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Synthesis and optical properties of triphenylene-based conjugated dendrons

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ABSTRACT

Conjugated dendrons based on triphenylene building blocks have been synthesized. Such dendrons exhibit broader absorption wavelength range and higher absorption coefficients than their phenyl analogs. They also possess extended excited state lifetimes and high fluorescence quantum yields in dilute solutions. In the solid state, these dendrons are highly aggregated, resulting in significantly broadened and red-shifted emissions, whose decay transients depend strongly on the detection wavelength.

1. Introduction

Dendrimers possess a multibranched structure that radiates out from a central core.[1] Such a structure not only represents a fundamentally new macromolecular architecture, but also offers an enormous opportunity for creating novel functional materials.[1,2] One characteristic of dendritic molecules is the presence of numerous peripheral end groups that all converge to a single core. Such a structure, with characteristics similar to those found in photosynthetic centers, naturally suggests itself as a potential molecular antenna suitable for transferring energy from the surface to the core. Indeed, a large number of light-harvesting dendrimer (LHD) systems,[3] including both conjugated[4–6] and non-conjugated[7–10] skeletons, have been synthesized and their excitation energy-transfer dynamics have been thoroughly explored.[11–15] For dendrimers with flexible linkages, there is negligible electronic interaction among chromophores and their excitation energy-transfer dynamics are characterized by the through-space dipole–dipole processes.[16] Conjugated dendrimers, on the other hand, exhibit certain electronic couplings among chromophoric branches, leading to delocalized (or relaxed) excited states, which enhance coherent or through-bond energy transfer.[17,18] Goodson et al. has shown elegantly that a dendrimer with more strongly coupled chromophores may form an excitation domain as large as the dendrimer itself and thus exhibits faster energy migration through a coherent process.[19–21] Even for *meta*-branched phenylacetylene (PA) dendrimers, which possess localized optical excitation due to the lack of conjugation through *meta*-positions, some excited state delocalization has also been firmly established.[17,18] Energy transfer in these PA dendrimers occurs through a hybrid energy-transfer process where excited state delocalization is followed by through-space Coulombic transfer between delocalized excited states and localized acceptors.[17] Clearly, an LHD with strongly electronic coupled intra-branch processes can enhance energy migration, which is further validated by the fact that conjugated polymers, the ultimate systems with strongly electronic coupled chromophores, are extraordinarily efficient excitation energy conductors.[22–26]

In search for LHDs with enhanced and directional energy migration, conjugated dendrimers with an unsymmetrical branching structure have also been studied.[27,28] Such dendrimers possess a broad absorption wavelength range, efficient and ultrafast energy-transfer dynamics, confirming that unsymmetrically branched conjugated dendrimers are novel attractive photosynthetic antenna mimics.[29] Here we report a new unsymmetrically branched conjugated dendron based on triphenyleneacetylene (TPA)s. The triphenylene chromophore was chosen for the following considerations: (1) Triphenylene-based π-conjugated systems are known to exhibit longer excited state lifetimes than their phenyl analogs, and should therefore foster through-bond energy migration.[30] (2) TPA dendrimers, by virtue of the more extended π-conjugation associated with the planar-fused triphenylene unit, should also exhibit broader absorptions in the visible range. In addition, triphenylene rings have numerous sites available for functionalization/substitution, thus providing means for further enhancement in absorption range. (3) Triphenylene derivatives are one of the most common discotic mesogens,[31] which have

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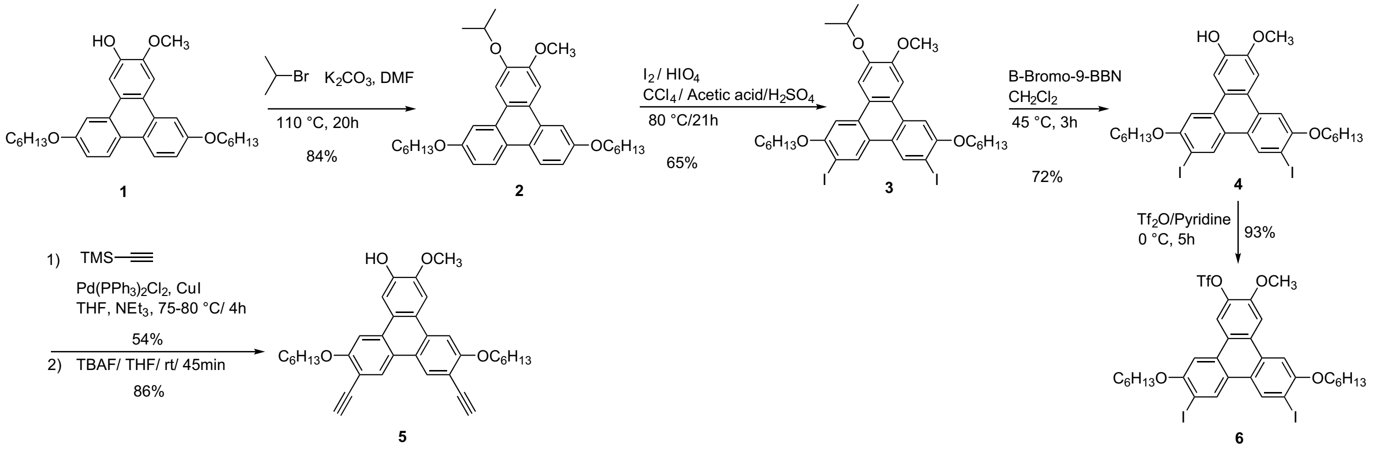


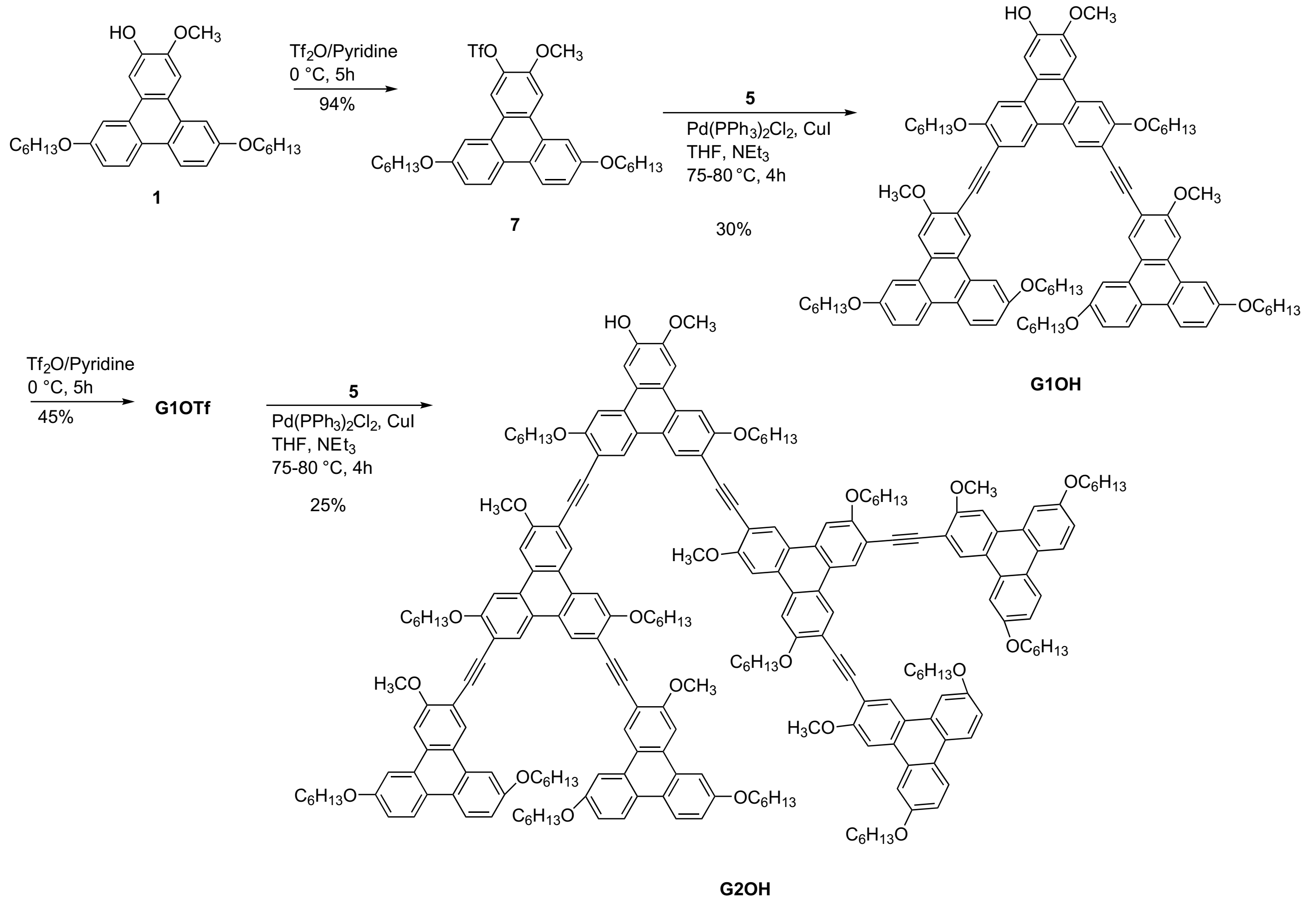
Scheme 1. Synthesis of AB_2-functionalized triphenylene building blocks.

a tendency to form π-stacked discotic liquid crystalline phases that facilitate charge transport.[32] While the shape-persistent nature of conjugated TPA dendrimers may prevent intra-dendrimer π-stacking, particularly at low generations, π-stacking of triphenylene rings from neighboring dendrimers in bulk is possible and thus may enhance energy and hole transport. It should be noted that while a number of triphenylene derivatives and polymers have been studied,[33] dendrimers based on triphenylene building blocks have not yet been realized.[34] The reported triphenylene-based dendrons thus represent the first such example.[35]

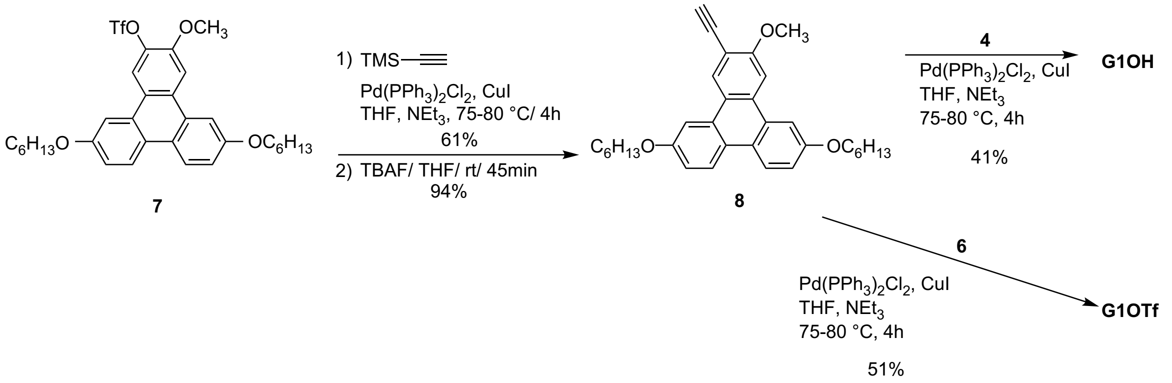
2. Results and discussion

2.1. Synthesis of monodendrons

The synthesis of TPA dendrons requires AB_2-functionalized triphenylene derivatives as the building block molecules. We have developed a synthetic approach to such triphenylene derivatives and a preliminary communication has been previously reported.[36] Adopting the same approach, three AB_2-functionalized triphenylene derivatives **4**, **5**, and **6** were synthesized according to Scheme 1.



Scheme 2. Synthesis of triphenylene-based dendrons.



Scheme 3. An alternative approach to **G1OTf**.

Compound **1** was synthesized according to a literature procedure.[36] After introduction of the isopropyl protection group, compound **2** was subjected to iodination and subsequent deprotection, yielding an AB_2-functionalized triphenylene derivative **4**, from which compound **5** or **6** was prepared in two steps and one step, respectively. It should be noted that the attempts to prepare **4** directly from compound **1** by iodination were not successful.

Using compound **5** as the building block molecule, the buildup of the TPA dendrons involves only two sets of reaction conditions: (a) conversion of a phenol to a triflate; and (b) palladium-catalyzed cross-coupling of a triflate with an acetylene. As shown in Scheme 2, the iterative synthesis starts with peripheral triphenylene unit **1**. The conversion of phenol (**1**) to triflate (**7**) is trivial, and high yield (94%) was obtained. The cross-coupling of **7** with **5** did give the desired first-generation dendron **G1OH**, but with a relatively low yield of 30%. Triphenylenetriflates appear to be much less reactive than their phenyl analog and some unreacted **7** was always recovered even after running the reaction for a prolonged period of time and at an elevated temperature. Fortunately, the desire product **G1OH** can be relatively easily isolated from the unreacted

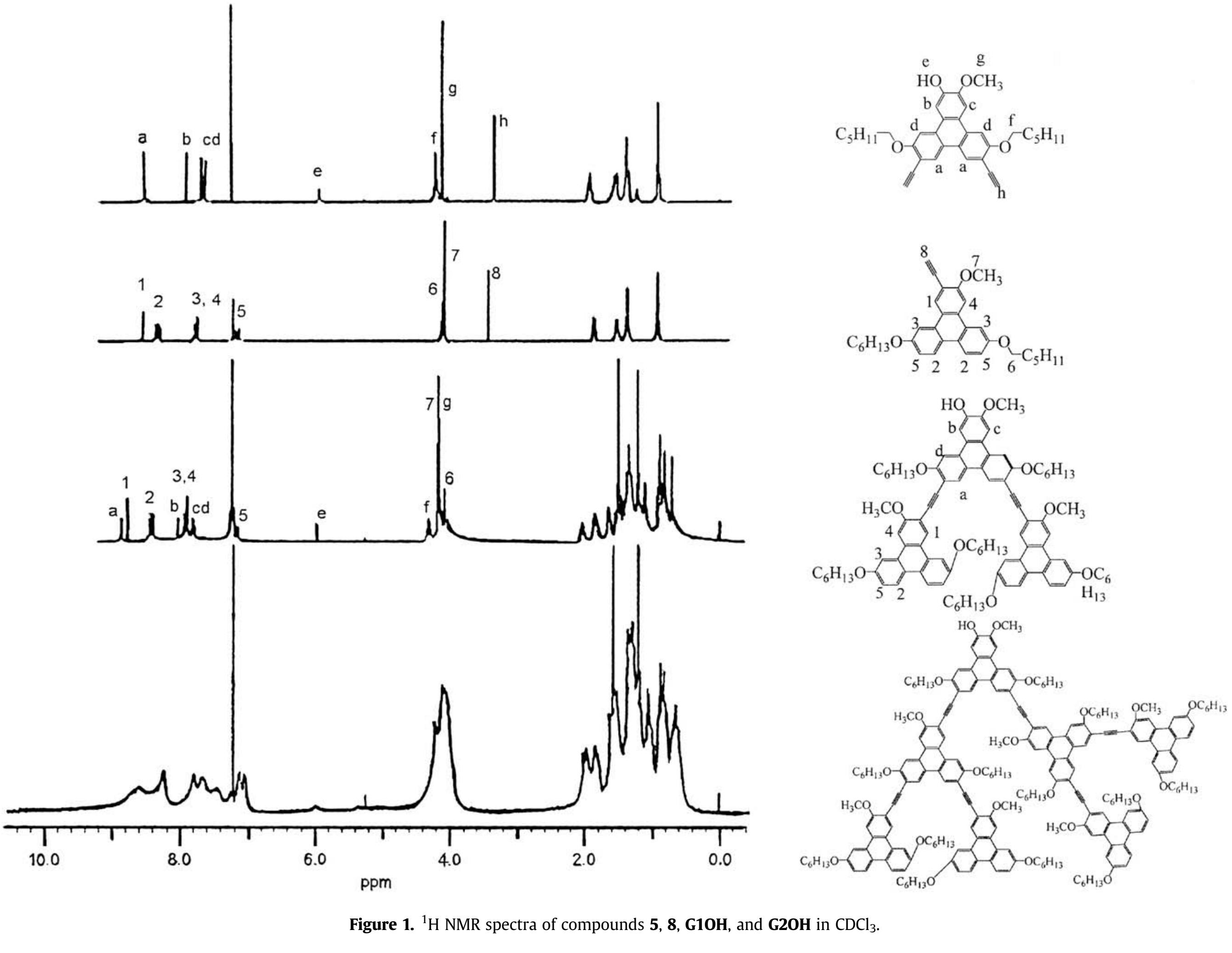


Figure 1. ^{1}H NMR spectra of compounds **5**, **8**, **G1OH**, and **G2OH** in $CDCl_3$.

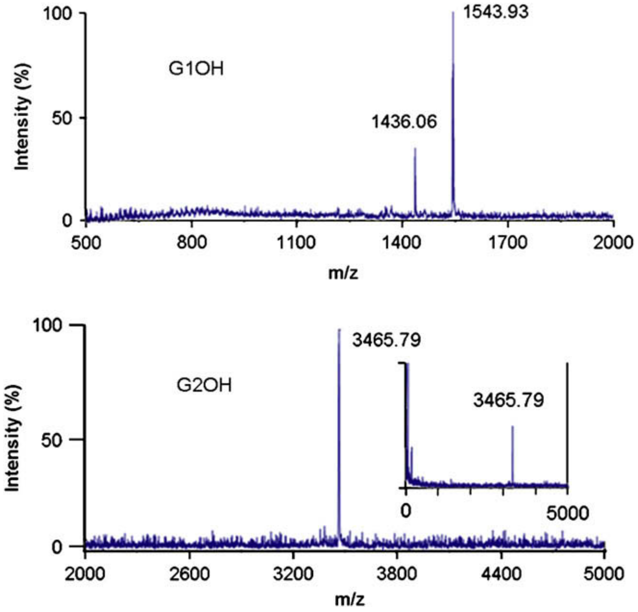


Figure 2. MALDI-TOF mass spectra of TPA dendrons.

triflate due to the presence of the polar hydroxy group in the product. Repeating the two sets of reactions on **G1OH**, second-generation dendron **G2OH**, which contains seven triphenylene units, was successfully prepared. Due to the low reaction yields and the anticipated difficulty in product purification, higher generation dendrons were not pursued.

While the synthetic approach shown in Scheme 2 led to desired dendrons, the low reaction yields are a concern. As mentioned earlier, triphenylene triflate such as **7** may not be sufficiently reactive. On the other hand, one cannot add excess **5** to push the coupling reaction forward as that will result in mono-coupled side product, which is very difficult to be separated from the desired product. The triflate group in compound **7**, however, can be converted to an ethynyl group in reasonably good yields as excess trimethylsilylacetylene can be used. As shown in Scheme 3, compound **8** was synthesized in 56% overall yield from **7**. The yield of the coupling reaction between compound **8** and **4**, which gives **G1OH**, however, is only slightly improved over the coupling reaction between **7** and **5**. Nevertheless, this approach is still valuable as **G1OTf** can be synthesized in one step by the cross-coupling of **8** with compound **6** in 51% yield.

2.2. Structural characterizations

With two long alkyl chains attached to each triphenylene unit, all triphenylene derivatives (**1**–**8**) and the two dendrons (**G1OH** and **G2OH**) are soluble in common organic solvents such as chloroform, THF, and DMF. Their structures and purity are confirmed by thin-layer chromatography, ^{1}H and ^{13}C NMR, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, elemental analysis, and HPLC analysis (see Supplementary data).

^{1}H NMR spectrum acquired in chloroform-*d* ($CDCl_3$) of **G1OH** gives adequately dispersed signals (Fig. 1). To help assign the signals, ^{1}H NMR spectra of compounds **5** and **8**, representing the core and the surface components, respectively, are also shown in Figure 1. When the core and two surface units are joined together, the chemical shifts of protons a and protons 1 (see proton labeling in Fig. 1), both of which are closest to the connection site, are affected most with a downfield shift of 0.34 and 0.23 ppm, respectively. A smaller downfield shift of 0.1 ppm is also seen for protons 2. The chemical shifts for the rest of the aromatic protons are essentially not affected, thus the assignment for all aromatic signals is straightforward and is shown in Figure 1. The core hydroxyl proton appears at 5.98 ppm while no alkyne proton signals, shown at chemical shifts around 3.4 ppm for both compounds **5** and **8**, are observed, indicating complete coupling of the core building block molecule **5**.

While **G1OH** gives sharp and resolved ^{1}H NMR signals, **G2OH** shows overlapped and broad signals. Considering the fact that sharp aromatic signals are observed for their phenyl analog dendrons, even up to the fourth generation, the significant broadening

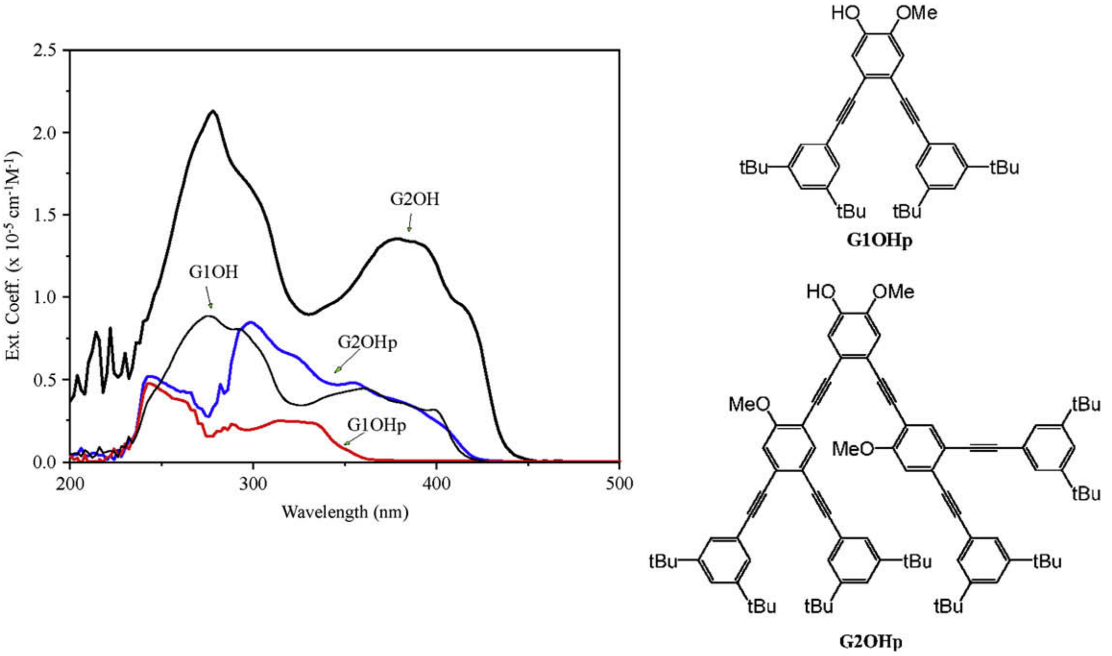


Figure 3. UV–vis absorption spectra of triphenylene-based dendrons and their phenyl analogs (whose chemical structures are also shown) in chloroform solutions.

Table 1
Fluorescence quantum yields of triphenylene derivatives measured in dilute chloroform solutions

Compound no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**G1OH**	**G2OH**
λ_{ex} (nm)	276	268	284	280	286	270	272	276	362	378
ϕ_{fl}	0.05	0.03	0.006	0.003	0.17	0.004	0.002	0.12	0.55	0.66

of signals for **G2OH** is likely due to severe aggregation,[37] a consequence of strong π–π stacking among triphenylene rings. The aggregation by π–π stacking is also supported by the observation that all aromatic proton signals of **G2OH** are up-field shifted compared to those of **G1OH**.[38] While broad and weak, the core hydroxyl signal (at around 6.0 ppm) is still discernible.

The ^{13}C NMR spectra of both dendrons give sharp signals, although strong signal overlapping is seen, particularly in the aromatic region of **G2OH**, which results in clusters of signals. The signals in the range of 80–100 ppm correspond to alkynyl carbons. Terminal alkyne carbons in **5** and **8** give two signals at 80.5 and 81.3 ppm, respectively. These signals have disappeared in the ^{13}C NMR spectra of **G1OH** and **G2OH**. Instead, two peaks at 90.6 and 91.1 ppm are observed for **G1OH**, consistent with its two internal alkynyl carbons. For **G2OH**, a cluster of signals centered at 91.1 ppm is observed, again consistent with the existence of multiple internal alkynyl carbons. The signals in the range of 150–160 ppm are attributed to hexyloxy-binding aryl carbons as well as those methoxyl-binding aryl carbons, which are *ortho* to an ethynyl substituent. **G1OH** and **G2OH** show 3 and 5 such signals, respectively, in that range, which is consistent with their structures. The hydroxyl-binding carbon and the methoxy-binding carbon at the core triphenylene unit appear at 146.0 and 147.2 ppm for **G1OH**. For **G2OH**, these two signals are much weaker but clearly noticeable (see Supplementary data for ^{13}C NMR spectra). The hexyloxy carbons give six signals at 14.0, 22.7, 25.8, 29.5, 31.7, and 68.3 ppm, while the methoxy carbon appears at 56.0 ppm for both **G1OH** and **G2OH**.

Both **G1OH** and **G2OH** have been subjected to MALDI-MS analysis. As shown in Figure 2, **G1OH** gives two peaks at 1436.06 and 1543.93, which correspond to M+H$^+$ (1436) and M+Ag$^+$ (1544), respectively. **G2OH** shows only one signal at 3465.79, which is attributed to M+Ag$^+$ (3465.8). These results provide an unambiguous confirmation of the structures of both dendrons.

2.3. Optical and photophysical properties

The optical properties of all triphenylene derivatives and monodendrons were studied by UV–vis absorption, steady-state and time-resolved fluorescence measurements in both chloroform solutions and as solid films.

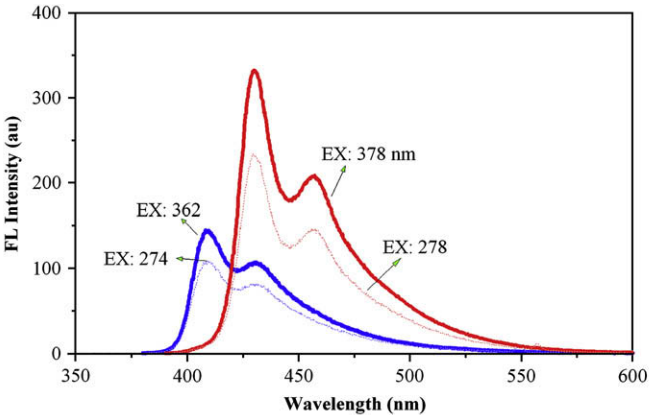


Figure 4. Fluorescence emission spectra of **G1OH** (blue) and **G2OH** (red) in chloroform excited at different wavelengths.

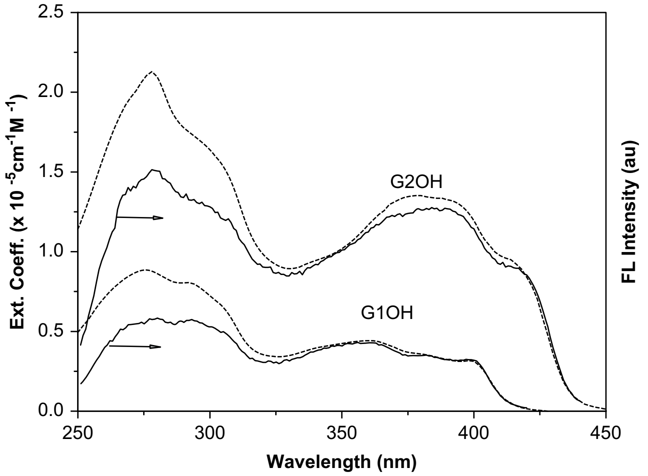


Figure 5. Fluorescence excitation (solid lines) and absorption (dotted lines) spectra of TPA dendrons.

The absorption spectra of **G1OH** and **G2OH**, and their phenyl analogs (**G1OHp**, **G2OHp**) in chloroform solutions are shown in Figure 3. Compared to their phenyl-based dendrons, triphenylene-based dendrons exhibit much broader absorption wavelength range and much higher absorption coefficients. Both **G1OH** and **G2OH** exhibit two broadly defined peaks; one in the range of 230–315 nm, which can be attributed to the absorption of localized triphenylene π-system, and the other at higher wavelengths due to the more delocalized π-system extending over multiple triphenylene units. From **G1OH** to **G2OH**, the extinction coefficients are approximately doubled in the range of 230–315 nm, reflecting roughly twice as many triphenylene units in **G2OH** as in **G1OH**. In longer wavelength range, however, **G2OH** shows a much broader absorption peak with absorption coefficients well exceeding twice those of **G1OH**.

Both **G1OH** and **G2OH** are highly fluorescent when dissolved in dilute chloroform solution (absorbance at λ_{max} less than 0.1), particularly when excited at wavelengths over 350 nm. The fluorescence quantum yields in solutions for **G2OH** and **G1OH** are found to be 0.66 (at 378 nm) and 0.55 (at 362 nm), respectively, which are significantly higher than those of simple triphenylene fluorophores whose quantum yields are usually one order of magnitude smaller.[39] We have measured the fluorescence quantum yields for all triphenylene derivatives shown in Schemes 1 and 2 and the results are listed in Table 1. For triphenylene chromophores without an externally attached π-substituent, such as compounds **1**–**4**, **6**, and **7**, low fluorescence quantum yields (<0.05) are obtained. Iodo or triflate substituent tends to lower further the fluorescence quantum yield, presumably due to their electron-withdrawing nature, which may bring about charge transfer transitions. When there is at least one external π-system attached to the triphenylene chromophore, such as compounds **5** and **8**, the fluorescence quantum yields are significantly increased. The more extended the external π-systems, the higher the fluorescence quantum yield. Clearly, a substituent with π-electrons is not a mere perturber of the triphenylene core. Instead, it extends the dimension of the π-system, and changes completely the symmetry of the π electronic states.[40] The symmetry-forbidden S_0–S_1 transition of the triphenylene core,[41] which accounts for its weak long wavelength absorption and low fluorescence quantum yield is replaced with symmetry-allowed 0–0 transitions, thus leading to higher fluorescence quantum yields.

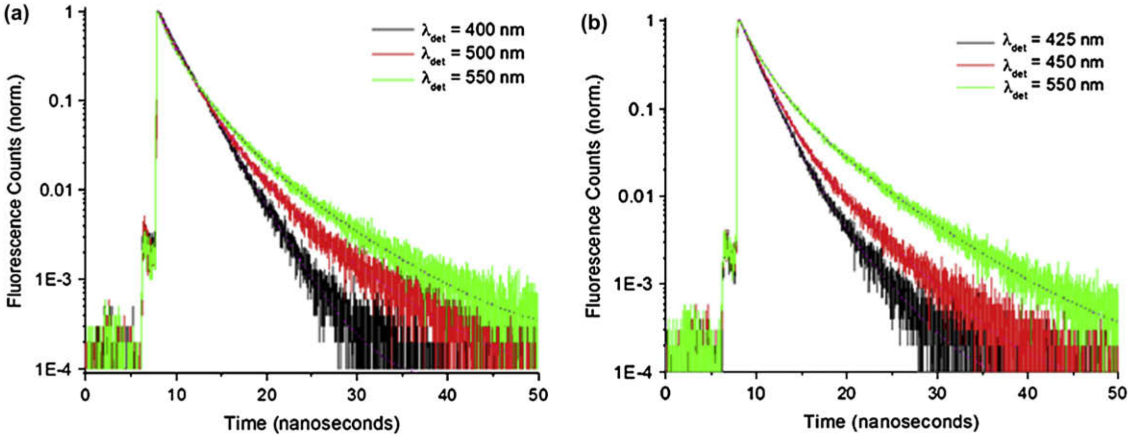


Figure 6. Fluorescence decay curves for **G1OH** (a) and **G2OH** (b) in $CHCl_3$ solution and measured at different detection wavelengths. The excitation wavelength is 300 nm. The dotted lines are fits based on a sum of exponential decay components, which are given in Table 2.

Table 2
Fluorescence lifetimes for **G1OH** and **G2OH** in $CHCl_3$ at different detection wavelengths. The excitation wavelength is 300 nm

	λ (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
G1OH	400	0.907	2.15	0.093	3.50	2.27
	450	0.801	1.98	0.199	3.46	2.28
	500	0.803	1.84	0.197	4.25	2.31
	550	0.756	1.67	0.244	4.90	2.46
G2OH	420	0.892	1.64	0.108	3.25	1.81
	500	0.887	1.76	0.113	4.49	2.07
	550	0.788	1.92	0.212	5.60	2.70

Figure 4 shows the solution emission spectra of **G1OH** and **G2OH**, both excited at two different wavelengths chosen from the two different absorption regions. Similar to what was observed on their dendritic phenyl analogs; red-shifted emissions are observed when the dendron size increases. It is also noted that the emission spectra of both dendrons are independent of the excitation wavelengths.

To estimate the energy-transfer efficiency of these dendrons to the emitting state, the excitation spectra of **G1OH** and **G2OH**, measured at emission wavelengths of 430 and 456 nm, respectively, were collected and together with their respective absorption spectra are shown in Figure 5. The excitation spectra were normalized to best match their corresponding absorption spectra in the long wavelength range. The energy-transfer efficiency (ϕ_{ET}) at a specific wavelength is estimated by comparing the intensities of the excitation profile and the absorption spectrum at that wavelength. The ϕ_{ET} over a spectral wavelength range is defined as the ratio of the areas under the fluorescence and absorption profiles. As shown in Figure 5, the excitation spectra of **G2OH** and **G1OH** resemble their respective absorption spectra. For excitation wavelengths greater than 325 nm, the energy-transfer efficiencies are found to be well over 90%. In the wavelength range of 250–325 nm where the absorption is dominated by the localized triphenylene π-system, moderate energy-transfer efficiencies are obtained: 81% for **G2OH** and 66% for **G1OH**.

Time-resolved fluorescence studies of **G*n*OH** in dilute ($\sim 10^{-6}$ M) chloroform solution (Fig. 6) show that the fluorescence decays for **G*n*OH** deviate from single exponential decays. A sum of two exponentials is needed to get a good fit to the data. Table 2 lists the fluorescence lifetimes and their associated coefficients. The averaged lifetimes shown in Table 2 were obtained by summing the individual time constants weighted by its amplitude (A_1 and A_2) in the fit.

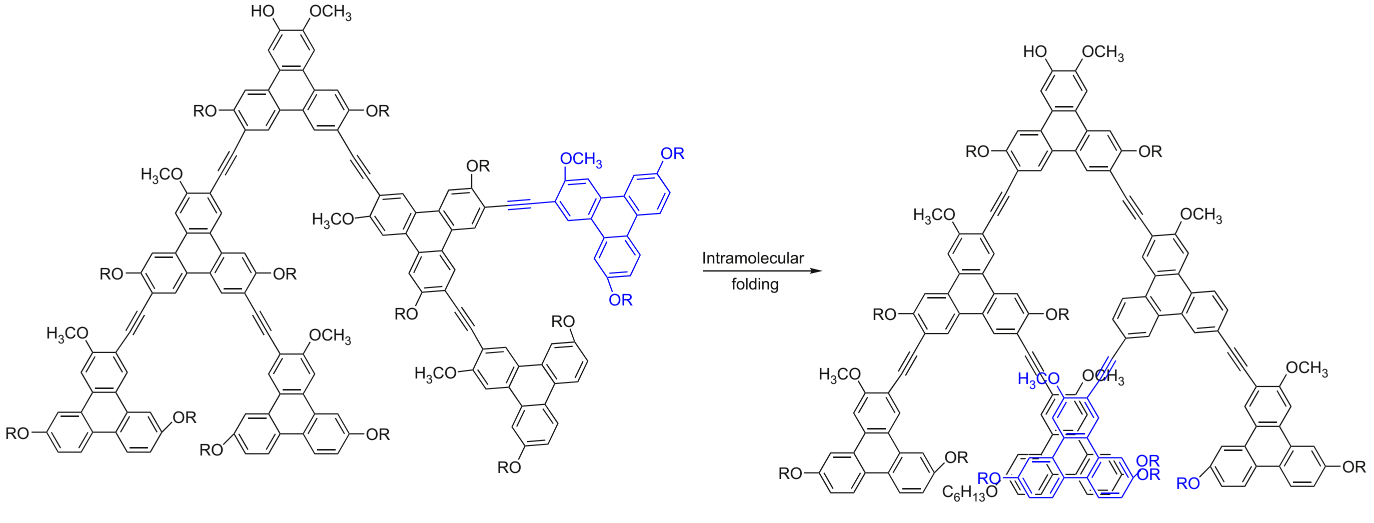


Figure 7. Intramolecular triphenylene aggregation of **G2OH**.

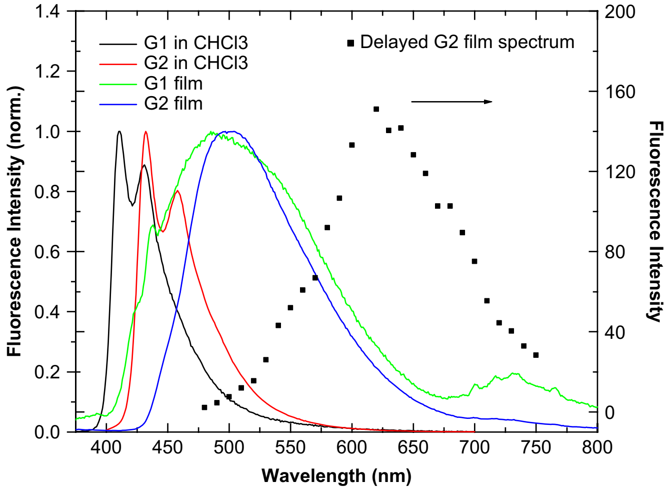


Figure 8. Comparison of fluorescence spectra for **G1OH** and **G2OH** dendrons in $CHCl_3$ solution and as thin films. The dotted line represents the 'delayed' spectrum for the **G2OH** film obtained as described in the text.

Compared to their respective phenyl analogs, **G1OHp** and **G2OHp**, both of which show a single exponential fluorescence decay with a fluorescence lifetime of 1.7 and 2.0 ns, respectively,[27b] **G*n*OH**s exhibit slightly longer fluorescence lifetimes and a bi-exponential decay behavior. It is also noted that there is some dispersion in the lifetime decay with the detection wavelength. The transients tend to show longer decay components as the detection wavelength increases, which suggests that the solution contains an aggregated species, which has a red-shifted emission. This is particularly true for **G2OH**. For example, the average fluorescence decay lifetime for **G2OH** increases from 1.81 to 2.70 ns when the detection wavelength changes from 425 to 550 nm. One question is whether the association is intermolecular or intramolecular (or both). For **G1OH**, we believe that only intermolecular aggregation is possible because the rigidity of the dendron prevents the two peripheral triphenylene rings from π-stacking. For **G2OH**, however, intramolecular aggregation is possible because the peripheral triphenylene chromophores have enough rotational flexibility to form a co-facial π-stacked association, as shown in Figure 7.

As stated earlier, both **G1OH** and **G2OH** show high fluorescence quantum yields. It is thus reasonable to assume that the initial fast component seen in the decay curves of Figure 6 is due to a radiative decay process. Coupled with their fluorescence quantum yields, the fluorescence decay rate constants for **G1OH** and **G2OH**, calculated using their τ_1 values obtained at detection wavelengths of 450 nm and 500 nm, are 2.8×10^8 and 3.7×10^8 s^{-1}, respectively. These rates are two orders of magnitudes higher than that of triphenylene,[41] reflecting again a symmetry-allowed S_0–S_1 transition in these dendrons. It is interesting to note that **G2OH** has faster initial decay (smaller τ_1 values except for 550 nm detection wavelength) than **G1OH**, which qualitatively is consistent with the observed increase in both the $S_0 \rightarrow S_1$ absorption and the fluorescence quantum yield. These results are again likely consequences of the fact that **G2OH** has a more extended π-conjugated system beyond the triphenylene chromophore and thus shows fluorescence properties more of a linear extended π-system than a highly symmetrical planar PAH system. Indeed, the fluorescence quantum yield, fluorescence lifetime, and fluorescence rate constant of **G2OH** are not significantly different from a linear triphenylene-containing PE polymer (0.27, 0.71 ns, and 3.8×10^8 S^{-1}, respectively).[30]

Fluorescence decay studies were also carried out on **G*n*OH** films. Both dendrons form uniform films by drop casting. The fluorescence spectra of the films are bathochromically shifted by 75–100 nm and are much broader than the solution spectra as shown in Figure 8. The broad, red-shifted structureless emission is suggestive of excimer or exciplex formation through inter-dendron interactions. To better highlight the photophysical aggregation effect, a delayed fluorescence spectrum for **G2OH** film was obtained by integration of the decay curves from 1.5 to 10 ns. The 'delayed' spectrum (see the dotted line in Fig. 8) is red-shifted with respect to the full steady-state film spectrum, clearly indicating a distribution of emitting species in the film.

Figure 9 shows the fluorescence decay curves of **G1OH** and **G2OH** films at different detection wavelengths. The fluorescence decays of these dendron films show a complex behavior with tri-exponential fitting. The time constants for each component and their associated contributions in the fitting are listed in Table 3. The averaged lifetimes shown in Table 3 were obtained by summing the individual time constants weighted by its amplitude (A_n) in the fit. Compared to their corresponding solution data shown in Table 2, the fluorescence decay of the dendron films is approximately one order of magnitude faster. The dispersion of the transients with detection wavelength is also stronger for the film than the solution. These results indicate that **G*n*OH** dendrons are highly aggregated in the thin film, presumably due to the strong π–π interactions among triphenylene rings.

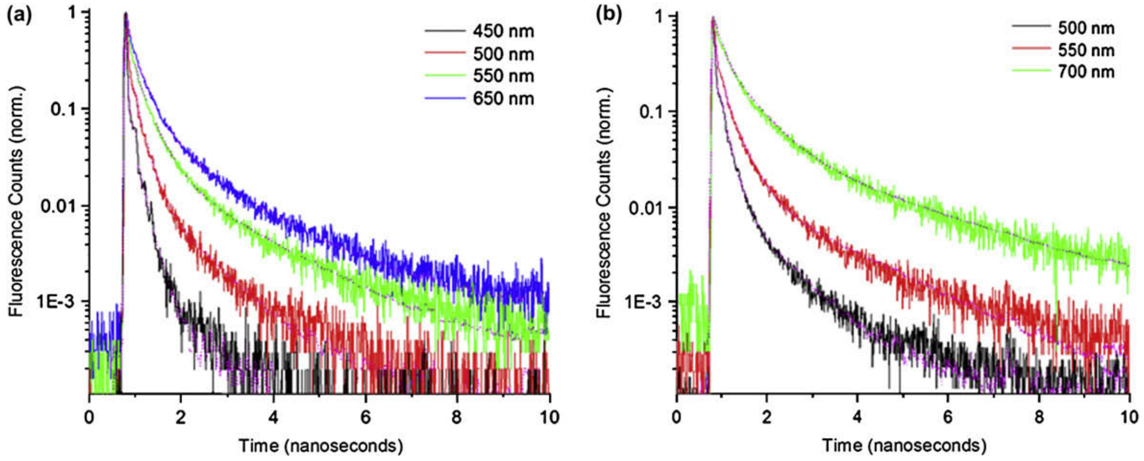


Figure 9. Fluorescence decay profiles of **G1OH** and **G2OH** films under different detection wavelengths (λ_{ex}=300 nm). The dotted lines are fits based on a sum of exponential decay components, which are given in Table 3.

Table 3
Fluorescence lifetimes for **G1OH** and **G2OH** films

	λ (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{avg} (ns)
G1OH	500	0.90	0.03	0.097	0.20	0.007	0.84	0.05
	550	0.79	0.06	0.19	0.32	0.016	1.46	0.13
	650	0.70	0.07	0.27	0.33	0.035	1.48	0.19
G2OH	500	0.92	0.03	0.076	0.187	0.005	0.83	0.04
	550	0.85	0.05	0.14	0.32	0.009	1.77	0.10
	650	0.69	0.11	0.27	0.58	0.04	2.52	0.33

3. Conclusions

Conjugated dendrons based on triphenylene building block units have been synthesized. Such dendrons exhibit broader absorption wavelength range and higher absorption coefficients than their phenyl analogs. Although aggregation occurs even in solutions, these dendrons exhibit moderate to high fluorescence quantum yields and long fluorescence lifetimes. In the solid state, these dendrons are highly aggregated, resulting in significantly broadened and red-shifted emissions. The strong aggregation may lead to unique discotic liquid crystallinity and, possibly, high charge transporting properties, both of which are being explored.

4. Experimental section

4.1. General

All reagents and solvents were obtained from either Aldrich or Fisher and were used as received unless otherwise stated.

^{1}H NMR spectra were recorded on Varian Unity 400 MHz. UV–vis absorption spectra were recorded using a Hewlett–Packard 8452A diode array spectrophotometer. The fluorescence emission spectra were measured using a Shimadzu RF-5301PC spectrofluorophotometer. Fluorescence quantum yields were determined using quinine sulfate in 1 N H_2SO_4 ($\phi_{fl}\approx0.55$) as the standard. Time-dependent fluorescence measurements were performed using the technique of time-correlated single photon counting (TCSPC). A Voyager DE Pro (Perceptive Biosystems/ABI) MALDI-TOF mass spectrometer was used for mass measurement, operating in the reflector mode. A mixture of silver trifluoroacetate/dithranol (1,8-dihydroxyanthrone) (1:25 w/w) was used as the matrix. HPLC analysis was performed on a PerSeptive Biosystems Inc. system equipped with C-18 column, peaks being detected with a UV detector.

*4.1.1. Compound **2***

A mixture of compound **1** (4.37 g, 9.21 mmol), 2-bromopropane (2.27 g, 18.46 mmol), K_2CO_3 (5.09 g, 36.83 mmol), and anhydrous DMF (200 mL) was stirred at 110 °C for 20 h. The resulting mixture was poured into 200 mL water and was then extracted with dichloromethane. The organic extracts were washed with water, dried over anhydrous $MgSO_4$, and the solvent was then evaporated. The crude product was purified by flash chromatography eluting with 5:1 hexane/ethyl acetate to give the product as a brownish yellow solid (3.98 g, 84%, mp 82–85 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (dd, J=1.2, 9.2 Hz, 2H), 7.94 (s, 1H), 7.88 (s, 1H), 7.86 (d, J=2.4 Hz, 1H), 7.82 (d, J=2.8 Hz, 1H), 7.20 (t, J=2.4 Hz, 1H), 7.18 (t, J=2.4 Hz, 1H), 4.81 (m, 1H), 4.15 (t, J=6.6 Hz, 4H), 4.08 (s, 3H), 1.87 (m, 4H), 1.49 (s, 3H), 1.47 (s, 3H), 1.38 (m, 12H), 0.91 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.4, 150.5, 147.3, 129.6, 124.5, 124.1, 123.1, 114.2, 109.4, 106.7, 105.1, 71.5, 68.0, 55.9, 31.6, 29.3, 25.7, 22.5, 22.0, 14.0. MALDI-TOF mass analysis: calcd for $C_{34}H_{44}O_4$ 516.71, found $[M]^+$ 516.56. Anal. Calcd for $C_{34}H_{44}O_4$: C, 79.03%; H, 8.58%. Found: C, 79.12%; H, 8.63%.

*4.1.2. Compound **3***

A mixture containing compound **2** (3.05 g, 5.90 mmol), iodine (1.38 g, 5.44 mmol), periodic acid (0.82 g, 3.59 mmol), CCl_4 (36 mL), acetic acid (94 mL), and H_2SO_4 (20%, 38 mL) was refluxed at 80 °C for 21 h. After cooling to room temperature, to the above reaction mixture was slowly added a NaOH (2 N) solution until the acidic mixture became neutral. The resulting mixture was extracted with dichloromethane three times and the combined organic extracts were washed with $NaHSO_3$ solution and then with water. After dried over $MgSO_4$, the organic solvent was stripped off. The resulting crude product was purified by chromatography on silica gel using 10% ethyl acetate in hexane as the eluent to give the product as a light brown solid (2.94 g, 65%, mp 116–119 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, J=4.0 Hz, 2H), 7.87 (s, 1H), 7.79 (s, 1H), 7.60 (s, 1H), 7.57 (s, 1H), 4.82 (m, 1H), 4.20 (m, 4H), 4.09 (s, 3H), 1.94 (m, 4H), 1.61 (m, 4H), 1.49 (s, 3H), 1.48 (s, 3H), 1.40 (m, 8H), 0.93 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.2, 150.8, 147.5, 133.2, 129.4, 124.0, 123.5, 123.1, 122.9, 109.6, 104.8, 103.3, 86.8, 72.1, 69.1, 56.1, 31.7, 29.2, 25.9, 22.6, 22.3, 14.1. MALDI-TOF mass analysis: calcd for $C_{34}H_{42}I_2O_4$ 768.50, found $[M]^+$ 768.51, $[M-I]^+$ 642.61, $[M-2I]^+$ 514.70. Anal. Calcd for $C_{34}H_{42}I_2O_4$: C, 53.14%; H, 5.51%. Found: C, 53.27%; H, 5.68%.

*4.1.3. Compound **4***

The sample of 4.8 mL of *B*-bromo-9-BBN (1 M solution of dichloromethane, 4.8 mmol) was added dropwise to a dichloromethane solution of compound **3** (3.33 g, 4.34 mmol in 60 mL of CH_2Cl_2) under refluxing. The resulting mixture was refluxed at 45 °C for another 3 h. The reaction mixture was washed with 3 N NaOH solution (three times) and then with water. The organic layer was collected and dried over $MgSO_4$. The crude product obtained by solvent evaporation was further purified by chromatography on silica gel using 25% ethyl acetate in hexane as the eluent to give the product as white solid (2.26 g, 72%, mp 135–137 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, J=6.0 Hz, 2H), 7.90 (s, 1H), 7.68 (s, 1H), 7.54 (s, 1H), 7.50 (s, 1H), 5.93 (s, 1H), 4.17 (m, 4H), 4.12 (s, 3H), 1.93 (m, 4H), 1.61–1.40 (m, 12H), 0.93 (t, J=6.8 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.4, 146.8, 145.7, 133.5, 133.3, 129.6, 129.4, 124.2, 123.2, 123.1, 107.5, 103.6, 103.3, 103.0, 86.9, 86.8, 69.2, 55.9, 31.7, 29.2, 25.9, 22.7, 14.1. MALDI-TOF mass analysis: calcd for $C_{31}H_{36}I_2O_4$ 726.42, found $[M]^+$ 726.15, $[M-I]^+$ 600.32, $[M-2I]^+$ 474.48. Anal. Calcd for $C_{31}H_{36}I_2O_4$: C, 51.26%; H, 5.00%. Found: C, 51.42%; H, 5.13%.

*4.1.4. Compound **5***

A mixture of **4** (0.94 g, 1.29 mmol), trimethylsilylacetylene (0.46 mL, 3.20 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 g, 0.07 mmol), CuI (0.04 g, 0.21 mmol), triethylamine (2 mL), and anhydrous THF (25 mL) was stirred under nitrogen at 60 °C for 4 h and was then poured into dichloromethane. The resulting mixture was passed through Celite. The filtrate was washed with aqueous HCl (1 N) and then water (two times). The organic layer was separated and dried over $MgSO_4$. After stripping off the solvent, the resulting solid was washed with methanol to give trimethylsilyl-protected **5** as a greenish yellow solid (0.46 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J=6.0 Hz, 2H), 7.95 (s, 1H), 7.75 (s, 1H), 7.69 (s, 1H), 7.66 (s, 1H), 5.93 (s, 1H), 4.21 (m, 4H), 4.12 (s, 3H), 1.92 (m, 4H), 1.61–1.39 (m, 12H), 0.92 (m, 6H), 0.31 (d, J=1.2 Hz, 18H). ^{13}C NMR (400 MHz, $CDCl_3$): 158.2, 147.3, 146.2, 130.0, 129.0, 128.7, 125.1, 123.9, 122.3, 122.1, 112.8, 108.2, 104.4, 104.2, 104.0, 101.6, 99.0, 69.1, 68.7, 56.1, 31.7, 29.4, 29.3, 25.8, 22.7, 14.1, 0.1. The desilylation was carried out by adding a sample of TBAF (0.24 g, 0.76 mmol) to a THF solution of the above greenish yellow solid (0.21 g, 0.31 mmol in 20 mL THF). The mixture was stirred at room temperature for 45 min and was then poured into water. It was extracted with methylene chloride. The organic extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo to give a crude product, which was purified by passing through a short silica gel column, eluting with 1:1 CH_2Cl_2/hexane to afford the title compound as a sticky brown solid (0.14 g, 86%, mp 127–130 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J=6.4 Hz, 2H), 7.92 (s, 1H), 7.71 (s, 1H), 7.68 (s, 1H), 7.65 (s, 1H), 5.94 (s, 1H), 4.23 (m, 4H), 4.12 (s, 3H), 3.36 (d, J=1.6 Hz, 2H), 1.93 (m, 4H), 1.58–1.39 (m, 12H), 0.92 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.7, 147.0, 145.9, 129.9, 129.7, 128.8, 128.6, 124.4, 123.4, 121.5, 121.4, 111.1, 107.8, 103.7, 103.3, 81.2, 80.5, 68.8, 55.7, 31.7, 29.2, 25.7, 22.6, 14.0. MALDI-TOF mass analysis: calcd for $C_{35}H_{38}O_4$ 522.67, found $[M]^+$ 522.63. Anal. Calcd for $C_{35}H_{38}O_4$: C, 80.43%; H, 7.33%. Found: C, 80.25%; H, 7.41%.

4.1.5. Compound ***6***

A 0.11 mL sample of trifluromethanesulfonic anhydride (0.65 mmol) was added slowly to the solution of compound **4** (0.22 g, 0.30 mmol) in 10 mL of anhydrous pyridine at 0 °C. The resulting mixture was warmed to room temperature and stirred for 5 h, and was then poured into water. The aqueous solution was extracted with dichloromethane. The organic layer was washed consecutively with 10% HCl solution, water, and then dried over $MgSO_4$. After stripping off the solvent, the resulting solid was washed with methanol to give the product as off-white solids (0.24 g, 93%, mp 148–150 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.59 (s, 1H), 8.15 (s, 1H), 7.81 (s, 1H), 7.51 (s, 1H), 7.37 (s, 1H), 4.20 (m, 4H), 4.13 (s, 3H), 1.95 (m, 4H), 1.62–1.41 (m, 12H), 0.94 (t, J=7.2 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 155.7, 149.8, 138.4, 133.5, 133.2, 129.6, 128.4, 128.0, 123.9, 122.9, 122.7, 120.4, 117.2, 116.7, 105.4, 103.5, 102.7, 89.4, 88.0, 69.4, 56.2, 31.7, 29.2, 25.9, 22.7, 14.1. MALDI-TOF mass analysis: calcd for $C_{32}H_{35}F_3I_2O_6S$ 858.49, found $[M]^+$ 858.34, $[M+Ag]^+$ 967.23, $[M-I]^+$ 732.47, $[M-Tf]^+$ 725.41. Anal. Calcd for $C_{32}H_{35}F_3I_2O_6S$: C, 44.77%; H, 4.11%. Found: C, 44.96%; H, 4.23%.

4.1.6. Compound ***7***

Compound **7** was prepared by a procedure similar to the synthesis of **6**. Compound **7** is a greenish yellow solid (4.89 g, 94%, mp 125–128 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J=9.6, 11.6 Hz, 2H), 8.21 (s, 1H), 7.89 (s, 1H), 7.77 (s, 1H), 7.65 (s, 1H), 7.24 (dd, J=2.0, 8.4 Hz, 1H), 7.20 (dd, J=2.4, 8.8 Hz, 1H), 4.13 (m, 4H), 4.09 (s, 3H), 1.88 (m, 4H), 1.54–1.38 (m, 12H), 0.92 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 157.9, 157.6, 150.0, 138.7, 130.5, 128.9, 128.6, 124.4, 124.3, 124.0, 123.1, 117.2, 115.9, 107.5, 106.1, 68.3, 56.2, 31.7, 29.4, 25.8, 22.6, 14.1. MALDI-TOF mass analysis: calcd for $C_{32}H_{37}F_3O_6S$ 606.69, found $[M]^+$ 606.54, $[M+Ag]^+$ 713.43, $[M-Tf]^+$ 474.60. Anal. Calcd for $C_{32}H_{37}F_3O_6S$: C, 63.35%; H, 6.15%. Found: C, 63.21%; H, 6.32%.

4.1.7. Compound ***8***

The synthetic procedures for compound **8** are similar to those of compound **5**. Compound **8** is a yellow solid (0.20 g, 94%, mp 115–117 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.36 (dd, J=9.2, 15.2 Hz, 2H), 7.80 (dd, J=2.4, 7.6 Hz, 2H), 7.76 (s, 1H), 7.21 (dd, J=2.8, 9.2 Hz, 1H), 7.16 (dd, J=2.8, 9.2 Hz, 1H), 4.12 (m, 4H), 4.09 (s, 3H), 3.44 (s, 1H), 1.87 (m, 4H), 1.54–1.38 (m, 12H), 0.93 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 158.8, 157.9, 157.5, 131.7, 129.9, 129.2, 129.1, 124.6, 124.4, 124.1, 123.5, 122.8, 115.9, 111.5, 107.5, 105.7, 103.4, 81.5, 80.4, 68.3, 56.0, 31.7, 29.4, 25.8, 22.6, 14.1. MALDI-TOF mass analysis: calcd for $C_{33}H_{38}O_3$ 482.65, found $[M]^+$ 482.71. Anal. Calcd for $C_{33}H_{38}O_3$: C, 82.12%; H, 7.94%. Found: C, 82.03%; H, 8.08%.

4.1.8. Dendron ***G1OH***

A sample of triethylamine (0.04 mL, 0.28 mmol) was added to the mixture of compound **7** (0.07 g, 0.12 mmol), compound **5** (0.03 g, 0.06 mmol), $Pd(PPh_3)_2Cl_2$ (0.0033 g, 0.0047 mmol), CuI (0.0007 g, 0.0036 mmol), and DMF (10 mL) at room temperature. The resulting mixture was stirred under N_2 at 75 °C for overnight. After cooling to room temperature, the mixture was poured into water and was then extracted with CH_2Cl_2. The organic layer was washed with an aqueous HCl solution, water and then was dried over $MgSO_4$. Solvent evaporation yielded the crude product, which was purified by chromatography on silica gel eluting with hexane/ethyl acetate (3:1) (yellowish brown solid, 0.025 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, J=6.4 Hz, 2H), 8.79 (s, 2H), 8.46 (s, 1H), 8.44 (s, 1H), 8.42 (s, 1H), 8.39 (s, 1H), 8.04 (s, 1H), 7.96 (s, 2H), 7.93 (d, J=2.4 Hz, 2H), 7.91 (s, 2H), 7.84 (s, 1H), 7.82 (s, 1H), 7.80 (s, 1H), 7.27 (dd, J=2.4, 11.2 Hz, 2H), 7.18 (dd, J=2.4, 8.8 Hz, 2H), 5.98 (s, 1H), 4.34 (m, 8H), 4.20 (s, 3H), 4.18 (s, 3H), 4.16 (s, 3H), 4.10 (t, J=6.6 Hz, 4H), 2.07–0.74 (m, 66H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 158.5, 157.9, 157.8, 157.5, 147.2, 146.1, 131.1, 129.9, 129.6, 129.4, 129.1, 128.7, 128.5, 125.0, 124.6, 124.3, 124.0, 123.9, 123.7, 122.8, 122.5, 122.3, 115.7, 115.6, 113.6, 113.2, 108.1, 107.4, 106.0, 104.5, 104.2, 103.8, 103.5, 91.1, 90.6, 69.2, 68.9, 68.3, 56.1, 55.9, 31.7, 31.6, 29.7, 29.5, 25.8, 22.7, 22.5, 14.0. MALDI-TOF mass analysis: calcd for $C_{97}H_{110}O_{10}$ 1435.91, found $[M]^+$ 1436.06, $[M+Ag]^+$ 1543.93. Anal. Calcd for $C_{97}H_{110}O_{10}$: C, 81.14%; H, 7.72%. Found: C, 80.78%; H, 8.02%.

G1OH by the alternative route shown in Scheme 3: Triethylamine (7 mL) was added into a mixture containing compound **4** (0.0598 g, 0.0823 mmol), compound **8** (0.0812 g, 0.1682 mmol), $Pd(PPh_3)_2Cl_2$ (0.0049 g, 0.0069 mmol), CuI (0.0021 g, 0.011 mmol), and DMF (5 mL) at room temperature. The resulting mixture was stirred under N_2 at 75 °C for 21 h and then poured into a 3 M hydrochloric acid solution. After extraction with methylene chloride (3×100 mL), the combined organic extracts were washed with water (3×50 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuo to give a crude product, which was then purified by column chromatography eluting with hexane/ethyl acetate (3:1) to give the pure product as yellowish brown solid (0.048 g, 41%).

4.1.9. Dendron ***G1OTf***

The synthetic procedures are similar to those of compound **6** or **7**. **G1OTf** is a yellow solid (0.007 g, 45%, mp 232–240 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.78 (s, 1H), 8.69 (s, 2H), 8.39–8.31 (m, 4H), 8.19 (s, 1H), 7.88 (s, 2H), 7.82–7.78 (m, 4H), 7.68 (s, 2H), 7.59 (s, 1H), 7.21 (dt, J=8.0, 2.4 Hz, 2H), 7.14 (dt, J=8.8, 2.4 Hz, 2H), 4.31 (m, 8H), 4.18 (s, 3H), 4.17 (s, 3H), 4.14 (s, 3H), 4.08 (t, J=6.6 Hz, 4H), 2.07–0.72 (m, 66H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 158.6, 158.2, 157.9, 157.5, 150.2, 138.9, 131.3, 130.5, 129.6, 129.4, 129.2, 128.9, 128.6, 128.5, 124.6, 124.3, 124.1, 123.7, 122.8, 122.4, 117.5, 115.8, 115.5, 115.3, 114.3, 113.4, 113.3, 107.4, 106.3, 106.1, 105.1, 104.1, 103.5, 91.7, 91.3, 90.7, 90.5, 69.3, 69.1, 68.2, 56.3, 56.1, 31.7, 31.6, 29.5, 29.4, 25.9, 25.8, 22.7, 22.5, 14.0. MALDI-TOF mass analysis: calcd for $C_{98}H_{109}F_3O_{12}S$ 1567.97, found $[M]^+$ 1567.99, $[M+Ag]^+$ 1675.80, $[M-Tf]^+$ 1435.06, $[M-Tf+Ag]^+$ 1543.96.

G1OTf by the alternative route shown in Scheme 3: Triethylamine (7 mL) was added into a mixture containing compound **6** (0.0668 g, 0.0778 mmol), compound **8** (0.0761 g, 0.1577 mmol), $Pd(PPh_3)_2Cl_2$ (0.0048 g, 0.0068 mmol), CuI (0.0024 g, 0.013 mmol), and DMF (5 mL) at room temperature. The resulting mixture was stirred under N_2 at 65 °C for 5 h and then poured into a 3 M hydrochloric acid solution. After extraction with methylene chloride (3×100 mL), the combined organic extracts were washed with water (3×50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, and evaporated in vacuo to give a crude product, which was then purified by column chromatography eluting with hexane/CH_2Cl_2 (1:1) to give the pure product as yellow solid (0.062 g, 51%).

4.1.10. Dendron ***G2OH***

A sample of triethylamine (0.01 mL, 0.071 mmol) was added to the mixture of **G1OTf** (0.0334 g, 0.0213 mmol), compound **5** (0.0081 g, 0.0155 mmol), $Pd(PPh_3)_2Cl_2$ (0.001 g, 0.001 mmol), CuI (0.001 g, 0.005 mmol), and DMF (2 mL) at room temperature. The resulting mixture was stirred under nitrogen at 85 °C for overnight. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic extract was washed with an aqueous HCl solution, dried over $MgSO_4$, and was then stripped off solvent. The resulting crude product was purified by chromatography eluting with hexane/CH_2Cl_2 (1:1) to give the pure product as yellowish brown solid (0.0178 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90–8.20 (br), 7.80–7.40 (br), 7.15–7.00 (br), 5.96 (s, 1H), 4.40–3.90 (br), 2.05–0.50 (br). ^{13}C NMR (400 MHz, $CDCl_3$): δ 158.6, 158.5, 157.8, 157.6, 157.5, 157.4, 130.9, 130.6, 129.5, 129.3, 129.1, 124.4, 124.2, 123.9, 123.6, 123.3, 122.7, 115.7, 115.4, 113.8, 113.6, 113.0, 107.0, 106.0, 103.4, 91.6, 91.4, 91.1, 90.6, 68.8, 68.2, 56.0, 31.7, 31.6, 29.7, 29.5, 25.9, 22.7, 14.1. MALDI-TOF mass analysis: calcd for $C_{229}H_{254}O_{22}$ 3466.63 $[M+Ag]^+$, found 3465.78 $[M+Ag]^+$. Anal. Calcd for $C_{229}H_{254}O_{22}\cdot 2H_2O$: C, 81.03%; H, 7.66%. Found: C, 80.96%; H, 7.77%.

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Supplementary data

Copies of ^{1}H NMR, ^{13}C NMR of all new compounds and HPLC traces of compound **1**, **G1OH** and **G2OH** are provided. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.017.

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