron increases.<sup>69,70</sup> The 1,2,3-triazole moiety formed during the 'click' reactions can be reckoned as an electron-accepting group in general. However, no discernible redox features could be assigned to the reduction of the triazole ring. The detailed redox potential data for **9a-d** are listed in Table 1.

# 2.3. Interfacial self-assembly behavior

The dendro[60]fullerenes **9a–d** were envisioned to have two regions that behave oppositely upon solvation in common organic solvents. The  $C_{60}$  core generally tends to show very poor solubility (solvophobic), whereas the Fréchet-dendron units are more solvent compatible (solvophilic) in nature. If this held true, the dendro[60]fullerenes would aggregate into hierarchically ordered supramolecular nanostructures, with the solvent amphiphilicity being a major driving force.<sup>65</sup> Also, the shape of molecular building components could be a key factor determining the morphology of self-aggregation. Several theoretical models have been developed to account for the morphological features of self-assemblies for amphiphiles.<sup>66–68</sup> According to the shapes of the  $C_{60}$ – $G_n$ –X (**9a–e**) building blocks, five scenarios of self-assembly morphologies (see Fig. 4) are considered most likely among numerous possible outcomes.

Supramolecular self-assemblies of dendro[60]fullerenes **9a–d** were prepared on surfaces by spin-coating. In the procedure, a few drops of the diluted solution of a corresponding dendro[60]fullerene in chloroform (ca.  $10^{-5}$ – $10^{-6}$  M) were first



Figure 1. Comparison of <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra for dendro[60]fullerenes 9a-e.

spin-cast on freshly cleaved mica surfaces at room temperature (spinning rate 2000 rpm). The resulting surfaces were further spun for a few more minutes, and the interfacial assemblies formed on mica were examined by atomic force microscopy (AFM) operating in non-contact mode.

Figure 5 shows the AFM images that depict the morphologies of the supramolecular assemblies by **9a–d** prepared from their diluted



Figure 2. UV-vis absorption spectra for dendro[60]fullerenes 9a-e measured in chloroform at room temperature.

chloroform solutions under neutral conditions. The assemblies of **9b**  $(C_{60}-G_1-H)$  show an interesting surface pattern characterized by closely packed and cross-linked 'worm-like' nano-cylinders (see Fig. 5a). The heights of these cylinders were measured to be in the range of 40-100 nm. A molecular modeling study suggests that  $C_{60}$ - $G_1$ -H (**9b**) assumes a 'wedge-like' molecular shape, which should pack into cylindrical micelles according to the amphiphilic packing model.<sup>67</sup> Given that the span of  $C_{60}$ – $G_1$ –H (**9b**) is calculated to be only 2.5 nm, these cylindrical nanostructures must be made up of multiple layers of micelles. For  $C_{60}$ -G<sub>2</sub>-H (**9d**), the morphology of interfacial assembly is markedly different; semi-spheroid nano-aggregates with randomly distributed sizes were observed (Fig. 5c) across the surfaces examined. Considering that the molecular shape of C<sub>60</sub>-G<sub>2</sub>-H resembles a 'truncated cone' more than a 'wedge' as a consequence of increased dendron generation, a spherical packing geometry would thus be a favored scenario, even though the shapes of assemblies of 9d, which are observed experimentally appear random and undefined. For *n*-decyl terminated dendro[60]fullerenes ( $C_{60}$ - $G_n$ - $C_{10}$ ) **9a** (*n*=1), **9c** (n=2), and **9e** (n=3), spin-coating led to the formation of amorphous thin films with randomly structured aggregates across the surface. Such morphological features imply that the dendro[60]fullerenes very likely assemble in a lamellar architecture (as predicted in Fig. 4b) because of their good solubility in chloroform, although other morphological possibilities should not be ruled out in this case.

It was puzzling to us initially that no discrete spherical micellar structures as predicted in Fig. 4d and e were observed in the



Figure 3. Cyclic voltammograms of dendro[60]fullerenes 9a-d.

#### Table 1

Redox potentials  $^a$  for  $\mathbf{9a-d}$  measured in o-dichlorobenzene solutions at room temperature

Entry	$E_{\rm pc}$ (V)	E <sub>pa</sub> (V)
9a	-0.69, -1.12, -1.69	-0.41, -0.81, -1.40
9b	-0.75, -1.12, -1.68	-0.40, -0.81, -1.40
9c	-0.80, -1.28, -1.67	-0.46, -0.845, -1.41
9d	-0.72, -1.03 (sh), -1.20	-0.50, -0.89, -1.03 (sh)

<sup>a</sup> Potentials versus Ag/AgCl; working electrode: glassy carbon; counter electrode: Pt: 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in o-DCB: scan rate: 100 mV s<sup>-1</sup>.

interfacial assemblies of **9a-e** under neutral conditions. Especially, in the cases of the dendro[60]fullerenes with higher-generation dendrons (G<sub>2</sub> and G<sub>3</sub>), molecular modeling suggests that these molecules assume a shape of a 'truncated cone' that in theory should lead to the formation of spherical assemblies.<sup>67</sup> Conducting similar spin-coating procedures using acidified solutions of 9a-e in chloroform, however, gave results in sharp contrast to those observed under neutral conditions. In these experiments, trifluoroacetic acid (TFA) was first added to the solutions of 9a-e in excess amounts. The solutions were then spin-coated on mica surfaces at room temperature. The interfacial assemblies prepared under these conditions were examined by AFM, and the results are shown in Figure 6. All of the acidified dendro[60]fullerenes 9a-e yielded discrete spherical nano-aggregates on the surface. The acid is believed to have protonated either the 1,2,3-triazole or the pyrrolidine ring or both. By doing so, the solvophobicity at the focal moieties of the dendron units was further exaggerated. This seems to be a key factor leading to the formation of spherical nano-assemblies. Notably, for the  $C_{60}$ – $G_n$ –H type of dendro[60]fullerenes (**9b** and **9d**), the nanospheres formed vary significantly in size, while the  $C_{60}$ – $G_n$ – $C_{10}$  type of molecules (**9a**, **9c**, and **9e**) afforded ordered arrays of nanospheres with relatively uniform sizes.

Statistical analysis on the vertical diameters of the nanospheres for each sample in Figure 6 is quite informative in terms of their possible morphologies and hierarchical orders. Fig. 7a and b reveals the effect of *n*-decyl chains on the size



**Figure 4.** Possible self-assembly morphologies for dendro[60]fullerenes. (a) Cylinder, (b) bilayer lamella, (c) bilayer vesicle, (d) monolayer spherical micelle, and (e) multi-layer spherical micelle.



Figure 5. AMF images of interfacial self-assemblies of 9a-e. Samples were prepared by spin-coating neutral solutions (ca. 10<sup>-5</sup>-10<sup>-6</sup> M) on freshly cleaved mica surfaces.

distributions of the nanospheres. It is clearly seen that the C<sub>60</sub>–G<sub>n</sub>–H molecules gave rise to much wider size distributions than those of the C<sub>60</sub>–G<sub>n</sub>–C<sub>10</sub> molecules. The fact that the phenyl peripheral groups in C<sub>60</sub>–G<sub>n</sub>–H have sufficient affinity for C<sub>60</sub> cages via  $\pi$ – $\pi$  stacking can be used to explain this result, hence allowing for the formation of multilayer micelles (as shown in Fig. 4e). For the C<sub>60</sub>–G<sub>n</sub>–C<sub>10</sub> (*n*=1–2) molecules, the size distributions of the spherical micelles formed on surfaces are rather narrow and monodispersed. Moreover, the average sizes of the nanospheres fit well the estimated diameters of monolayer micelles based upon molecular modeling studies.<sup>71</sup> The comparison

results in Fig. 7a and b clearly indicate that the peripheral *n*-decyl groups can form effective insulating layers to prevent the formation of multilayer nano-aggregates during the process of amphiphilic self-assembly. For  $C_{60}-G_3-C_{10}$  (**9e**), the size distribution of nanospheres is much broader than **9a** and **9c**. This is likely due to the increased conformational flexibility of the  $G_3$  dendron moiety. Nevertheless, a trend showing that the average sizes of spherical micelles assembled by  $C_{60}-G_n-C_{10}$  molecules progressively increase with growing dendron generation can be clearly seen in Fig. 7d. This result underscores the viability of using the 'bottom-up' approach to gain control over the size and



Figure 6. AMF images of interfacial self-assemblies for 9a-e under acidic conditions. Samples were prepared by spin-coating acidified solutions (ca. 10<sup>-5</sup>-10<sup>-6</sup> M with excess TFA) on freshly cleaved mica surfaces.



Figure 7. Statistical analysis of vertical diameter distributions for the spherical nano-assemblies of 9a-e prepared from spin-coating their acidified solutions on mica.

morphology of dendro[60]fullerene based supramolecular self-assembly.

#### 3. Conclusions

In conclusion, synthetic access to a series of 1,2,3-triazole-linked dendro[60]fullerenes **9a–e** using a Cu(1)-catalyzed [3+2] cycloaddition 'click' protocol was successfully developed. Electronic absorption and electrochemical properties of these compounds were characterized by UV–vis and cyclic voltammetric analyses. Most importantly, the amphiphilic self-assembly behavior of these compounds on surfaces was investigated and found to be dependent on three important molecular parameters: acidity, dendron generation, and the nature of peripheral groups. Under controllable conditions, these dendro[60]fullerene molecules can yield four different self-assembly morphologies, multilayer cylinder, lamella, monolayer spherical micelle, and multilayer spherical micelle. Our results suggest a new and useful approach to the controlled synthesis of complex supramolecular systems composed of C<sub>60</sub> and dendrimers.

# 4. Experimental

# 4.1. General

Chemicals and reagents were purchased from commercial suppliers and used as-received unless noted otherwise. [60]Fullerene (purity 99.5+%) was purchased from MTR Ltd. THF was distilled from sodium/benzophenone. Et<sub>3</sub>N, benzene, and toluene were distilled from LiH. All reactions were performed in standard,

dry glassware in an inert atmosphere of N<sub>2</sub>. Evaporation and concentration were done at H<sub>2</sub>O-aspirator pressure. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from VWR International. Thin-layer chromatography (TLC) was carried out with silica gel 60 F254 covered on plastic sheets and visualized by UV light or KMnO<sub>4</sub> stain. Melting points (mps) were measured with a Fisher-Jones melting point apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on the Bruker Avance 500 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million downfield from the signal of the internal reference SiMe<sub>4</sub>. Coupling constants (J) are given in hertz. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. UV-vis spectra were recorded on an Agilent 8453 spectrophotometer. APCI mass spectra (MS) were measured on an Agilent 1100 series LCMSD spectrometer, and MALDI-TOF mass spectra on an Applied Biosystems Voyager instrument with dithranol as the matrix. Cyclic voltammetric experiments were performed on an Epsilon electrochemical analyzer, and AFM imaging was conducted on a QScope 250 scanning probe microscope in non-contact (tapping) mode.

#### 4.2. Methyl 3,5-bis(decyloxy)benzoate (2a)

To an oven-dried round-bottom flask were added methyl 3,5dihydroxybenzoate (1) (500 mg, 3.0 mmol), 1-bromodecane (2.65 g, 12.0 mmol),  $K_2CO_3$  (3.4 g, 25 mmol), a phase transfer catalyst 18-crown-6 (157 mg, 0.6 mmol), and acetone (15 mL). The mixture was refluxed for 24 h and then cooled to room temperature. The solvent was evaporated in vacuo, and the residue was diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic solution was sequentially washed with H<sub>2</sub>O, aq NaOH (2 M), and H<sub>2</sub>O again. The organic layer was dried over MgSO<sub>4</sub>, concentrated in vacuo, and the resulting crude product was purified by silica flash chromatography (hexanes/ CH<sub>2</sub>Cl<sub>2</sub> 3:1) to afford compound **2a** (1.27 g, 2.83 mmol, 95%) as white needle-like crystals. Mp 52.5 °C. IR (neat): 2921, 2850, 1722, 1599 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.16 (d, *J*=2.6 Hz, 2H, Ar–H), 6.63 (t, *J*=2.5 Hz, 1H, Ar–H), 3.97 (t, *J*=6.4 Hz, 4H, OCH<sub>2</sub>), 3.89 (s, 3H, ester CH<sub>3</sub>), 1.77 (m, 4H, decyl CH<sub>2</sub>), 1.44 (m, 4H, decyl CH<sub>2</sub>), 1.38–1.23 (m, 24H, decyl CH<sub>2</sub>), 0.88 (t, *J*=6.7 Hz, 6H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.3 (C=O), 160.5 (Ar C–O), 132.1, 107.9, 106.9, 68.6 (OCH<sub>2</sub>), 52.5 (OCH<sub>3</sub>), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.0, 23.0, 14.4 (decyl CH<sub>3</sub>); APCI-MS (positive mode) *m/z* calcd for C<sub>28</sub>H<sub>48</sub>O<sub>4</sub> 448.4, found 449.3 [M+H]<sup>+</sup>.

#### 4.3. 3,5-Bis(decyloxy)benzyl alcohol (2b)

A solution 2a (1.0 g, 2.23 mmol) in dry THF (40 mL) was added to an oven-dried round-bottom flask cooled at 0 °C. A pre-cooled slurry of LiAlH<sub>4</sub> (169 mg, 4.45 mmol) in dry THF (10 mL) was then added dropwise. After addition of LiAlH<sub>4</sub>, the reaction mixture was stirred at room temperature for 2 h, then quenched with a small amount of H<sub>2</sub>O to consume excess LiAlH<sub>4</sub> and neutralized with aq HCl (4 M). The solvent THF was removed in vacuo, and the resulting content was extracted with EtOAc and washed with saturated NH<sub>4</sub>Cl. The organic layer was dried over MgSO<sub>4</sub> and filtered. Evaporation of the solvent in vacuo afforded compound 2b (921 mg, 2.19 mmol, 98%) as a white solid. Mp 29 °C. IR (neat): 3364 (br, OH), 2919, 2851, 1590, 1466, 1128 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.48 (m, 2H, Ar-H), 6.37 (m, 1H, Ar-H), 4.56 (s, 2H, benzylic CH<sub>2</sub>), 3.91 (t, *I*=6.4 Hz, 4H, OCH<sub>2</sub>), 2.69 (br s, 1H, OH), 1.77 (m, 4H, decyl CH<sub>2</sub>), 1.46 (m, 4H, decyl CH<sub>2</sub>), 1.41-1.24 (m, 24H, decyl CH<sub>2</sub>), 0.92 (t, *J*=6.7 Hz, 6H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.6 (Ar C-O), 143.5, 10.5.2, 100.7, 68.2 (OCH<sub>2</sub>), 65.3 (benzylic CH<sub>2</sub>), 32.1, 29.82, 29.80, 29.64, 29.56, 29.5, 26.3, 22.9, 14.3 (decyl CH<sub>3</sub>); APCI-MS (positive mode) m/z calcd for C<sub>27</sub>H<sub>48</sub>O<sub>3</sub> 420.4, found 421.3 [M+H]<sup>+</sup> and 444.3 [M+Na]<sup>+</sup>.

# 4.4. 3,5-Bis(decyloxy)benzyl bromide (2c)

A solution of 2b (300 mg, 0.714 mmol) and CBr<sub>4</sub> (356 mg, 1.07 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added in an oven-dried roundbottom flask, and to this mixture was dropwise added a solution of PPh<sub>3</sub> (281 mg, 1.07 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. The content was then kept under stirring at room temperature for 3 h. The solvent was removed in vacuo and the residue was purified by silica flash chromatography (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 5:1) to yield compound 2c (345 mg, 0.715 mmol, 100%) as white shiny crystals. Mp 26.5 °C. IR (neat): 2923, 2853, 1596, 1165, 1057 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.53 (m, 2H, Ar-H), 6.40 (m, 1H, Ar-H), 4.42 (s, 2H, benzylic CH<sub>2</sub>), 3.94 (t, J=6.4 Hz, 4H, OCH<sub>2</sub>), 1.78 (m, 4H, decyl CH<sub>2</sub>), 1.46 (m, 4H, decyl CH<sub>2</sub>), 1.42–1.23 (m, 24H, decyl CH<sub>2</sub>), 0.91 (t, *J*=7.1 Hz, 6H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.7 (Ar C–O), 139.8, 107.7, 101.6, 68.4 (OCH<sub>2</sub>), 34.0 (benzylic CH<sub>2</sub>), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 23.0, 14.4 (CH<sub>3</sub>); APCI-LCMS (positive mode) m/z calcd for C<sub>27</sub>H<sub>47</sub>O<sub>2</sub><sup>79</sup>Br (<sup>81</sup>Br) 482.3 (484.3), found 483.3 (485.3)  $[M+H]^{+}$ .

#### 4.5. G<sub>1</sub>–C<sub>10</sub> dendron (3a)

G<sub>1</sub>–C<sub>10</sub> dendron (**3a**) (1.31 g, 1.35 mmol, 100%) was prepared as white needle-like crystals from methyl 3,5-dihydroxybenzoate (**1**) (231 mg, 1.38 mmol), **2c** (2.00 g, 4.15 mmol), K<sub>2</sub>CO<sub>3</sub> (0.762 g, 5.52 mmol), and 18-crown-6 (72 mg, 0.28 mmol) following the same etherification procedure as described in the synthesis of **2a**. Mp 58.5 °C. IR (neat): 2922, 2853, 1726, 1595, 1163, 1051 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.32 (d, *J*=2.6 Hz, 2H, Ar–H), 6.82 (m, 1H, Ar–H), 6.59 (m, 4H, Ar–H), 6.44 (m, 2H, Ar– H), 5.00 (s, 4H, benzylic CH<sub>2</sub>), 3.96 (t, *J*=6.4 Hz, 8H, decyl OCH<sub>2</sub>), 3.92 (s, 3H, ester CH<sub>3</sub>), 1.80 (m, 8H, decyl CH<sub>2</sub>), 1.48 (m, 8H, decyl CH<sub>2</sub>), 1.43–1.26 (m, 48H, decyl CH<sub>2</sub>), 0.93 (t, *J*=7.1 Hz, 12H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.9 (*C*=0), 160.8, 160.0 (Ar *C*-0), 138.8, 132.2, 108.6, 107.4, 105.9, 101.1, 70.5 68.2 (one benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 52.3 (ester CH<sub>3</sub>), 32.2, 29.84, 29.82, 29.7, 29.6, 29.5, 26.3, 22.9, 14.3 (decyl CH<sub>3</sub>); APCI-MS (positive mode) *m*/*z* calcd for C<sub>62</sub>H<sub>100</sub>O<sub>8</sub> 972.7, found 973.7 [M+H]<sup>+</sup>.

# 4.6. G<sub>1</sub>-C<sub>10</sub> dendron (3b)

 $G_1-C_{10}$  dendron **3b** (476 mg, 0.50 mmol, 98%) was prepared as white solids from **3a** (500 mg, 0.514 mmol) and LiAlH<sub>4</sub> (100 mg, 2.63 mmol) following the same reduction procedure as described in the synthesis of **2b**. Mp 47 °C. IR (neat): 3500–3200 (br, OH), 2922, 2853, 1596, 1455, 1161 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.62 (m, 2H, Ar–H), 6.55 (m, 5H, Ar–H), 6.41 (m, 2H, Ar–H), 4.96 (s, 4H, benzylic CH<sub>2</sub>), 4.64 (s, 2H, benzylic CH<sub>2</sub>), 3.95 (t, *J*=6.4 Hz, 8H, decyl OCH<sub>2</sub>), 1.78 (m, 8H, decyl CH<sub>2</sub>), 1.46 (m, 8H, decyl CH<sub>2</sub>), 1.40–1.25 (m, 48H, decyl CH<sub>2</sub>), 0.90 (t, *J*=7.1 Hz, 12H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.8, 160.5 (two Ar *C*–0), 143.7, 139.3, 106.03, 106.01, 101.6, 101.1 (six aromatic carbon signals), 70.4, 68.4, 65.6 (two benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 32.2, 29.88, 29.86, 29.7, 29.62, 29.56, 26.4, 23.0, 14.4 (decyl CH<sub>3</sub>); APCI-MS (positive mode) *m*/*z* calcd for C<sub>61</sub>H<sub>100</sub>O<sub>7</sub> 944.8, found 945.7 [M+H]<sup>+</sup>.

# 4.7. G<sub>1</sub>-C<sub>10</sub> dendron (3c)

G<sub>1</sub>–C<sub>10</sub> dendron **3c** (314 mg, 0.312 mmol, 98%) was prepared as white shinny crystals from **3b** (300 mg, 0.318 mmol), CBr<sub>4</sub> (264 mg, 0.795 mmol), and PPh<sub>3</sub> (208 mg, 0.795 mmol) following the same bromination procedure as described in the synthesis of **2c**. Mp 42 °C. IR (neat): 2922, 2853, 1594, 1457, 1162, 1052 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.70 (m, 2H, Ar–H), 6.64 (m, 4H, Ar–H), 6.62 (m, 1H, Ar–H), 6.51 (m, 2H, Ar–H), 4.99 (s, 4H, benzylic CH<sub>2</sub>), 4.45 (s, 2H, benzylic CH<sub>2</sub>), 4.01 (t, *J*=6.4 Hz, 8H, decyl OCH<sub>2</sub>), 1.86 (m, 8H, decyl CH<sub>2</sub>), 1.56 (m, 8H, decyl CH<sub>2</sub>), 1.51–1.34 (m, 48H, decyl CH<sub>2</sub>), 1.02 (t, *J*=7.1 Hz, 12H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.7, 160.2 (two Ar C–O), 139.7, 139.0, 108.2, 105.8, 102.3, 100.9, 70.2, 68.1 (one benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 33.6 (benzylic CH<sub>2</sub>); 32.1, 29.82, 29.80, 29.64, 29.55, 29.49, 26.3, 22.9, 14.3 (decyl CH<sub>3</sub>); APCI-MS (positive mode) *m*/*z* calcd C<sub>61</sub>H<sub>99</sub>O<sub>6</sub><sup>9</sup>Br (<sup>81</sup>Br) 1006.7 (1008.7), found 1007.7 (1009.7) [M+H]<sup>+</sup>.

# 4.8. G<sub>1</sub>-C<sub>10</sub> dendron (3d)

A solution of 3c (200 mg, 0.199 mmol) and NaN<sub>3</sub> (139 mg, 2.14 mmol) in DMSO (5 mL) was added in an oven-dried roundbottom flask and heated up to 80–85 °C for 30 h. Afterwards, the content was cooled to room temperature and then quenched with slow addition of water (exothermic). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the organic layer was sequentially washed with H<sub>2</sub>O and saturated NH<sub>4</sub>Cl and then dried over MgSO<sub>4</sub>, and filtered. Removal of the solvent in vacuo afforded 3d (192 mg, 0.198 mmol, 100%) as a pale yellow liquid. IR (neat): 2923, 2853, 2099, 1595, 1457, 1164, 1058 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.64–6.54 (m, 7H, Ar–H), 6.45 (m, 2H, Ar–H), 4.98 (s, 4H, benzylic CH<sub>2</sub>), 4.28 (s, 2H, benzylic CH<sub>2</sub>), 3.97 (t, J=6.4 Hz, 8H, decyl OCH<sub>2</sub>), 1.81 (m, 8H, decyl CH<sub>2</sub>), 1.49 (m, 8H, decyl CH<sub>2</sub>), 1.44-1.26 (m, 48H, decyl CH<sub>2</sub>), 0.94 (t, *J*=6.7 Hz, 12H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.8, 160.5 (2Ar C-O), 139.0, 137.8, 107.4, 105.9, 102.1, 101.1, 70.4, 68.3 (one benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 55.0 (benzylic CH<sub>2</sub>N<sub>3</sub>), 32.1, 29.83, 29.81, 29.7, 29.6, 29.5, 26.3, 22.9, 14.3 (CH<sub>3</sub>); APCI-MS (positive mode) m/z calcd for C<sub>61</sub>H<sub>99</sub>O<sub>6</sub>N<sub>3</sub> 969.8, found 970.8 [M+H]<sup>+</sup>.

# 4.9. G<sub>1</sub>-H dendron (3e)

G<sub>1</sub>-H (**3e**) (1.98 g, 5.69 mmol, 95%) was prepared as white shinny crystals from methyl 3,5-dihydroxybenzoate (1.0 g, 6.0 mmol), benzyl bromide (4.07 g, 24.0 mmol), K<sub>2</sub>CO<sub>3</sub> (3.4 g, 24 mmol), and 18-crown-6 (156 mg, 0.6 mmol) following the same etherification procedure as described in the synthesis of **2a**. Mp 144 °C. IR (neat): 3032, 2950, 1719, 1594, 1153, 1054 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.43–7.20 (m, 10H, Ar–H), 7.30 (d, *J*=2.6 Hz, 2H, Ar–H), 6.80 (t, *J*=2.6 Hz, 1H, Ar–H), 5.07 (s, 4H, benzylic CH<sub>2</sub>), 3.90 (s, 3H, ester CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 166.9 (*C*=O), 160.0 (Ar *C*-O), 136.7, 132.3, 128.8, 128.3, 127.8, 108.6, 107.5, 70.5 (benzylic CH<sub>2</sub>), 52.5 (ester CH<sub>3</sub>); APCI-MS (negative mode) *m/z* calcd for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> 348.1, found 347.1 [M–H]<sup>-</sup>.

# 4.10. G<sub>1</sub>-H dendron (3f)

G<sub>1</sub>–H dendron (**3f**) (855 mg, 2.46 mmol, 93%) was prepared as a white solid from **3e** (1.00 g, 2.87 mmol) and LiAlH<sub>4</sub> (218 mg, 11.5 mmol) following the same reduction procedure as described in the synthesis of **2b**. Mp 81 °C. IR (neat): 3321 (OH), 3032, 2904, 2870, 1592 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.46–7.28 (m, 10H, Ar–H), 6.60 (m, 2H, Ar–H), 6.53 (m, 1H, Ar–H), 5.01 (s, 4H, benzylic CH<sub>2</sub>), 4.58 (s, 2H, benzylic CH<sub>2</sub>), 1.86 (br s, 1H, OH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.5 (Ar C–O), 143.7, 137.1, 128.9, 128.3, 127.8, 106.1, 101.6 (seven aromatic carbon signals), 70.4, 65.6 (two benzylic OCH<sub>2</sub>); APCI-MS (positive mode) *m*/*z* calcd for C<sub>21</sub>H<sub>20</sub>O<sub>3</sub> 320.1, found 343.1 [M+Na]<sup>+</sup>.

# 4.11. G<sub>1</sub>-H dendron (3g)

G<sub>1</sub>–H dendron (**3g**) (460 mg, 1.20 mmol, 77%) was prepared as white shinny crystals from **3f** (500 mg, 1.56 mmol), CBr<sub>4</sub> (571 mg, 1.72 mmol), and PPh<sub>3</sub> (451 mg, 1.72 mmol) following the same bromination procedure as described in the synthesis of **2c**. Mp 84 °C. IR (neat): 3032, 2927, 2875, 1594 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.48–7.50 (m, 10H, Ar–H), 6.87 (d, *J*=2.6 Hz, 2H, Ar–H), 6.80 (m, 1H, Ar–H), 5.16 (s, 4H, benzylic CH<sub>2</sub>), 4.56 (s, 2H, benzylic CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.4, 141.1, 136.9, 128.9, 128.4, 127.8, 108.5, 102.5 (eight aromatic carbon signals), 70.5 (benzylic OCH<sub>2</sub>), 33.9 (benzylic CH<sub>2</sub>Br); APCI-MS (negative mode) *m/z* calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub><sup>79</sup>Br (<sup>81</sup>Br) 382.1 (384.1), found 381.2 (383.1) [M–H]<sup>-</sup>.

# 4.12. G<sub>1</sub>-H dendron (3h)

G<sub>1</sub>–H dendron (**3h**) (62.7 mg, 0.182 mmol, 100%) was prepared as white solid from **3g** (69.8 mg, 0.182 mmol) and NaN<sub>3</sub> (118.5 mg, 1.82 mmol) following the same procedure as described in the synthesis of **3d**. Mp 69 °C. IR (neat): 3033, 2930, 2097, 1594, 1497, 1150, 1080 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.54–7.40 (m, 10H, Ar–H), 6.70 (m, 1H, Ar–H), 6.66 (m, 2H, Ar–H), 5.12 (s, 4H, benzylic OCH<sub>2</sub>), 4.33 (s, 2H, benzylic CH<sub>2</sub>N<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.5 (Ar *C*–O), 137.9, 136.9, 128.8, 128.3, 127.9, 107.4, 102.1 (seven aromatic carbons), 70.3 (benzylic CH<sub>2</sub>O), 55.0 (benzylic CH<sub>2</sub>N<sub>3</sub>); APCI-MS (positive mode) *m*/*z* calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>N<sub>3</sub> 345.1, found 345.3 [M]<sup>+</sup>.

#### 4.13. G<sub>2</sub>–C<sub>10</sub> dendron (4a)

 $G_2-C_{10}$  dendron (**4a**) (1.03 g, 0.51 mmol, 98%) was prepared as a white solid from methyl 3,5-dihydroxybenzoate (**1**) (87.0 mg, 0.521 mmol), **3c** (1.58 g, 1.57 mmol), K<sub>2</sub>CO<sub>3</sub> (273 mg, 1.98 mmol), and 18-crown-6 (26 mg, 0.10 mmol) following the same etherification procedure as described in the synthesis of **2a**. Mp 68 °C. IR (neat): 2923, 2853, 1725, 1595, 1161, 1052 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (m, 2H, Ar–H), 6.79 (m, 1H, Ar–H), 6.72 (m, 4H, Ar–H),

6.62 (m, 10H, Ar–H), 6.46 (m, 4H, Ar–H), 4.95 (m, 12H, benzylic OCH<sub>2</sub>), 3.96 (m, 23H, overlap of benzylic OCH<sub>2</sub>, decyl OCH<sub>2</sub> and ester CH<sub>3</sub>), 1.82(m, 16H, decyl CH<sub>2</sub>), 1.51 (m, 16H, decyl OCH<sub>2</sub>), 1.47–1.32 (m, 96H, decyl OCH<sub>2</sub>), 0.99 (t, *J*=7.1 Hz, 24H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.0 (*C*=O), 160.8, 160.5, 160.0 (three Ar *C*–O), 139.2, 139.1, 108.7, 107.8, 107.4, 106.7, 106.1, 102.0, 101.2 (eight aromatic carbon signals), 70.5 (benzylic OCH<sub>2</sub>), 66.4 (decyl OCH<sub>2</sub>), 52.5 (ester CH<sub>3</sub>), 32.2, 29.88, 29.86, 29.7, 29.62, 29.57, 26.4, 23.0, 14.4 (decyl CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) *m/z* calcd for C<sub>130</sub>H<sub>204</sub>O<sub>16</sub> 2022.5, found 2017.3 [M]<sup>+</sup>.

# 4.14. G<sub>2</sub>–C<sub>10</sub> dendron (4b)

G<sub>2</sub>-C<sub>10</sub> dendron (**4b**) (484 mg, 0.243 mmol, 98%) was prepared as a white solid from **4a** (500 mg, 0.247 mmol) and LiAlH<sub>4</sub> (37 mg, 0.98 mmol) following the same reduction procedure as described in the synthesis of 2b. Mp 124.5 °C. IR (neat): 3600-3200 (br, OH), 2922, 2852, 1595, 1453, 1159, 1054 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.70 (m, 4H, Ar–H), 6.61(m, 12H, Ar–H), 6.55 (m, 1H, Ar– H), 6.46 (m, 4H, Ar-H), 4.95 (s, 8H, benzylic OCH<sub>2</sub>), 4.94 (s, 4H, benzylic OCH<sub>2</sub>), 4.60 (s, 2H, benzylic OCH<sub>2</sub>), 3.97 (t, J=6.4 Hz, 16H, decyl OCH2), 1.82 (m, 16H, decyl CH2), 1.51 (m, 16H, decyl CH2), 1.47-1.30 (m, 96H, decyl CH<sub>2</sub>), 0.97 (t, J=6.7 Hz, 24H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.6, 160.3, 160.1 (three Ar C–O), 143.9, 139.5, 139.2, 106.4, 105.83, 105.75, 101.7, 101.3, 101.0 (nine aromatic carbon signals), 70.2, 70.0, 68.2 65.2 (three benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 32.1, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 14.3 (decyl CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd for C<sub>129</sub>H<sub>204</sub>O<sub>15</sub> 1994.5, found 1992.9 [M]+.

#### 4.15. G<sub>2</sub>–C<sub>10</sub> dendron (4c)

G<sub>2</sub>-C<sub>10</sub> dendron (**4c**) (490 mg, 0.238 mmol, 98%) was prepared as white needle-like crystals from 4b (500 mg, 0.251 mmol), CBr<sub>4</sub> (125 mg, 0.376 mmol), and PPh<sub>3</sub> (99 mg, 0.38 mmol) following the same bromination procedure as described in the synthesis of 2c. Mp 118 °C. IR (neat): 2922, 2853, 1595, 1453, 1162, 1053 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.70 (m, 4H, Ar–H), 6.65 (m, 2H, Ar–H), 6.60 (m, 1H, Ar-H), 6.58 (m, 8H, Ar-H), 6.43 (m, 6H, Ar-H), 4.99 (s, 4H, benzylic OCH<sub>2</sub>), 4.98 (s, 8H, benzylic OCH<sub>2</sub>), 4.44 (s, 2H, benzylic CH<sub>2</sub>Br), 3.96 (t, *J*=6.4 Hz, 16H, decyl OCH<sub>2</sub>), 1.79 (m, 16H, decyl CH<sub>2</sub>), 1.47 (m, 16H, decyl CH<sub>2</sub>), 1.42–1.26 (m, 96H, decyl CH<sub>2</sub>), 0.91 (t, J=7.1 Hz, 24H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.8, 160.5, 160.3 (three Ar C-O), 140.0, 139.24, 139.18, 108.5, 106.7, 106.0, 102.4, 101.9, 101.1 (nine aromatic carbon signals), 70.5, 70.4, 68.3 (two benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 33.8 (benzylic CH<sub>2</sub>Br), 32.2, 29.9 (2×), 29.7, 29.60, 29.55, 26.3, 23.0, 14.4 (CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd for C<sub>129</sub>H<sub>203</sub>O<sup>79</sup><sub>14</sub>Br 2058.4, found 2054.9 [M]+.

# 4.16. G<sub>2</sub>-C<sub>10</sub> dendron (4d)

G<sub>2</sub>-C<sub>10</sub> dendron (**4d**) (244 mg, 0.121 mmol, 100%) was prepared as a pale yellow liquid from **4c** (250 mg, 0.121 mmol) and NaN<sub>3</sub> (79 mg, 1.21 mmol) following the same procedure as described in the synthesis of **3d**. IR (neat): 2922, 2853, 2099, 1595, 1455, 1163, 1053 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.71 (m, 4H, Ar–H), 6.64– 6.56 (m, 13H, Ar–H), 6.44 (m, 4H, Ar–H), 5.01 (s, 4H, benzylic OCH<sub>2</sub>), 4.99 (s, 8H, benzylic OCH<sub>2</sub>), 4.29 (s, 2H, benzylic CH<sub>2</sub>N<sub>3</sub>), 3.97 (t, *J*=6.7 Hz, 16H, decyl OCH<sub>2</sub>), 1.80 (m, 16H, decyl CH<sub>2</sub>), 1.48 (m, 16H, decyl CH<sub>2</sub>), 1.42–1.24 (m, 96H, decyl CH<sub>2</sub>), 0.93 (t, *J*=6.7 Hz, 24H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.8, 160.5, 160.4 (three Ar C–O), 139.3, 139.2, 137.9, 107.5, 106.6, 106.0 (nine aromatic carbon signals), 70.4, 70.3, 68.3 (two benzylic OCH<sub>2</sub> and one decyl OCH<sub>2</sub>), 55.1 (benzylic CH<sub>2</sub>N<sub>3</sub>), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 14.4 (CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd  $C_{129}H_{203}O_{14}N_3$  2019.5, found 2017.5 [M]<sup>+</sup>.

# 4.17. G<sub>2</sub>-H dendron (4e)

G<sub>2</sub>–H dendron (**4e**) (210 mg, 0.272 mmol, 91%) was prepared as white crystals from methyl 3,5-dihydroxybenzoate (**1**) (50 mg, 0.30 mmol), **3g** (344 mg, 0.9 mmol), K<sub>2</sub>CO<sub>3</sub> (165 mg, 1.2 mmol), and 18-crown-6 (7.8 mg, 0.03 mmol) following the same etherification procedure as described in the synthesis of **2a**. Mp 99 °C. IR (neat): 3030, 2874, 1712, 1593 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.51–7.37 (m, 22H, Ar–H), 6.85 (m, 1H, Ar–H), 6.76 (m, 4H, Ar–H), 6.66 (m, 2H, Ar–H), 5.09 (s, 8H, benzyl OCH<sub>2</sub>), 5.06 (s, 4H, benzyl OCH<sub>2</sub>), 3.97(s, 3H, ester CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 166.9 (*C*=O), 160.4, 159.9 (two Ar *C*–O), 139.1, 137.0, 132.3, 128.8, 128.2, 127.7, 108.7, 107.4, 106.6, 101.9 (10 aromatic signals), 70.3 (benzylic OCH<sub>2</sub>), 52.5 (ester CH<sub>3</sub>); APCI-MS (positive mode) *m*/*z* calcd for C<sub>50</sub>H<sub>44</sub>O<sub>8</sub> 772.3, found 773.4 [M+H]<sup>+</sup>.

# 4.18. G<sub>2</sub>-H dendron (4f)

G<sub>2</sub>–H dendron (**4f**) (3.41 mg, 4.58 mmol, 80%) was prepared as a colorless liquid from **4e** (4.42 g, 5.72 mmol) and LiAlH<sub>4</sub> (869 mg, 22.9 mmol) following the same reduction procedure as described in the synthesis of **2b**. IR (neat): 3404 (br, OH), 3032, 2873, 1593, 1497, 1147 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.43–7.27 (m, 20H, Ar–H), 6.66 (d, *J*=2.6 Hz, 4H, Ar–H), 6.61 (m, 2H, Ar–H), 6.57 (m, 2H, Ar–H), 6.51 (m, 1H, Ar–H), 5.03 (s, 8H, benzylic OCH<sub>2</sub>), 4.96 (s, 4H, benzylic OCH<sub>2</sub>), 4.39 (s, 2H, benzylic OCH<sub>2</sub>) (OH signal was not observed due to rapid proton exchange); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.5, 160.4 (two Ar C–O), 139.6, 137.1, 128.9, 128.3, 127.8, 106.7, 106.1, 101.9, 101.7 (nine aromatic carbon signals, one coincidental peak not observed), 70.4, 70.3, 65.6 (three benzylic OCH<sub>2</sub>); APCI-MS (positive mode) *m*/*z* calcd for C<sub>49</sub>H<sub>44</sub>O<sub>7</sub> 744.3, found 745.4 as [M+H]<sup>+</sup>.

# 4.19. G<sub>2</sub>-H dendron (4g)

 $G_2$ –H (**4g**) (380 mg, 0.471 mmol, 67%) was prepared as white needle-like crystals from **4f** (523 mg, 0.703 mmol), CBr<sub>4</sub> (350 mg, 1.05 mmol), and PPh<sub>3</sub> (276 mg, 1.05 mmol) following the same bromination procedure as described in the synthesis of **2c**. Mp 125.5 °C. IR (neat): 3030, 2879, 1559 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.43–7.28 (m, 20H, Ar–H), 6.66 (m, 4H, Ar–H), 6.61 (d, *J*=2.6 Hz, 2H, Ar–H), 6.57 (m, 2H, Ar–H), 6.51 (m, 1H, Ar–H), 5.03 (s, 8H, benzylic OCH<sub>2</sub>), 4.96 (s, 4H, benzylic OCH<sub>2</sub>), 4.40 (s, 2H, benzylic CH<sub>2</sub>Br); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.5, 160.3 (two Ar *C*–O), 140.1, 137.1, 128.9, 128.3, 127.8, 108.5, 106.7, 102.5, 102.0 (nine aromatic carbon signals, one coincidental signal not observed), 70.5, 70.4 (two benzylic OCH<sub>2</sub>), 33.9 (benzylic CH<sub>2</sub>Br); APCI-MS (positive mode) *m*/*z* calcd for C<sub>49</sub>H<sub>43</sub>O<sub>6</sub><sup>79</sup>Br (<sup>81</sup>Br) 806.2 (808.2), found 807.3 (809.3) [M+H]<sup>+</sup>.

# 4.20. G<sub>2</sub>-H dendron (4h)

G<sub>2</sub>–H dendron (**4h**) (142 mg, 0.185 mmol, 100%) was prepared as a white solid from **4g** (150 mg, 0.186 mmol) and NaN<sub>3</sub> (121 mg, 1.86 mmol) following the same procedure as described in the synthesis of **3d**. Mp 110 °C. IR (neat): 3032, 2922, 2095, 1593, 1051 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.45–7.28 (m, 20H, Ar–H), 6.67 (m, 4H, Ar–H), 6.57 (m, 2H, Ar–H), 6.55 (m, 1H, Ar–H), 6.54 (m, 2H, Ar–H), 5.03 (s, 8H, benzylic OCH<sub>2</sub>), 4.97 (s, 4H, benzylic OCH<sub>2</sub>), 4.25 (s, 2H, benzylic CH<sub>2</sub>N<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.8, 160.7 (two Ar C–O), 139.7, 138.3, 137.3, 129.1, 128.6, 128.1, 107.8, 107.0, 102.4, 102.2 (10 aromatic carbon signals), 70.7, 70.6 (two benzylic OCH<sub>2</sub>), 55.3 (benzylic CH<sub>2</sub>N<sub>3</sub>); APCI-MS (positive mode) m/z calcd for C<sub>49</sub>H<sub>43</sub>O<sub>6</sub>N<sub>3</sub> 769.3, found 770.4 [M+H]<sup>+</sup> and 787.4 [M+H<sub>2</sub>O]<sup>+</sup>.

#### 4.21. G<sub>3</sub>-C<sub>10</sub> dendron (5a)

G<sub>3</sub>-C<sub>10</sub> dendron (**5a**) (0.91 g, 0.221 mmol, 66%) was prepared as a waxy solid from methyl 3,5-dihydroxybenzoate (1) (55.0 mg, 0.329 mmol), 4c (2.02 g, 0.981 mmol), K<sub>2</sub>CO<sub>3</sub> (181 mg, 1.31 mmol), and 18-crown-6 (8.6 mg, 0.033 mmol) following the same etherification procedure as described in 2a. IR (neat): 2924, 2854, 1723, 1595, 1451, 1163, 1053 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.33 (m, 2H, Ar-H), 6.85 (m, 1H, Ar-H), 6.72 (m, 12H, Ar-H), 6.61-6.57 (m, 22H, Ar-H), 6.42 (m, 8H, Ar-H), 5.04 (s, 4H, benzylic OCH<sub>2</sub>), 4.99 (s, 8H, benzylic OCH<sub>2</sub>), 4.97 (s, 16H, benzylic OCH<sub>2</sub>), 3.94 (m, 32H, decyl OCH<sub>2</sub>), 1.77 (m, 32H, decyl CH<sub>2</sub>), 1.46 (m, 32H, decyl CH<sub>2</sub>), 1.29–1.35 (m, 192H, decyl CH<sub>2</sub>), 0.90 (t, *J*=6.7 Hz, 48H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 166.9 (C=O), 160.9, 160.8, 160.5, 160.3 (four Ar C-O), 139.6, 139.3, 132.5, 109.0, 107.8, 106.5, 106.0, 102.0 101.7 (nine aromatic carbon signals, three coincidental peaks not observed), 70.4, 70.3, 68.3 (two benzylic and one decyl OCH<sub>2</sub>, two coincidental peaks not observed), 55.1 (ester CH<sub>3</sub>), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 14.4 (CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) *m*/*z* calcd for C<sub>266</sub>H<sub>412</sub>O<sub>32</sub> 4122.1, found 4121.1 [M]<sup>+</sup>.

#### 4.22. G<sub>3</sub>-C<sub>10</sub> dendron (5b)

G<sub>3</sub>-C<sub>10</sub> dendron (**5b**) (505 mg, 0.123 mmol, 99%) was prepared as a waxy solid from 5a (511 mg, 0.124 mmol) and LiAlH<sub>4</sub> (23.5 mg, 0.621 mmol) following the same reduction procedure as described in the synthesis of 2b. IR (neat): 3398 (br, OH), 2922, 2853, 1595, 1452, 1160, 1054 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.67 (m, 12H, Ar-H), 6.62 (m, 1H, Ar-H), 6.59-6.55 (m, 20H, Ar-H), 6.50 (m, 2H, Ar-H), 6.39 (m, 10H, Ar-H), 4.96 (s, 4H, benzylic OCH<sub>2</sub>), 4.94 (s, 8H, benzylic OCH<sub>2</sub>), 4.93 (s, 16H, benzylic OCH<sub>2</sub>), 4.63 (s, 2H, benzylic OCH<sub>2</sub>), 4.59 (s, 1H, OH), 3.93 (t, J=6.7 Hz, 32H, decyl OCH<sub>2</sub>), 1.77 (m, 32H, decyl CH<sub>2</sub>), 1.42 (m, 32H, decyl CH<sub>2</sub>), 1.40–1.26 (m, 192H, decyl CH<sub>2</sub>), 0.87 (t, *J*=6.7 Hz, 48H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 161.0, 160.7, 160.6, 160.5 (four Ar C–O), 139.7, 139.5, 139.4 128.9, 128.0, 127.0, 107.0, 106.6, 105.5, 102.0, 101.5, 101.0 (12 aromatic carbon signals), 70.4, 70.3, 70.2, 68.5, 65.8 (four benzylic and one decyl OCH<sub>2</sub>), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 14.4 (CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd for C<sub>265</sub>H<sub>412</sub>O<sub>31</sub> 4093.1, found 4106.7 [M+H<sub>2</sub>O]<sup>+</sup>.

# 4.23. G<sub>3</sub>-C<sub>10</sub> dendron (5c)

G<sub>3</sub>-C<sub>10</sub> dendron (**5c**) (434 mg, 0.104 mmol, 95%) was prepared as a waxy solid from 5b (450 mg, 0.11 mmol), CBr<sub>4</sub> (54.6 mg, 0.164 mmol), and PPh<sub>3</sub> (43.3 mg, 0.165 mmol) following the same bromination procedure as described in the synthesis of 2c. IR (neat): 2922, 2853, 1594, 1453, 1161, 1053 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.74 (m, 8H, Ar–H), 6.69 (m, 2H, Ar–H), 6.63–6.61 (m, 25H, Ar-H), 6.58 (m, 2H, Ar-H), 6.44 (m, 8H, Ar-H), 5.02 (s, 2H, benzylic CH<sub>2</sub>Br), 5.01 (s, 8H, benzylic OCH<sub>2</sub>), 4.99 (s, 16H, benzylic OCH<sub>2</sub>), 4.46 (s, 4H, benzylic OCH<sub>2</sub>), 3.98 (t, *J*=6.7 Hz, 32H, decyl OCH<sub>2</sub>), 1.86 (m, 32H, decyl CH<sub>2</sub>), 1.50 (m, 32H, decyl CH<sub>2</sub>), 1.49-1.35 (m, 192H, decyl CH<sub>2</sub>), 0.96 (t, J=6.7 Hz, 48H, decyl CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  161.0, 160.8, 160.7, 160.5 (four Ar C–O), 139.7, 139.4, 139.3, 108.7, 107.9, 106.9, 106.6, 106.2, 102.7, 102.3, 101.9, 100.7 (12 aromatic carbon signals), 70.7, 70.5, 68.3, 68.2 (three benzylic and one decyl OCH<sub>2</sub>, one coincidental peak not observed), 34.2 (benzylic CH<sub>2</sub>Br), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 14.4 (CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd for  $C_{265}H_{411}^{79}BrO_{30}$  4155.0, found 4012.5  $[M-C_{10}H_{21}]^+$ .

# 4.24. G<sub>3</sub>-C<sub>10</sub> dendron (5d)

G<sub>3</sub>–C<sub>10</sub> dendron (**5d**) (265 mg, 0.064 mmol, 97%) was prepared as a waxy solid from 5c (275 mg, 0.066 mmol) and NaN<sub>3</sub> (43 mg, 0.66 mmol) following the same procedure as described in the synthesis of 3d. IR (neat): 2923, 2853, 2099, 1595, 1455, 1162, 1055 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>);  $\delta$  6.72 (m, 12H, Ar–H), 6.61– 6.59 (m. 22H, Ar-H), 6.46 (m. 3H, Ar-H), 6.45 (m. 8H, Ar-H), 5.01 (s. 4H, benzylic OCH<sub>2</sub>), 4.99 (s, 8H, benzylic OCH<sub>2</sub>), 4.98 (s, 16H, benzylic OCH<sub>2</sub>), 4.29 (s, 2H, benzylic CH<sub>2</sub>N<sub>3</sub>), 3.97 (t, *J*=6.7 Hz, 32H, decyl OCH<sub>2</sub>), 1.80 (m, 32H, decyl CH<sub>2</sub>), 1.48 (m, 32H, decyl CH<sub>2</sub>), 1.47-1.45 (m, 192H, decyl CH<sub>2</sub>), 0.93 (t, *J*=6.7 Hz, 48H, decyl CH<sub>3</sub>);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  160.9, 160.8, 160.5, 160.4 (four Ar C-O), 139.9, 139.7, 139.4, 139.3, 107.0, 106.9, 106.2, 106.0, 102.4, 102.1, 101.5, 101.3 (12 aromatic carbon signals), 70.4, 70.3, 68.3, 68.2 (three benzylic and one decyl OCH<sub>2</sub>), 55.2 (benzylic CH<sub>2</sub>N<sub>3</sub>), 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9, 14.4 (CH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd for C<sub>265</sub>H<sub>411</sub>N<sub>3</sub>O<sub>30</sub> 4118.1, found 4087.3 [M-N<sub>2</sub>]<sup>+</sup>.

#### 4.25. 4-(Trimethylsilyl)ethynylbenzaldehyde (7)

An oven-dried round-bottom flask was purged with N2 and to it were added 4-bromobenzaldehyde (6) (530 mg, 2.86 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (100 mg, 14.3 mmol), CuI (54.5 mg, 28.6 mmol), and DBU (521 mg, 3.40 mmol) in dry benzene (10 mL) under the protection of N<sub>2</sub>. Trimethylsilylacetylene (TMSA) (563 mg, 5.70 mmol) in benzene (3 mL) was added dropwise in 0.5 h. and the reaction mixture was kept under reflux for another 0.5 h. After cooling down to room temperature, the mixture was filtered through a Celite plug. The resulting organic solution was concentrated in vacuo to give the crude product, which was purified by silica flash chromatography (hexanes/EtOAc 25:1) to yield compound 7 (509 mg, 2.51 mmol, 86%) as a pale yellow solid. IR (neat): 2957, 2737, 2156, 1699, 1600, 1563 cm  $^{-1};~^{1}{\rm H}$  NMR (500 MHz, CDCl3):  $\delta$  10.01 (s, 1H, CHO), 7.82 (d, J=8.8 Hz, 2H, Ar-H), 7.61(d, J=8.8 Hz, 2H, Ar-H), 0.28 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 191.6 (C=O), 135.9, 132.7, 129.6, 104.1, 99.2, 0.1 (Si(CH<sub>3</sub>)<sub>3</sub>); GC-MS m/z (%) calcd for C<sub>12</sub>H<sub>14</sub>OSi 202.1, found 201.8 (16, [M]<sup>+</sup>), 187 (100, [M–CH<sub>3</sub>]<sup>+</sup>).

# 4.26. C<sub>60</sub> adduct (8)

To an oven-dried round-bottom flask purged with  $N_{\rm 2}$  were charged C<sub>60</sub> (712 mg, 0.989 mmol), benzaldehyde **7** (100 mg, 0.50 mol), and sarcosine (446 mg, 5.00 mol) in dry toluene (70 mL). The mixture was refluxed for 24 h. Afterwards, the solvent was evaporated off under reduced pressure, and the residue was purified by silica chromatography (hexanes/toluene 4:1) to afford compound 8 (108 mg, 0.114 mmol, 23%) as a dark brown solid. Mp >300 °C. IR (neat): 2947, 2840, 2782, 2159 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.78 (br s, 2H, Ar-H), 7.52 (d, J=8.3 Hz, 2H, Ar-H), 5.00 (d, J=9.6 Hz, 1H), 4.95 (s, 1H), 4.29 (d, J=9.0 Hz, 1H), 2.82 (s, 3H, NCH<sub>3</sub>), 0.25 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 156.0, 153.8, 153.1, 152.8, 147.33, 147.31, 146.6, 146.40, 146.36, 146.30, 146.26, 146.22, 146.18, 146.14, 145.99, 145.97, 145.77, 145.64, 145.62, 145.51, 145.43, 145.39, 145.35, 145.31, 145.28, 145.27, 145.21, 144.37, 144.68, 144.43, 144.41, 143.20, 143.06, 142.74, 142.67, 142.63, 142.61, 142.31, 142.27, 142.18, 142.14, 142.08, 142.06, 141.91, 141.7, 141.6, 140.28, 140.25, 140.01, 139.64, 137.4, 136.9, 136.6, 135.9, 135.8 (totally 54 carbon signals observed for the 60 chemically nonequivalent fullerene carbons), 132.4, 132.3, 123.6 (three signals observed for the four aryl carbons), 105.1, 95.3 (two alkynl carbons), 89.3 (CH), 69.0 (CH<sub>2</sub>), 40.0 (NCH<sub>3</sub>), 0.2 (Si(CH<sub>3</sub>)<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/z calcd for C<sub>74</sub>H<sub>19</sub>NSi 949.1287, found 950.7477 [M+H]+.

# 4.27. General synthetic procedure for triazole-linked dendro[60]fullerenes (9a–e) via a 'click' reaction

To a solution of compound **8** (1 equiv) in THF was added TBAF (1 equiv, 1 M in THF), and the mixture was stirred at room temperature for 5 min. To this mixture were added Cul (0.3 equiv) and azido-dendron (1 equiv). The reaction mixture was kept under stirring at room temperature overnight. The solvent THF was then removed in vacuo, and the residue was diluted in CHCl<sub>3</sub>, washed with saturated NH<sub>4</sub>Cl, and dried over anhydrous MgSO<sub>4</sub>. Suction filtration followed by flash chromatography (hexanes/CHCl<sub>3</sub> 1:1 and then hexanes/CHCl<sub>3</sub>/EtOAc 5:1:0.5) afforded the corresponding dendro[60]fullerene product.

# 4.28. Dendro[60]fullerene (9a, C<sub>60</sub>-G<sub>1</sub>-C<sub>10</sub>)

Dendro[60]fullerene **9a** (115 mg, 0.062 mmol, 72%) was prepared according to the general 'click' reaction procedure, using compound **8** (80 mg, 0.084 mmol), TBAF (0.08 mL, 1 M in THF), Cul (1.6 mg, 0.0084 mmol), and azido-dendron **3d** (81.6 mg, 0.084 mmol). The isolated product was a dark brown waxy solid. IR (neat): 3032, 2929, 1594 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.86 (m, 4H), 7.63 (s, 1H, triazole H), 6.57 (m, 1H), 6.50 (m, 6H), 6.36 (m, 2H), 5.45 (s, 2H), 4.99 (d, *J*=6.9 Hz, 1H), 4.95 (s, 1H), 4.89 (s, 4H), 4.27 (d, *J*=6.9 Hz, 1H), 3.95 (t, *J*=6.7 Hz, 8H), 2.82 (s, 3H), 1.74 (m, 8H), 1.42 (m, 8H), 1.37–1.25 (m, 48H), 0.88 (t, *J*=7.1 Hz, 12H). Meaningful <sup>13</sup>C NMR spectrum could not be acquired due to low concentration. MALDI-TOF MS (dithranol as the matrix) *m/z* calcd for C<sub>132</sub>H<sub>112</sub>N<sub>4</sub>O<sub>6</sub> 1849.9, found 1848.8 [M]<sup>+</sup>.

# 4.29. Dendro[60]fullerene (9b, C<sub>60</sub>-G<sub>1</sub>-H)

Dendro[60]fullerene 9b (34.2 mg, 0.028 mmol, 38%) was prepared according to the general 'click' reaction procedure, using compound 8 (70 mg, 0.074 mmol), TBAF (0.07 mL, 1 M in THF), CuI (1.4 mg, 0.0074 mmol), and azido-dendron **3h** (25.5 mg, 0.074 mmol). The isolated product was a dark brown solid. IR (neat): 2921, 2852, 2782, 1595, 1451 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.90 (m, 4H), 7.64 (s, 1H, triazole H), 7.44–7.27 (m, 10H), 6.61 (m, 1H), 6.53 (m, 2H), 5.49 (s, 2H), 5.03 (d, J=9.6 Hz, 1H), 5.02 (s, 4H), 5.00 (s, 1H), 4.31 (d, *J*=9.6 Hz, 1H), 2.86 (s, 3H, NCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 160.7 (Ar C–O), 156.5, 154.3, 153.6, 153.5, 148.2, 147.6, 147.0, 146.7, 146.6, 146.53, 146.50, 146.43, 146.41, 146.37, 146.20, 145.81, 145.80, 145.7, 145.60, 145.55, 145.49, 145.43, 145.0, 144.9, 144.67, 144.66, 143.4, 143.3, 143.0, 142.84, 142.78, 142.6, 142.5, 142.44, 142.40, 142.39, 142.33, 142.31, 142.27, 142.2, 142.1, 142.0, 141.8, 140.5, 140.4, 140.2, 137.3, 137.1, 136.9, 136.8, 136.6, 136.2, 136.0 (totally 53 signals were observed out of 58 sp<sup>2</sup> carbons on the  $C_{60}$ cage and 2 phenyl carbons in this region), 131.0, 128.9, 128.4, 127.8, 120.0, 114.2, 107.5, 102.5 (9 aromatic carbon signals were observed out of 12 aromatic carbons), 83.6 (NCHPh on the pyrolidine ring), 70.4, 70.3 (two OCH<sub>2</sub>), 69.4 (NCH<sub>2</sub> on the pyrolidine ring), 54.6 (CH<sub>2</sub>N), 40.3 (NCH<sub>3</sub>); MALDI-TOF MS (dithranol as the matrix) m/zC<sub>92</sub>H<sub>30</sub>O<sub>2</sub>N<sub>4</sub> 1222.2, found 1223.3 [M+H]<sup>+</sup>.

### 4.30. Dendro[60]fullerene (9c, C<sub>60</sub>-G<sub>2</sub>-C<sub>10</sub>)

Dendro[60]fullerene **9c** (126 mg, 0.0430 mmol, 69%) was prepared according to the general 'click' reaction procedure, using compound **8** (60 mg, 0.063 mmol), TBAF (0.06 mL, 1 M in THF), Cul (1.2 mg, 0.0063 mmol), and azido-dendron **4d** (127 mg, 0.063 mmol). The isolated product was a dark brown waxy solid. IR (neat): 2924, 2854, 1597, 1464 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (m, 4H), 7.62 (s, 1H, triazole H), 6.64 (m, 4H), 6.55–6.51 (m, 13H), 6.41 (m, 4H), 5.45 (s, 2H), 5.30 (s, 1H), 4.93 (m, 13H), 4.26 (d, *J*=9.6 Hz, 1H), 3.94 (t, *J*=6.4 Hz, 16H), 2.81 (s, 3H), 1.78

(m, 16H), 1.46 (m, 16H), 1.42–1.25 (m, 96H), 0.91 (t, *J*=6.4 Hz, 24H); Meaningful <sup>13</sup>C NMR spectrum could not be acquired due to low concentration and significant line broadening. MALDI-TOF MS (dithranol as the matrix) *m*/*z* calcd for  $C_{200}H_{214}O_{14}N_4$  2897.6, found 2894.5 [M]<sup>+</sup>.

# 4.31. Dendro[60]fullerene (9d, C<sub>60</sub>-G<sub>2</sub>-H)

Dendro[60]fullerene **9d** (63 mg, 0.038 mmol, 70%) was prepared according to the general 'click' reaction procedure, using compound **8** (52 mg, 0.055 mmol), TBAF (0.06 mL, 1 M in THF), Cul (1.0 mg, 0.005 mmol), and azido-dendron **4h** (42 mg, 0.055 mmol). The isolated product was a dark brown waxy solid. IR (neat): 3033, 2930, 1594 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.84 (m, 4H), 7.61 (s, 1H, triazole H), 7.44–7.28 (m, 20H), 6.62 (m, 4H), 6.53 (m, 3H), 6.49 (s, 2H), 5.44 (s, 2H), 5.00 (s, 8H), 4.99 (d, *J*=9.6 Hz, 1H), 4.94 (s, 1H), 4.92 (s, 4H), 4.27 (d, *J*=9.6 Hz, 1H), 2.81 (s, 3H). Meaningful <sup>13</sup>C NMR spectrum could not be acquired due to low concentration. MALDI-TOF MS (dithranol as the matrix) *m/z* calcd for C<sub>120</sub>H<sub>54</sub>N<sub>4</sub>O<sub>6</sub> 1647.4, found 1646.9 [M]<sup>+</sup>.

### 4.32. Dendro[60]fullerene (9e, C<sub>60</sub>-G<sub>3</sub>-C<sub>10</sub>)

Dendro[60]fullerene 9e (147 mg, 0.0290 mmol, 80%) was prepared according to the general 'click' reaction procedure, using compound 8 (35 mg, 0.037 mmol), TBAF (0.04 mL, 1 M in THF), CuI (1.0 mg, 0.005 mmol), and azido-dendron **5d** (120 mg, 0.029 mmol). The isolated product was a dark brown waxy solid. IR (neat): 3417, 2925, 2854, 1619, 1550, 1466 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.83 (m, 4H), 7.5 (s, 1H, triazole H), 6.67 (m, 8H), 6.66 (m, 4H), 6.62 (m, 20H), 6.55-6.41 (m, 5H), 6.41 (m, 8H), 5.45 (s, 2H), 5.30 (s, 1H), 4.95 (s, 16H), 4.93 (m, 9H), 4.89 (m, 4H), 4.26 (d, J=9,6 Hz, 1H), 3.94 (t, J=6.4 Hz, 32H), 2.78 (s, 3H), 1.79 (m, 32H), 1.45 (m, 32H), 1.42-1.25 (m, 192H), 0.91 (t, J=6.4 Hz, 48H). Meaningful <sup>13</sup>C NMR spectrum could not be acquired due to low concentration and significant line broadening. MALDI-TOF MS (dithranol as the matrix) m/z calcd for C<sub>336</sub>H<sub>422</sub>N<sub>4</sub>O<sub>30</sub> 4996.2, found 4993.3 [M]<sup>+</sup>.

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