

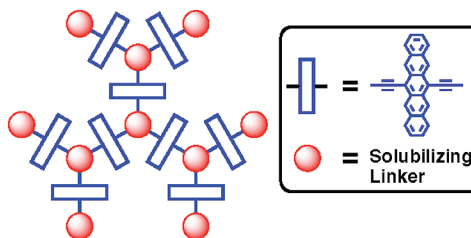
# Pentacene-Based Dendrimers: Synthesis and Thin Film Photoconductivity Measurements of Branched Pentacene Oligomers

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The synthesis of pentacene-based dendrimers has been achieved via esterification of 1,3,5-benzenetricarboxylic acid and unsymmetrical pentacene **4** possessing a hydroxy group. Dendrimers **1** ( $C_{183}H_{204}O_9Si_9$ ,  $2800 \text{ g mol}^{-1}$ ) and **2** ( $C_{540}H_{570}O_{30}Si_{24}$ ,  $8214 \text{ g mol}^{-1}$ ) are characterized by  $^1H$  and  $^{13}C$  NMR, IR, UV-vis, and fluorescence spectroscopy, as well as mass spectrometry. These branched oligomeric materials are benchtop stable and soluble in common organic solvents, allowing for solution cast formation of thin films. Photocurrent and photocurrent yield measurements of these films reveal improved efficiency in photogenerated conduction for dendrimers in comparison to linearly connected pentacene-based polymers.

## Introduction

The formation of oligo- and polymeric acene-based materials, such as those based on thiophene<sup>1</sup> and anthracene chromophores,<sup>2</sup> have provided materials with significantly enhanced properties for optoelectronic applications in comparison to that of their respective monomeric chromophore unit. It was thus envisioned that pentacene-based oligo- and polymers should offer technologically relevant materials with improved properties relative to pentacene. The formation of pentacene-based oligo- and polymers should also provide a means to address the solubility and stability issues associated with pristine pentacene, toward materials suitable for solution deposition of thin films. In recent years, several soluble, stable functionalized pentacene oligomers and polymers have appeared. Limited synthetic details have been reported in 2001 by Tokito and co-workers for random co-polymers of pentacene and fluorene synthesized via

Ni(0)-mediated Yamamoto-coupling.<sup>3</sup> In 2007, Okamoto et al. used a Sonogashira coupling of diethynylated benzenes to obtain co-polymers with pentacene, although a regiorandom mixture was obtained as a result of utilizing a mixture of 2,9- and 2,10-dibrominated isomers of 6,13-bis(triisopropylsilylethynyl)pentacene as the precursors.<sup>4</sup> In 2008, this methodology was extended to include Suzuki couplings for the synthesis of pentacene-fluorene co-polymers.<sup>5</sup> In 2007, a method of functionalizing pentacene with a silylacetylene afforded mono-, di-, tri-, and polymeric pentacene materials based on the formation of ester linkages.<sup>6</sup> In 2008, the desymmetrization of pentacene was achieved such that the pentacene core could be functionalized with two different acetylides.<sup>7</sup> This synthetic protocol was then optimized to a one-pot protocol and employed for the synthesis of conjugated dimers that showed impressive photo-

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conductive gain.<sup>8</sup> With these studies as a foundation, we turned our attention to branched structures, namely dendrimers, that incorporate pentacene chromophores. It was predicted that dendrimers should improve the chromophore organization in comparison to linearly connected polymers, ultimately increasing  $\pi$ - $\pi$  interactions that are crucial to materials performance.

Dendrimers are a versatile class of branched, 3-dimensional, defined-length oligomers<sup>9</sup> that have been synthetically targeted for a range of applications, such as biomedicine,<sup>10</sup> catalysis,<sup>11</sup> and light-harvesting.<sup>12</sup> Recently, their use in the field of organic electronics as semiconductive materials for light-emitting diodes and photovoltaic cells has come to the forefront.<sup>13</sup> Dendritic structures offer the potential of enhanced performance for semiconductors through the ability to control the local environment of the chromophore within the macromolecular shell, as well as providing 3-dimensional ordering of the chromophores.<sup>14</sup> Since 3-dimensional arrangement of chromophores in the solid state strongly influences the electronic properties of a material and thus device performance, dendritic molecules can afford new and enhanced properties as a result of this controlled geometrical organization.<sup>15</sup> For example, the spatial organization of dendrimers has been used to create dipole alignment of polarized chromophores for nonlinear optical applications,<sup>16</sup> and oligothiophene dendrimers<sup>17a</sup> have been used by Bäurele and co-workers for applications in solar cells with promising power-conversion efficiencies.<sup>17b</sup> Furthermore, Müllen's giant polyphenylene dendrimers highlight how unique physical properties can be dictated by precise spatial arrangement of functional groups.<sup>18</sup> We report herein the synthesis of the first pentacene-based dendrimers, as well as an evaluation and comparison of their photoconductivity performance versus linear polymers.

## Results and Discussion

Synthetically, the targeted dendrimers **1**–**3** derive from the combination of a functionalized pentacene linking group and a 1,3,5-benzenetricarboxylate moiety that serves as both the core and the 1  $\rightarrow$  3 branching unit (Figure 1).<sup>19</sup>

It was envisioned that the assembly of these materials would rely on a simple esterification reaction between the alcohol

moiety of pentacene building block **4** and a branched unit bearing carboxylic acid moieties (Scheme 1). Thus, a 3-fold EDC-mediated esterification of 1,3,5-benzenetricarboxylic acid with **4**<sup>6b</sup> gave the first generation dendrimer **1** in excellent yield (86%).

The synthesis of a second generation of dendrimer **2** employed a divergent approach that required the synthesis of dendron **5** to serve as the arms (Scheme 1). Mono-ol **5** was obtained from dendrimer **1** via kinetic desilylation, using a procedure analogous to that developed in synthesis of mono-ol **4**.<sup>6b</sup> Thus, subjecting dendrimer **1** to dilute HCl in THF provided dendron **5** in 33% yield, as well as diol **6** (9%) and recovered starting material **1** (58%). The reaction time was optimized to minimize the formation of diol **6** while allowing for recycling of the recovered starting material **1** to build up reasonable quantities of the necessary precursor **5**. The subsequent EDC-mediated esterification of 1,3,5-benzenetricarboxylic acid with mono-ol **5** afforded dendrimer **2**.

Synthetic attempts were made toward the third generation dendrimer **3**, but these proved to be challenging. Obviously, the methodology used for the synthesis of dendrimer **2** is not amenable to dendrimer **3**. Namely, the kinetic desilylation of one of six TBS ethers of dendrimer **2** to obtain dendron **7** with one free alcohol would be low-yielding at best and is further complicated by a difficult separation between starting material and the various poly-ol products. Thus, an alternative route was investigated in which dendrimer **2** was employed as a precursor to the core of dendrimer **3**. Specifically, a 2-fold esterification of 1,3,5-benzenetricarboxylic acid with 2 equiv of mono-ol **4** provided a monocarboxylic acid equivalent in the form of dendron **8a** and/or **8b**, instead of the expected monocarboxylic acid **8c** (Scheme 2). The yields of this reaction were highly solvent-dependent, with the best conditions affording 32% yield using a combination of THF and CH<sub>2</sub>Cl<sub>2</sub>. It was intended that **8a** and/or **8b** would be used in an esterification reaction with hexa-ol core **9** to provide dendrimer **3** (see Figure 1 for structure). Unfortunately, global removal of the TBS ethers of dendrimer **2** using HCl in THF (as optimized for the synthesis of **5**)<sup>6b</sup> gave significant hydrolysis of the ester groups, as documented by <sup>1</sup>H NMR spectroscopy and MALDI MS. At this point, with no obvious means to effectively generate **9**, synthetic efforts to dendrimer **3** were abandoned.

Dendrimers **1** and **2** were isolated by column chromatography as blue solids, which are readily soluble in common organic solvents, including CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and THF (>50 mg/mL in all cases). Dendrimers **1** and **2** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, UV-vis, and fluorescence spectroscopy, as well as mass spectrometry.<sup>20</sup> MALDI HRMS analysis of **1** showed a base peak (M<sup>+</sup>) at *m/z* 2797.3470, as expected for C<sub>183</sub>H<sub>204</sub>O<sub>9</sub>Si<sub>9</sub> (Figure 2). In the case of ESI MS analysis for **2**, signals of M<sup>4+</sup> and M<sup>5+</sup> were observed at *m/z* 2053.4 and 1642.7, respectively, for C<sub>540</sub>H<sub>570</sub>O<sub>30</sub>Si<sub>24</sub> (Figure 3). MALDI MS analysis of **2** revealed signals for M<sup>+</sup> and M<sup>2+</sup> in addition to signals consistent with aggregates such as [2M]<sup>+</sup> and [3M]<sup>+</sup>.

NMR spectroscopy provided convincing evidence of product purity for both **1** and **2**, and it was particularly useful for dendrimer **2**. A comparison of the <sup>1</sup>H NMR spectra of **1**, **4**, and **5** shows that in each case the benzylic protons have a unique chemical shift depending on whether they are adjacent to an alcohol, an ester, or a silyl ether functional group.<sup>20</sup> Examination of the <sup>1</sup>H NMR spectrum of **2** shows no evidence of incomplete

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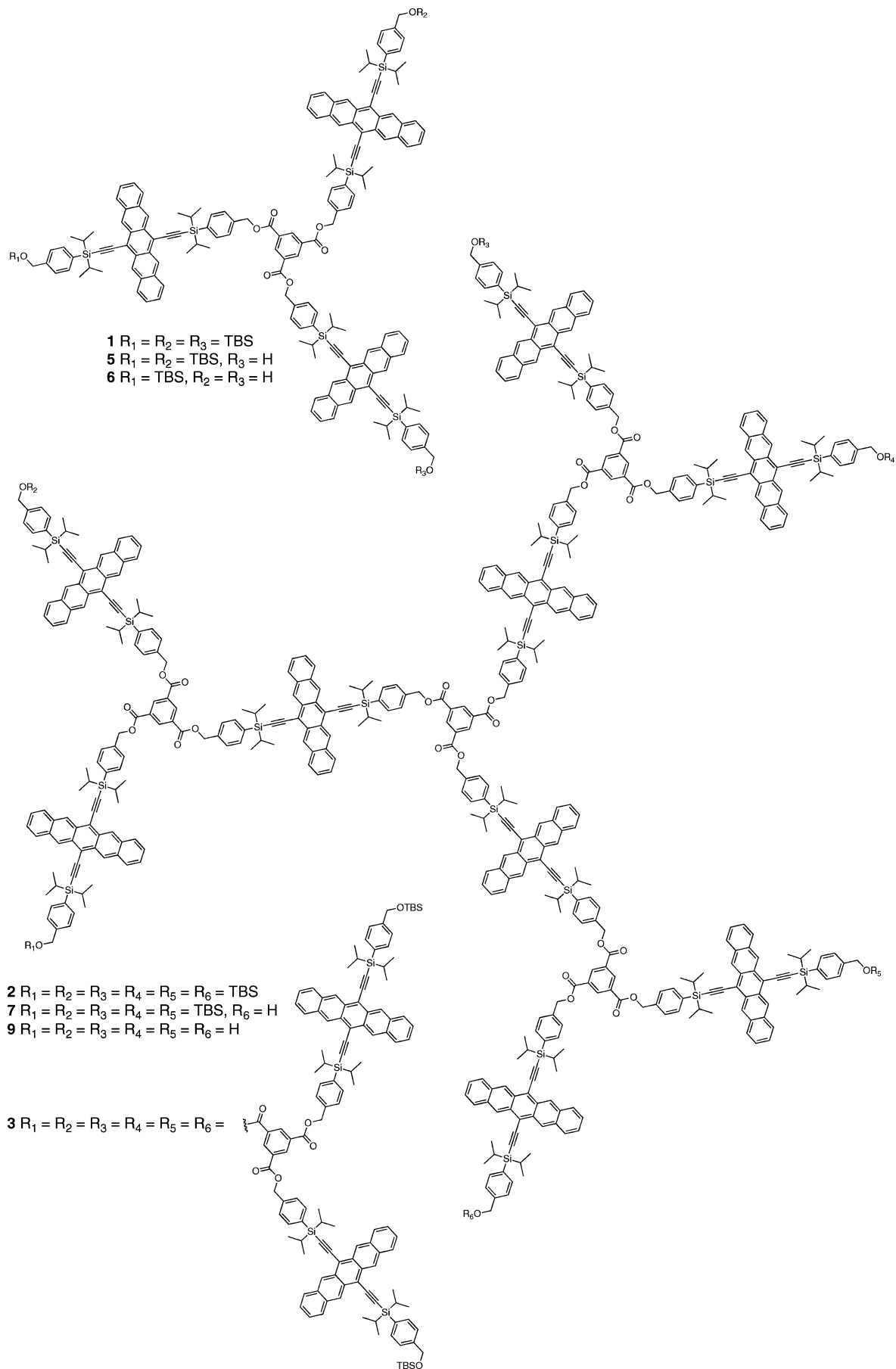
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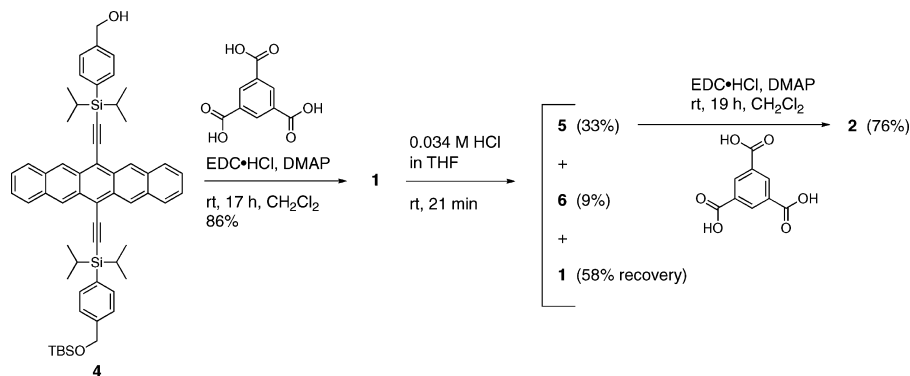
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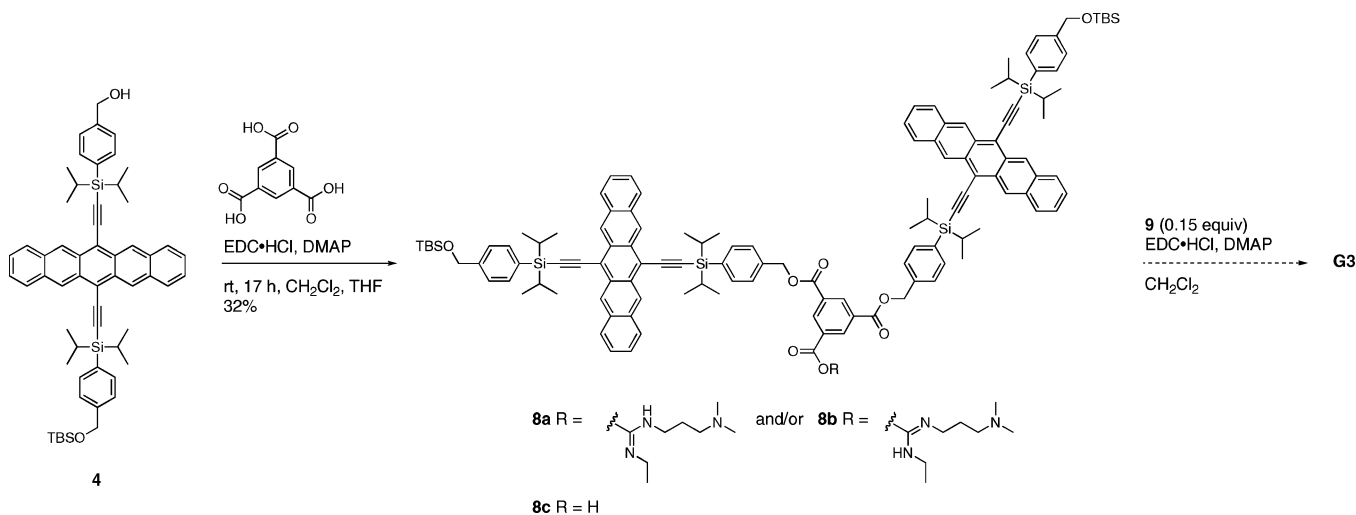


**FIGURE 1.** Pentacene-based dendrimers **1–3** and building blocks **5–7, 9**.

## SCHEME 1. Synthesis of Pentacene-Based Dendrimers 1 and 2



## SCHEME 2. Attempted Synthesis of Pentacene-Based Dendrimer 3



esterification, i.e., there are no signals present that would be consistent with benzyl alcohol protons of an uncoupled dendron. Likewise, no additional signals in the  $^{13}\text{C}$  NMR spectrum were observed that would be consistent with an aromatic core bearing a free carboxylic acid.

Thermal stability of the dendrimers was assessed by thermal gravimetric analysis (TGA), and no significant weight loss (i.e., <5% weight loss) was observed below 395 and 430 °C for 1

and 2, respectively. Analysis by differential scanning calorimetry (DSC) showed an exotherm at 370–375 °C for both 1 and 2, which was assigned to decomposition in both cases. The thermal stability of 1 and 2 is analogous to that of previously reported oligomers and polymers,<sup>6,8</sup> which show enhanced thermal stability in comparison to monomeric pentacenes.<sup>6–8,21</sup>

The solution-state UV–vis and fluorescence spectra of dendrimers 1 and 2 in  $\text{CH}_2\text{Cl}_2$  are shown in Figure 4a. Both

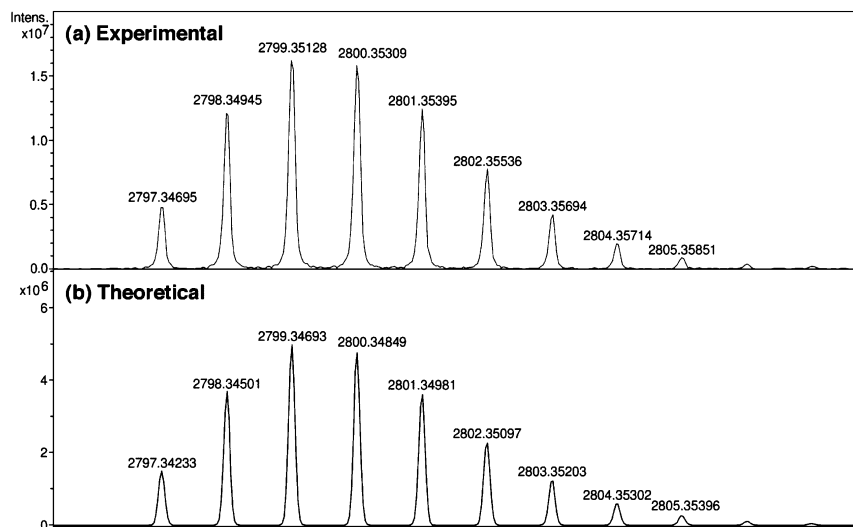


FIGURE 2. (a) Experimental high-resolution MALDI mass spectrum of 1. (b) Theoretical isotopic envelope for  $\text{C}_{187}\text{H}_{204}\text{O}_9\text{Si}_9$  ( $\text{M}^+$ ).

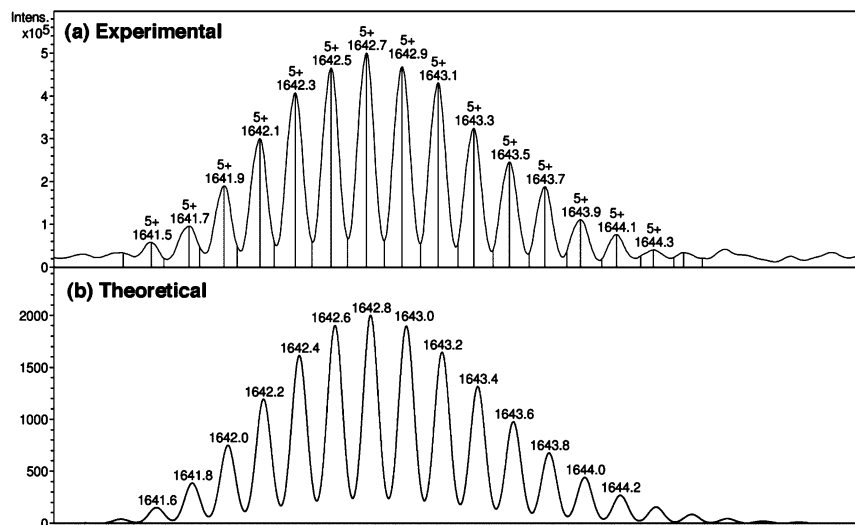


FIGURE 3. (a) Experimental ESI mass spectrum of dendrimer 2. (b) Theoretical isotopic envelope for  $C_{540}H_{570}O_{30}Si_{24} (M^{5+})$ .

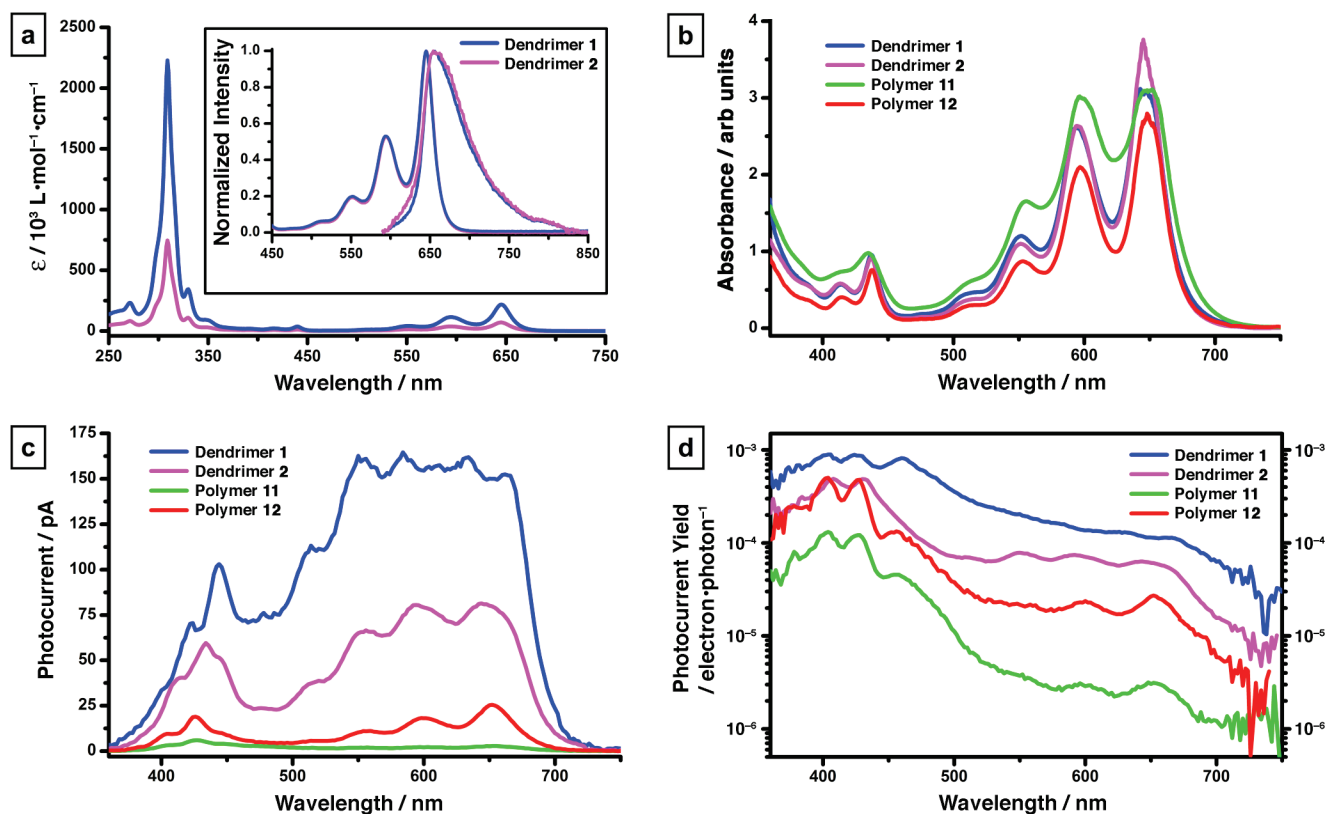


FIGURE 4. (a) Absorption spectra of dendrimers 1 and 2. Inset: absorption (left trace) and emission spectra (right trace, normalized to unity) of dendrimers 1 and 2 using  $\lambda_{exc} = 551$  nm, illustrating the small Stokes shift (all measurements in  $CH_2Cl_2$ ). (b) Spectral data (360–750 nm) for thin films of dendrimers 1 and 2 and polymers 11 and 12. (c) Photocurrent spectra as a function of irradiation wavelength. (d) Photocurrent yield as a function of irradiation wavelength.

dendrimers have analogous absorption spectra in terms of profile and  $\lambda_{max}$  values. Similar to other functionalized pentacene derivatives, the absorption spectra of 1 and 2 show an intense high-energy absorption at 309 nm, along with a series of low intensity, long wavelength absorptions with the lowest energy transition at  $\lambda_{max} = 645$  nm. The molar absorptivity of dendrimer

2 ( $\epsilon = 2\,230\,000$ ) for the most intense absorption (309 nm) is approximately three times larger than that of 1 ( $\epsilon = 747\,000$ ), as expected on the basis of the number of pentacene chromophores in each molecule. Solution-state fluorescence reveals a small Stokes shift of only 9 nm for both dendrimers (inset of Figure 4a), suggesting that minimal molecular rearrangement occurs upon photoexcitation of the molecule. Although the fluorescence spectra of dendrimers 1 and 2 appear similar to that of building block 10 (Figure 5), the quantum yield of fluorescence ( $\Phi_F$ )<sup>22</sup> in  $CH_2Cl_2$  decreases as a result of the

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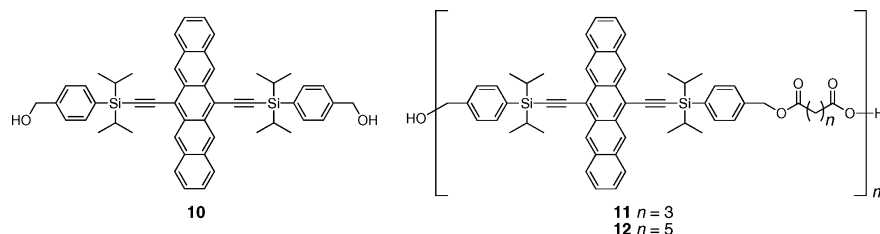


FIGURE 5. Structures of pentacene monomer **10** and linearly connected pentacene-based polymers **11** and **12**.

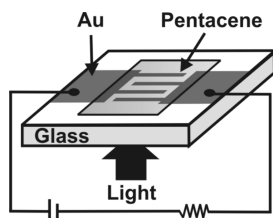


FIGURE 6. Schematic representation of a pentacene-based photodetector.

oligomerization process, i.e., upon going from monomer **10** ( $\Phi_F = 0.14$ )<sup>6b</sup> to **1** ( $\Phi_F = 0.04$ ) to **2** ( $\Phi_F = 0.03$ ).<sup>23</sup> The shape of the emission trace is also solvent-dependent. Emission from  $\text{CH}_2\text{Cl}_2$  provides a broad emission trace, whereas some vibrational fine structure is observed in solvents such as THF and toluene.<sup>20</sup> This solvent effect has also been observed for various other oligoacenes.<sup>24</sup>

The semiconducting properties of the new pentacene dendrimers were assessed in comparison to those of linearly connected polymers **11** and **12** to evaluate the effect of branched structures (see Figure 5 for structures) by preparing photodetectors (Figure 6).<sup>25</sup> Thin films (ca. 0.2–0.3  $\mu\text{m}$ ) for device analysis were obtained by spin-casting solutions of **1**, **2**, **11**, and **12** (0.5–1 wt % in  $\text{CHCl}_3$ ) onto interdigitated gold electrodes that were fabricated by lift-off photolithography on 1 cm  $\times$  1 cm fused-silica substrates. The electrode thickness, width, and separation were 0.2, 10, and 20  $\mu\text{m}$ , respectively, with a total active area of 3 mm  $\times$  3 mm.<sup>20</sup> A brief thermal annealing process (ca. 15 min) at 75  $^\circ\text{C}$  under a nitrogen atmosphere gave relatively smooth, amorphous films, as shown by atomic force microscopy.<sup>20</sup> Film coverage extended over a portion of the bare fused-silica substrate allowing for UV–vis absorption measurements of the actual films used in the devices (Figure 4b and Table 1). Solid-state absorption of these thin films (Figure 4b) were red-shifted by <10 nm compared to the solution-state spectra. The samples were illuminated through the substrate using light from a 50 W tungsten-halogen bulb passing through a 0.25 m grating monochromator, giving a maximum optical power of about 6.2  $\mu\text{W}$  at 650 nm over a 4 nm bandwidth. The spot size on the sample was kept within the active area of the device. A voltage bias of 100 V was applied to the photodetector structure producing an electric field

TABLE 1. Solution and Solid-State Photophysical Properties of Dendrimers **1** and **2**, Polymers **11** and **12**, and Monomer **10**

compounds	$\lambda_{\text{max}}$ , nm ( $\epsilon/M^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{max,em}}$ , nm	$\Phi_F^a$
dendrimer <b>1</b> (in $\text{CH}_2\text{Cl}_2$ )	271 (82 100), 309 (747 000), 330 (109 000), 346 (30 200), 393 (8 270), 416 (8 890), 440 (12 200), 552 (14 200), 594 (37 600), 645 (70 700)	654	0.04
dendrimer <b>1</b> (film) <sup>b,c</sup>	413, 437, 551, 594, 645		
dendrimer <b>2</b> (in $\text{CH}_2\text{Cl}_2$ )	271 (233 000), 309 (2 230 000), 330 (345 000), 347 (92 400), 392 (18 900), 417 (21 400), 440 (37 000), 552 (41 800), 594 (114 000), 645 (218 000)	654	0.03
dendrimer <b>2</b> (film) <sup>b,c</sup>	413, 437, 551, 594, 645		
polymer <b>11</b> (in $\text{CH}_2\text{Cl}_2$ )	271, 309, 330, 440, 552, 594, 645		
polymer <b>11</b> (film) <sup>b,c</sup>	435, 552, 597, 648		
polymer <b>12</b> (in $\text{CH}_2\text{Cl}_2$ )	271, 309, 330, 440, 552, 594, 645		
polymer <b>12</b> (film) <sup>b,c</sup>	414, 438, 552, 597, 648		
monomer <b>10</b> (in $\text{CH}_2\text{Cl}_2$ )	271 (22 600), 309 (285 000), 330 (40 200), 440 (4 330), 551 (4 940), 594 (13 400), 645 (25 900)	653	0.14
monomer <b>10</b> (film) <sup>b,c</sup>	414, 438, 554, 598, 652		

<sup>a</sup> Emission quantum yields determined using  $\lambda_{\text{exc}} = 652$  nm and cresyl violet perchlorate in MeOH ( $\Phi_F = 0.67$  at  $5.9 \times 10^{-7}$  M) as a standard (see ref 22). <sup>b</sup> Thin film cast from  $\text{CHCl}_3$  onto fused silica glass. <sup>c</sup> Solid-state UV–vis data only available for absorptions at wavelengths greater than 400 nm.

of  $10^5$  V  $\text{cm}^{-1}$  across the electrodes. The incident light was modulated by a mechanical chopper at 13 Hz, and the resulting photocurrent signal was measured using a lock-in amplifier across a 1  $\Omega$  load resistor. The incident light power on the sample was measured using a calibrated power meter, and the absorbed light power at each wavelength was determined by subtracting the power transmitted through the pentacene-based material from the incident power, corrected for the shadowing effect of the electrodes.

Photodetectors using dendrimers **1** and **2** and polymers **11** and **12** as the active material were fabricated and used to measure photoconductive yield as a function of wavelength using a traditional monochromator and lock-in technique (Figure 4c,d).<sup>26</sup> Photocurrent yield is defined as the ratio between the photogenerated electron flow rate and the absorbed photon rate. The photocurrent yield was calculated using the following equation:

$$\text{photocurrent yield} = \frac{I}{\frac{e}{P_{\text{abs}}}} \frac{1}{h\nu} \quad (1)$$

where  $I$  is the photocurrent,  $e$  is the electron charge,  $P_{\text{abs}}$  is the absorbed light power in the active region between the electrodes,  $h$  is Planck's constant, and  $\nu$  is the frequency of the light.

(22) Measured using cresyl violet perchlorate in methanol as a standard ( $\Phi_F = 0.67$  at  $5.9 \times 10^{-7}$  M). See: Isak, S. J.; Eyring, E. M. *J. Phys. Chem.* **1992**, *96*, 1738–1742.

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Photocurrent measurements of thin films of dendrimers **1** and **2** revealed photoconduction onset at ca. 700 nm (Figure 4c) corresponding to the absorption edge for these materials (Figure 4b), potentially indicating a band-to-band photogeneration mechanism<sup>27</sup> as opposed to excitonic (Onsager) models.<sup>28</sup> Photocurrent yields for dendrimer **1** and **2** revealed yields as high as  $9 \times 10^{-4}$  and  $4 \times 10^{-4}$ , respectively (Figure 4d). These efficiencies are up to an order of magnitude greater than those observed for linearly connected polymers **11** and **12**. While these results show that these dendritic materials are able to act as semiconductive materials with enhanced efficiency compared to linearly connected pentacene materials, the photocurrent yields are still low. The lack of any substantial red-shift for the solid-state UV-vis spectra compared to that of the solution-state data supports the lack of any substantial  $\pi$ -stacking interaction. Thus, even though a dendritic structure seems to provide improved performance, both dendrimers **1** and **2** still suffer from inefficient solid-state packing between the pentacene chromophores.

An additional observation is noted with respect to the wavelength dependence of the photoconductive yield (Figure 4d). The dendrimer geometry provides a flatter response in the photocurrent yield as a function of wavelength, with a change of approximately only 1 order of magnitude over the range of 360–650 nm compared to that of the polymers, which exhibit a change of approximately 2 orders of magnitude. Thus, the dendrimers not only provide improved efficiency but also a photodetector with photoresponse that is less susceptible to minor changes in the wavelength of photoexcitation.

## Conclusion

In summary, we have developed methodology for synthesizing branched pentacene oligomers with defined-length in the form of dendrimers. These materials are soluble in common organic solvents and stable in the presence of air, allowing for facile purification and solution deposition to afford thin films. Although no evidence of increased  $\pi$ - $\pi$  interactions is observed by UV-vis spectroscopic analysis, the ordering of the chromophore using a dendritic geometry afforded materials whose thin films exhibited photocurrent yields superior to those of the corresponding linearly connected pentacene polymers.

## Experimental Section

Reagents were purchased in reagent grade from commercial suppliers and used without further purification. Compounds **4**, **10**, and polymers **11** and **12** have been previously reported.<sup>6</sup> THF was distilled from sodium/benzophenone ketyl;  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{CaH}_2$ . Anhydrous  $\text{MgSO}_4$  was used as the drying agent after aqueous workup. Evaporation and concentration in vacuo was done at water-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of nitrogen.

**Dendrimer 1.** To a solution of **4** (0.960 g, 1.09 mmol), 1,3,5-benzenetricarboxylic acid (0.0690 g, 0.328 mmol), and EDC·HCl (0.522 g, 2.73 mmol) in  $\text{CH}_2\text{Cl}_2$  (12 mL) was added DMAP (0.334 g, 2.73 mmol). The solution was stirred at rt for 24 h before being poured into saturated aq  $\text{NaHCO}_3$  (120 mL). The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL, 25 mL), washed with saturated aq

$\text{NaHCO}_3$  (120 mL), saturated aq  $\text{NH}_4\text{Cl}$  ( $2 \times 120$  mL), and saturated aq  $\text{NaCl}$  (100 mL), and dried ( $\text{MgSO}_4$ ), and the solvent was removed in vacuo. Column chromatography (silica gel, 2:1  $\text{CH}_2\text{Cl}_2$ /hexanes) afforded dendrimer **1** (0.786 g, 86%) as a blue solid. The excess **4** was recovered by flushing the column with  $\text{CH}_2\text{Cl}_2$ .  $R_f = 0.58$  (2:1  $\text{CH}_2\text{Cl}_2$ /hexanes). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 271 (82 100), 309 (747 000), 330 (109 000), 346 (30 200), 393 (8 270), 416 (8 890), 440 (12 200), 552 (14 200), 594 (37 600), 645 (70 700) nm. Fluorescence ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{exc}} = 551$  nm):  $\lambda_{\text{max,em}} = 654$  nm,  $\Phi_F = 0.04$ . IR ( $\text{CH}_2\text{Cl}_2$ , cast) 3049 (w), 2953 (s), 2890 (m), 2863 (s), 2136 (m), 1732 (m), 1462 (m), 1228 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.47 (s, 6H), 9.44 (s, 6H), 9.05 (s, 3H), 8.09–8.02 (m, 12H), 8.02–7.96 (m, 12H), 7.61 (d,  $J = 7.7$  Hz, 6H), 7.52 (d,  $J = 7.6$  Hz, 6H), 7.50–7.43 (m, 12H), 5.53 (s, 6H), 4.88 (s, 6H), 1.68–1.54 (m, 12H), 1.48 (d,  $J = 7.4$  Hz, 18H), 1.46 (d,  $J = 7.2$  Hz, 18H), 1.35 (d,  $J = 7.3$  Hz, 18H), 1.32 (d,  $J = 7.2$  Hz, 18H), 1.03 (s, 27H), 0.19 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 142.9, 136.7, 135.7, 135.3, 134.9, 133.8, 132.44, 132.41, 131.4, 131.3, 130.73, 130.70, 128.7, 128.6, 127.7, 126.4, 126.22, 126.19, 125.5, 118.4, 118.1, 106.0, 105.8, 105.6, 105.1, 67.3, 64.9, 26.0, 18.4, 18.25, 18.20, 18.16, 18.15, 12.10, 12.06, –5.3 (one signal not observed or coincident). HRMS MALDI  $m/z$  calcd for  $\text{C}_{183}\text{H}_{204}\text{O}_3\text{Si}_9$  ( $\text{M}^+$ ) 2797.3423, found 2797.3470. TGA:  $T_d \approx 395$  °C. DSC: decomposition, 370 °C (onset), 395 °C (peak).

**Dendrimer 2.** To a solution of **5** (0.410 g, 0.153 mmol), 1,3,5-tribenzenecarboxylic acid (0.010 g, 0.048 mmol), EDC·HCl (0.249 g, 1.30 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL) was added DMAP (0.227 g, 0.186 mmol). The solution was allowed to stir for 15 h at rt before being poured into saturated aq  $\text{NaHCO}_3$  (150 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL). The mixture was separated, and the organic was washed with saturated aq  $\text{NaHCO}_3$  (150 mL), saturated aq  $\text{NH}_4\text{Cl}$  (150 mL), and saturated aq  $\text{NaCl}$  (150 mL), and dried ( $\text{MgSO}_4$ ), and the solvent was removed in vacuo. Column chromatography (silica gel, 2:1  $\text{CH}_2\text{Cl}_2$ /hexanes  $\rightarrow$   $\text{CH}_2\text{Cl}_2$   $\rightarrow$  50:1  $\text{CH}_2\text{Cl}_2$ /EtOAc)<sup>29</sup> afforded dendrimer **2** (0.298 g, 76%) as a dark blue solid.  $R_f = 0.54$  (2:1  $\text{CH}_2\text{Cl}_2$ /hexanes). UV-vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ): 271 (233 000), 309 (2 230 000), 330 (345 000), 347 (92 400), 392 (18 900), 417 (21 400), 440 (37 000), 552 (41 800), 594 (114 000), 645 (218 000) nm. Fluorescence ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{exc}} = 551$  nm):  $\lambda_{\text{max,em}} = 654$  nm,  $\Phi_F = 0.03$ . IR ( $\text{CHCl}_3$ , cast) 3048 (w), 2952 (s), 2890 (m), 2863 (s), 2136 (m), 1731 (s), 1230 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.38 (br s, 12H), 9.35 (br s, 24H), 8.97 (br s, 12H), 8.01–7.95 (m, 36H), 7.95–7.89 (m, 36H), 7.53 (d,  $J = 7.2$  Hz, 24H), 7.45 (d,  $J = 7.5$  Hz, 12H), 7.43–7.35 (m, 36H), 5.45 (s, 24H), 4.82 (s, 12H), 1.62–1.47 (m, 36H), 1.47–1.34 (m, 108H), 1.31–1.20 (m, 108H), 0.96 (s, 54H), 0.13 (s, 36H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.8, 142.9, 136.7, 135.7, 135.3, 134.9, 133.82, 133.78, 132.42, 132.40, 131.4, 131.3, 130.72, 130.69, 128.6, 127.7, 126.4, 126.22, 126.17, 125.5, 118.5, 118.2, 118.1, 105.95, 105.89, 105.79, 105.6, 105.2, 105.1, 67.3, 64.9, 26.0, 18.4, 18.24, 18.19, 18.14, 12.10, 12.06, –5.3 (37 signals not observed or coincident). ESI MS (infused using 2:1  $\text{CH}_2\text{Cl}_2$ /MeOH with NaCl added)  $m/z$  calcd for the tallest isotope peak of  $\text{C}_{540}\text{H}_{570}\text{O}_{30}\text{Si}_{24}$  ( $\text{M}^{4+}$ ) 2053.4, found 2053.4; calcd for the tallest isotope peak of  $\text{C}_{540}\text{H}_{570}\text{O}_{30}\text{Si}_{24}$  ( $\text{M}^{5+}$ ) 1642.8, found 1642.7. TGA:  $T_d \approx 430$  °C. DSC: decomposition, 375 °C (onset), 398 °C (peak).

**Dendron 5.** To a solution of **1** (0.170 g, 0.0607 mmol) in dry THF (30 mL) was added dropwise an aqueous solution of HCl (~1.17 M, 0.83 mL, prepared by adding 10.0 mL of concentrated HCl (36%) to 90.0 mL of water) (equivalent to 0.034 M HCl in THF). The solution was allowed to stir for 21 min at rt and then poured into saturated aq  $\text{NaHCO}_3$  (100 mL) and extracted with

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(29) Dendrimer **2** behaved significantly different during TLC analysis and column chromatography. On TLC plates dendrimer **2** had the following  $R_f$  values: 0.54 (2:1  $\text{CH}_2\text{Cl}_2$ /hexanes), 1.0 ( $\text{CH}_2\text{Cl}_2$ ), 1.0 (50:1  $\text{CH}_2\text{Cl}_2$ /EtOAc). On column chromatography, very slow advancement of the band occurred with 2:1  $\text{CH}_2\text{Cl}_2$ /hexanes or  $\text{CH}_2\text{Cl}_2$ , and thus a more polar system (50:1  $\text{CH}_2\text{Cl}_2$ /EtOAc) was used.

CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The mixture was separated and the organic was washed with saturated aq NaHCO<sub>3</sub> (150 mL), saturated aq NaCl (150 mL), dried (MgSO<sub>4</sub>), and the solvent removed *in vacuo*. Column chromatography (silica gel, 2:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) afforded unreacted **1** (0.098 g, 58%), elution with 100:7 CH<sub>2</sub>Cl<sub>2</sub>/EtOAc afforded **5** (0.053 g, 33%) as a dark blue solid, and finally elution with 200:15 CH<sub>2</sub>Cl<sub>2</sub>/EtOAc afforded **6** (0.014 g, 9%). *R<sub>f</sub>* = 0.51 (23:1 CH<sub>2</sub>Cl<sub>2</sub>/EtOAc). IR (CHCl<sub>3</sub>, cast) 3043 (w), 2943 (s), 2890 (m), 2863 (s), 2136 (m), 1732 (s), 1229 (s), 743 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.44 (s, 4H), 9.41 (br s, 8H), 9.02 (s, 3H), 8.07–7.99 (m, 12H), 7.99–7.92 (m, 12H), 7.58 (d, *J* = 7.6 Hz, 6H), 7.54–7.47 (m, 6H), 7.47–7.40 (m, 12H), 5.50 (s, 6H), 4.86 (s, 4H), 4.78 (d, *J* = 5.7 Hz, 2H), 1.82 (t, *J* = 5.8 Hz, 1H), 1.66–1.51 (m, 12H), 1.49–1.39 (m, 36H), 1.36–1.25 (m, 36H), 1.01 (s, 18H), 0.17 (s, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 164.8, 142.9, 142.2, 136.7, 135.7, 135.6, 135.3, 134.9, 133.83, 133.81, 132.5, 132.44, 132.42, 131.4, 131.3, 130.74, 130.70, 128.66, 128.64, 127.7, 126.41, 126.37, 126.29, 126.26, 126.23, 126.18, 125.5, 118.5, 118.3, 118.2, 118.1, 106.0, 105.9, 105.8, 105.7, 105.5, 105.2, 105.1, 67.3, 65.3, 64.9, 26.0, 18.4, 18.25, 18.22, 18.20, 18.17, 18.15, 12.11, 12.07, –5.3 (22 signals not observed or coincident). HRMS MALDI *m/z* calcd for C<sub>177</sub>H<sub>190</sub>O<sub>8</sub>Si<sub>8</sub> (M<sup>+</sup>) 2683.2559, found 2683.2555.

**Diol 6.** Isolated as a byproduct from the synthesis of dendron **5** (see above for procedure) as a crude material. Further purification was done by dissolving this crude solid in minimal amount of CH<sub>2</sub>Cl<sub>2</sub> (ca. <0.5 mL) and adding hexanes (10 mL). The precipitate was filtered and washed with hexanes (2 × 2 mL) and the filtrate was discarded. The solid was then redissolved off the fritted funnel using CH<sub>2</sub>Cl<sub>2</sub> and filtered, this filtrate was concentrated *in vacuo*, and the resulting solid was dried under vacuum to afford **6** as a deep blue solid. Data for compound **6**: Blue solid. *R<sub>f</sub>* = 0.41 (100:7 CH<sub>2</sub>Cl<sub>2</sub>/EtOAc). IR (CHCl<sub>3</sub>, cast) 3600–3200 (br, w), 3048 (w), 2943 (s), 2890 (m), 2863 (s), 2136 (m), 1732 (s), 1230 (s), 743 (s)

cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 9.35 (s, 2H), 9.34 (s, 4H), 9.33 (s, 6H), 8.95 (br s, 3H), 7.98–7.92 (m, 12H), 7.92–7.86 (m, 12H), 7.50 (d, *J* = 7.6 Hz, 6H), 7.46 (d, *J* = 7.5 Hz, 4H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.41–7.35 (m, 12H), 5.42 (s, 6H), 4.79 (s, 2H), 4.74 (d, *J* = 4.6 Hz, 4H), 1.80 (t, *J* = 5.5 Hz, 2H), 1.60–1.46 (m, 12H), 1.38 (d, *J* = 7.3 Hz, 18H), 1.36 (d, *J* = 7.2 Hz, 18H), 1.25 (d, *J* = 7.3 Hz, 18H), 1.22 (d, *J* = 7.3 Hz, 18H), 0.94 (s, 9H), 0.11 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 164.8, 142.9, 142.2, 136.6, 135.64, 135.59, 135.3, 134.9, 133.8, 132.5, 132.4, 131.4, 131.3, 130.7, 128.6, 127.7, 126.42, 126.35, 126.27, 126.21, 126.17, 125.5, 118.4, 118.3, 118.2, 118.1, 105.91, 105.89, 105.77, 105.6, 105.5, 105.2, 105.1, 67.3, 65.3, 64.9, 26.0, 18.4, 18.22, 18.19, 18.17, 18.12, 12.1, –5.3 (29 signals not observed or coincident). HRMS MALDI *m/z* calcd for C<sub>171</sub>H<sub>176</sub>O<sub>9</sub>Si<sub>7</sub> (M<sup>+</sup>) 2569.1694, found 2569.1682.

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**Supporting Information Available:** Experimental procedures, additional spectroscopic and characterization data, <sup>1</sup>H and <sup>13</sup>C NMR spectra for new compounds, mass spectra for dendrimers, and additional AFM images of thin films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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