Layer-Block Dendrimers with Alternating Thienylenevinylene and Phenylenevinylene Units

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S *Supporting Information*

ABSTRACT: A series of new hybrid, layer-block π-conjugated dendrons and dendrimers with alternating thienylenevinylene and phenylenevinylene units has been prepared by means of an orthogonal and convergent-growth methodology that made use of the Horner–Wadsworth–Emmons (HWE) reaction. The placement of the thiophene and benzene rings can be accurately controlled to afford a large variety of dendritic structures, although access to compounds of high generation proved difficult. The optical properties of the synthesized dendrimers were determined by UV/vis and fluorescence spectroscopy, and the influence of the generation and nature of the core on the behavior of these materials was evaluated.
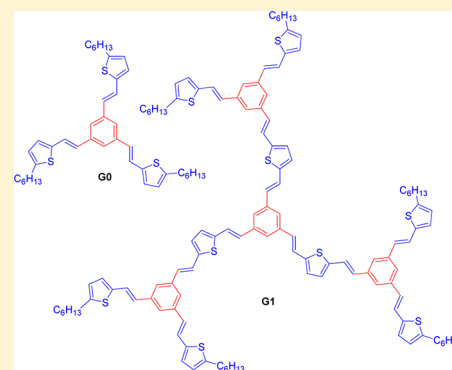
INTRODUCTION

Thiophene-based compounds have been highlighted as one of the most important types of materials in terms of applications in organic and molecular electronics.[1] These compounds are p-type semiconductors that show excellent optical, redox, self-organizing, and charge transport properties. Additionally, all of these optoelectronic characteristics are easily tunable in a convenient fashion by chemical modification.[2−4] As a consequence, oligo- and polythiophene derivatives have been extensively studied and currently play an important role in nanotechnology. For example, these materials have been used as organic light emitting diodes, organic field-effect transistors, and organic solar cells—among other electronic applications—and many are also liquid crystals and can be used as sensors.[5−10]

In the past decade the incorporation of thiophene into dendrimers has also been investigated.[11−13] As macromolecules, dendrimers have a high molecular weight but also provide several possible advantages over their analogous polymers, including well-defined and monodisperse structures and a higher degree of purity.[14−16] Dendrimers with polyconjugated branches have become particularly attractive materials for use in organic devices because of their good processability and high absorption intensity.[17−19] Through precise synthetic approaches, different chromophores can be incorporated into the branches, and this offers the possibility of engineering the final optical and electronic properties. Among the most widely studied dendrimers are those in which the backbone is fully conjugated: e.g., those comprised of phenylene, phenylenevinylene, phenyleneethynylene, and, more recently, thiophene units. All-thiophene-based dendrimers were reported for the first time by Advincula and co-workers.[20−22] Since then, the synthesis and properties of novel all-thiophene[23−28] as well as oligothiophene-based dendrimers with different cores, branching units, or positions of the oligothiophene units[29−42] have been widely described and interesting results have been reported for optoelectronic applications. Some of these dendrimers incorporate acetylene spacers within the arms in order to relieve steric strain and to allow more efficient conjugation of the π systems.[43−45]

On the other hand, π-conjugated thienylenevinylene dendrimers are also known. These compounds improve the inherent nonluminescent properties of longer oligo- and poly(thienylenevinylene)s in solution and thin films while retaining their attractive features for organic solar cells.[46] Thus, there is some interest in amending the poor photophysical properties of thienylenevinylene-based materials by structural modification to further develop various applications. The well-established optical properties of phenylenevinylene dendrimers and our significant experience in the synthesis of these systems[47] led us to design a new class of layer-block dendritic architecture containing thienylenevinylene and phenylenevinylene units within the arms. These hybrid materials were prepared using an efficient orthogonal and convergent-growth methodology based on the Horner–Wadsworth–Emmons (HWE) reaction. The synthetic strategy allows specific control over the placement of thiophene and benzene rings within the interior of the dendrimers, thus providing access to concentric layers of these two components around the central core. The periphery of the structures was always decorated with long alkyl chains (*n*-hexyl groups) in order to introduce specific
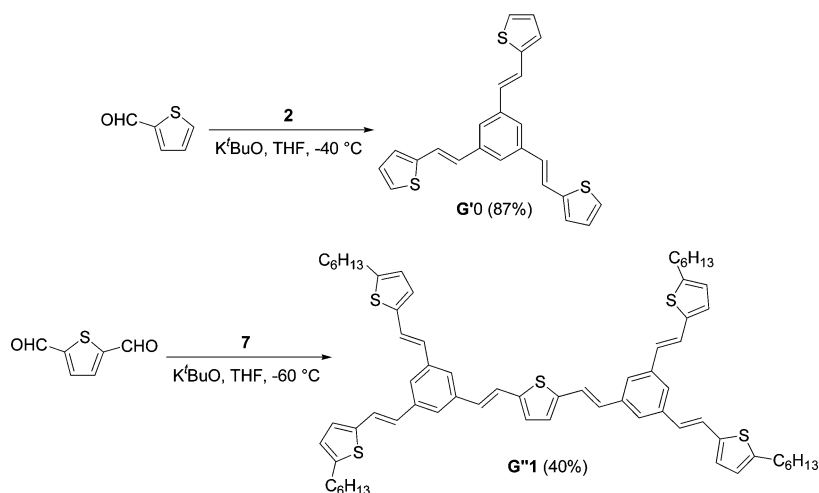
Scheme 1. Synthesis of Zero- and First-Generation Layer-Block Dendrimers with a Phenyl Ring as Central Core
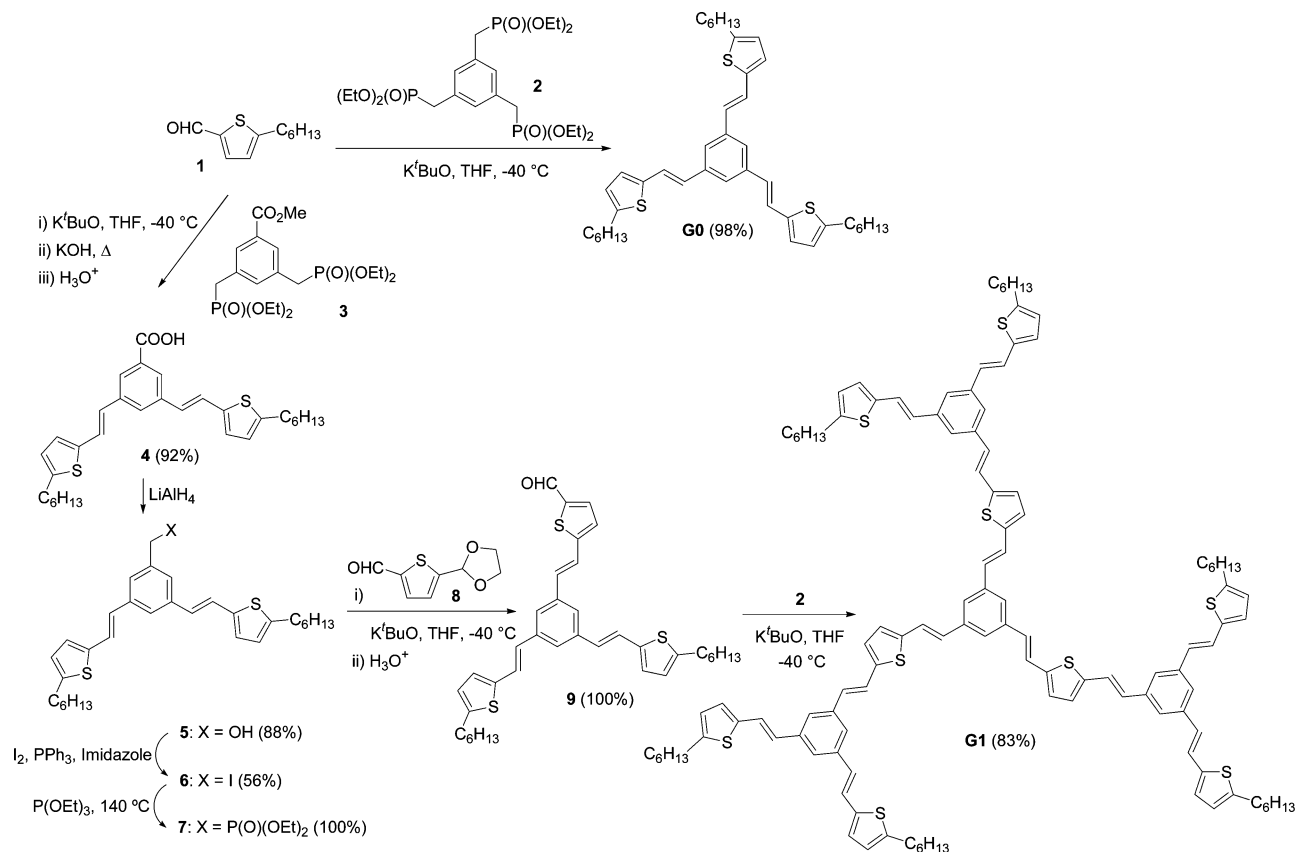
Scheme 2. Synthesis of Dendrimers G′0 and G″1

properties such as solubility in organic media. We also report a preliminary study of the optical properties (absorbance, emission, and fluorescence lifetime) of the resulting dendrimers.

■ RESULTS AND DISCUSSION

Synthesis of Zero- and First-Generation Dendrimers. The synthetic pathway to dendrimers that contain a phenyl ring as the central core is shown in Scheme 1. The preparation of the zero- and first-generation layer-block dendrimers was carried out by using a convergent, orthogonal approach in which the core and the dendrons were obtained separately and linked together in the final step.

In all cases the first step involves 5-hexyl-2-thiophenecarboxaldehyde (**1**), which bears a long-chain substituent aimed at improving the solubility and is the ultimate unit located at the periphery of the final branched molecules. 1,3,5-Tris-(diethoxyphosphorylmethyl)benzene (**2**) was used as the central core, and the zero-generation dendrimer **G0** was easily prepared in excellent yield (98%) by an HWE reaction in the presence of K^{t}BuO in THF at −40 °C. This low temperature guaranteed a good reaction yield by avoiding the undesired

Scheme 3. Synthesis of Dendron 13
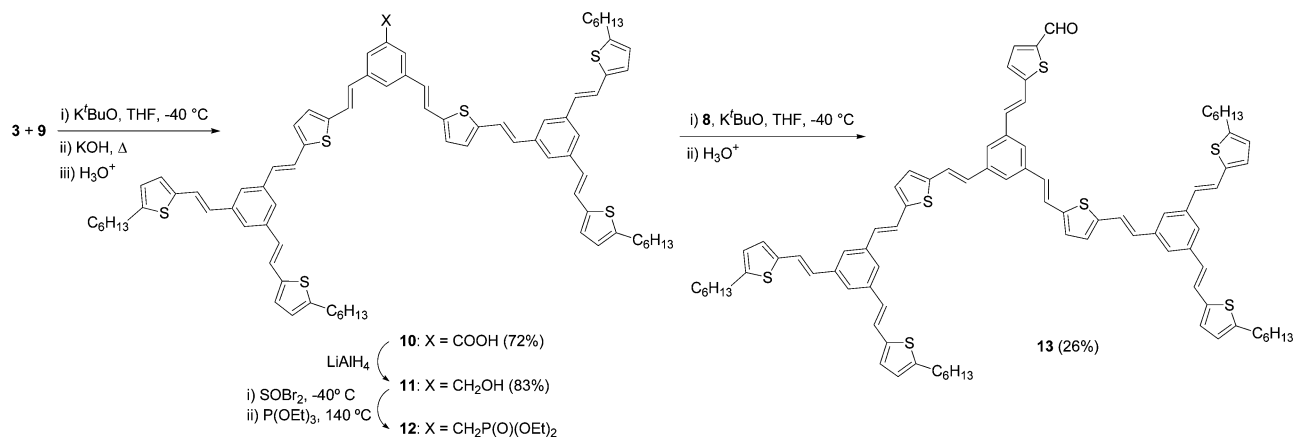
deformylation reaction that thienyl aldehydes often suffer under these reaction conditions.[48]

On the other hand, initial coupling of aldehyde **1** with methyl 3,5-bis(diethoxyphosphorylmethyl)benzoate (**3**) under the same conditions gave the carboxylic acid **4** (92%), and this compound was reduced with LiAlH₄ at 0 °C to afford the corresponding alcohol **5** in 88% yield. Subsequent treatment with iodine in the presence of PPh₃ and imidazole[49,50] gave the iodo derivative **6** in moderate yield (56%). Compound **6** was quantitatively converted into the benzyl phosphonate **7** by an Arbuzov reaction under standard conditions. A new HWE reaction with the aldehyde **8** followed by in situ deprotection of the ketal group gave the dendritic aldehyde **9**. Dendron **9** is the precursor of the first-generation dendrimer **G1**, the synthesis of which was achieved in good yield (83%) by a final HWE reaction with the triphosphonate **2**.

Additionally, with the aim of later analyzing the influence that the peripheral alkyl chains and the nature of the core had on the optical properties, we also synthesized the dendrimers **G′0** and **G″1** by following a similar protocol (Scheme 2). Whereas the commercially available 2-thiophenecarboxaldehyde was employed to obtain the dendrimer **G′0** in 87% yield by reaction with the core **2**, the also commercially available 2,5-thiophenedicarboxaldehyde was used as a core and was coupled with compound **7** to give the dendrimer **G″1** in 40% yield.

The structure and purity of each new compound was unequivocally established by a variety of analytical techniques. NMR experiments indicated the successful formation of the desired products. Signals in the ¹H NMR spectra were well-resolved, except for the first-generation dendrimer **G1**, and the observed ³J(H,H) coupling constants of ∼16.0 Hz for the vinylic protons clearly support the selective formation of *E*-configured double bonds.

All dendrons and dendrimers showed good solubility in common organic solvents, such as THF, chloroform, and dichloromethane, whereas they are somewhat insoluble in polar solvents such as MeOH and EtOH. Indeed, these poor solvents could be used to wash and clean the compounds.

Dendritic Structures of Higher Generation. In principle, the synthetic methodology described above can be further progressed through multiple cycles, although in practice higher molecules are difficult to synthesize because of the well-documented progressive reduction in the reactivity of the focal point in successive generations.[51,52] Starting from aldehyde **9** and proceeding to generation 2, dendrons **10** and **11**, which

bear a carboxyl and hydroxyl group at the focal point, respectively, were easily accessible (Scheme 3). However, the reaction of the latter with I₂/Ph₃P/imidazole to obtain the corresponding iodo derivative only led to a partial transformation. Instead, alcohol **11** was treated with thionyl bromide and DMF as catalyst at −40 °C to afford the desired benzyl bromide, which was directly used without further purification to prepare the corresponding phosphonate **12**. An HWE reaction of **12** with the aldehyde **8** gave the dendron **13**.

These higher structures led to reduced solubility in comparison to that of their lower generation counterparts. The NMR spectra also showed considerable line broadening, which has its origin in reduced segment mobility. Thus, assessment of the overall purity of these molecules proved difficult and the presence of small amounts of other compounds cannot be ruled out.

The MALDI-TOF and high-resolution mass spectrometry data proved to be decisive for monitoring the reactions and for identification of the compounds. The use of DCTB or dithranol as matrix in conjunction with a positive detection mode gave mass spectra that showed peaks corresponding to the radical ions [M]⁺, with an excellent match between the experimental and theoretical isotope distributions.

Dendron **13** is considered to be the precursor of the second-generation dendrimer. However, the HWE reaction of this compound with the core **2** at −40 °C did not afford the desired product. The MALDI-TOF spectrum of the crude product revealed the presence of a new structure formed by the reaction of only one molecule of dendron per molecule of core, together with appreciable amounts of both unreacted starting materials. Unfortunately, it was not possible to increase the temperature to complete the reaction because of the aforementioned decarbonylation of the thiophene aldehyde.

Optical Properties. The optical properties of the synthesized dendrimers were investigated by UV/vis and fluorescence spectroscopy in CH₂Cl₂ solutions at room temperature and at low concentration ($c = (3.0–7.0) \times 10^{-6}$ M). All compounds were photostable and did not undergo cis–trans isomerization under the analysis conditions, nor were aggregation or self-absorption effects observed. The data obtained are summarized in Table 1.

The meta arrangement through which the different units are linked prevents efficient delocalization throughout the conjugated backbone. As a result, the UV/vis spectra consisted of a superposition of the absorptions due to the different

Table 1. UV/Vis and Fluorescence Data

compd	UV/vis[a] λ_{max}, nm (ε, M^{-1} cm^{-1})	fluorescence[a] λ_{max}, nm	Φ_F[b]	Stokes shift, cm^{-1}	τ,[c] ns
G0	346 (74800)	422, 433	0.18	5205	4.4
G′0	335 (77300)	404, 424	0.29	5098	4.2
G″1	350 (96400), 404 (41100), 431 (27300)	446, 476	0.34	6150	0.9
G1	349 (193400), 410 (119400), 432 (93600)	450, 479	0.17	6431	0.8

[a]All spectra were recorded in CH$_2$Cl$_2$ solutions at room temperature at c = (3.0−7.0) × 10^{-6} M. [b]Fluorescence quantum yield (±10%) determined relative to quinine sulfate in 0.1 M H$_2$SO$_4$ as standard (Φ_F = 0.54); excitation at 347 nm. [c]Fluorescence lifetime recorded after excitation at 346 nm (**G0**), 335 nm (**G′0**), 350 nm (**G″1**), and 349 nm (**G1**), at c = 5.0 × 10^{-6} M.

chromophores and all compounds showed absorption wavelengths (λ_{max}) in the UV or visible region. Indeed, the molar extinction coefficients (ε) become much higher as the dendritic generation increases, a consequence of the increase in the number of light-absorbing units. In comparison with previously described all-phenylenevinylene ((E)-stilbenyl)-based dendrimers and dendrons,[53] the replacement of a benzene by a thiophene ring results in a bathochromic shift of the absorption bands, because thiophene is a more electron-rich aromatic ring than benzene. Regarding the zero-generation compound **G′0**, both the shape of the UV/vis spectrum and the ε value are very similar to those of **G0** (Figure 1a), and only a small blue shift in the λ_{max} value is observed, due to the absence of the weakly electron donating peripheral hexyl chain. On the other hand, the absorption bands of lower energy (404−432 nm) observed for **G″1** and **G1** (Figure 1b) can be easily assigned to the more conjugated 2,5-distyrylthiophene chromophores that are present in the structures of these molecules.

All compounds are fluorescent and emit light when irradiated, showing a typical response in the visible region. The Stokes shifts are large, although the magnitude decreases from the zero to the first generation, a situation that has also been observed in related conjugated structures.[51,53] As expected, the fluorescence behaviors of the structurally related pairs of dendrimers **G0**/**G′0** and **G″1**/**G1** are comparable because of the presence of the same chromophores in each pair

(Figure 1). The emission bands for **G″1** and **G1** are red-shifted and probably arise from the extended 2,5-distyrylthiophene units as a result of an energy transfer from the less conjugated branches. Importantly, the emission spectra obtained for **G″1** and **G1** by irradiation at the diverse absorption maxima are the same regardless of the excitation frequency, a fact that supports the energy transfer process from the less conjugated branches, which act as independent chromophores (Figure 2).[23]

The most important differences stem from the fluorescence quantum yields (Φ_f) and the fluorescence lifetimes (τ). Indeed, **G′0** presents a higher Φ_f value than **G0** despite their comparable chromophores and molecular sizes, a result that might be attributed to different fluorophore−solvent interactions due to the absence of the peripheral hexyl group in the former dendrimer.[54] However, it is worth noting that the influence of the hexyl chain on τ is negligible (τ = 4.2 ns for **G0** vs 4.4 ns for **G′0**). On the other hand, **G″1** has a higher Φ_f value than **G1**. In this case both compounds possess exactly the same type of chromophore and, therefore, the variation in the fluorescence intensity can only be explained by the variation in the molecular size. Similar behavior has previously been observed for other structurally rigid dendrimers[51,55−57] and has been explained as being due to the through-space interaction between the fluorescent units becoming more significant on increasing the molecular size, thus providing additional fluorescence quenching pathways. The τ values found for **G″1** (τ = 0.9 ns) and **G1** (τ = 0.8 ns) clearly indicate a shorter fluorescence lifetime of the 2,5-distyrylthiophene units from which the emission takes place in these dendrimers, a situation consistent with the occurrence of an energy transfer process.

■ CONCLUSIONS

In conclusion, we have prepared and characterized a new family of hybrid layer-block conjugated dendritic architectures with alternating thienylenevinylene and phenylenevinylene units. The convergent HWE protocol allowed precise control over the placement of thiophene and benzene rings within the interior of the dendrimers, giving access to concentric layers of these two components around the central core. The extension of this methodology to second-generation architectures proved difficult because of the well-documented progressive reduction in both the solubility and reactivity in successive generations. In
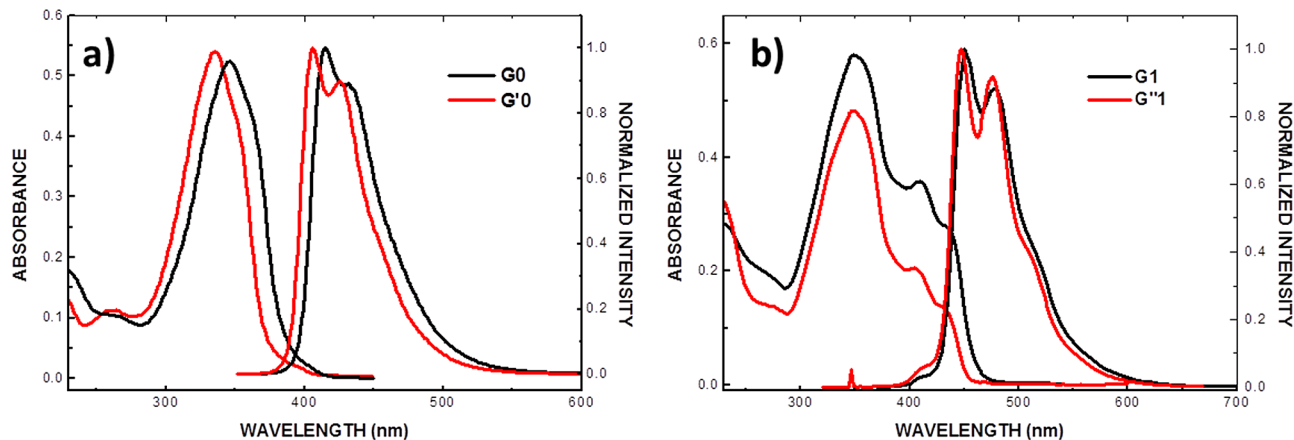
Figure 1. UV/vis and normalized emission spectra in CH$_2$Cl$_2$: (a) **G′0** (black, c = 7.0 × 10^{-6} M, λ_{exc} 346 nm) and **G0′** (red, c = 7.0 × 10^{-6} M, λ_{exc} 335 nm); (b) **G1** (black, c = 3.0 × 10^{-6} M, λ_{exc} 349 nm) and **G″1** (red, c = 5.0 × 10^{-6} M, λ_{exc} 350 nm).
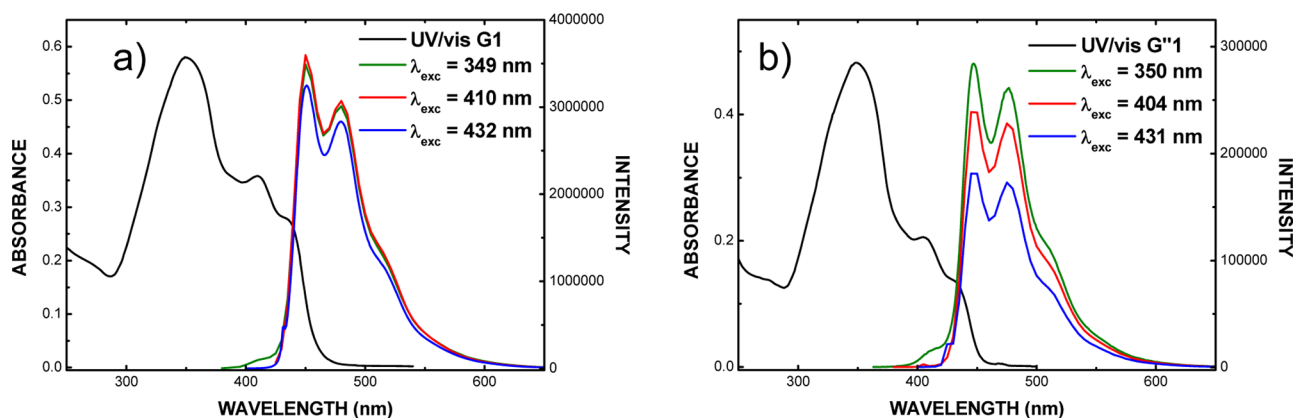
Figure 2. UV/vis and emission spectra in CH_2Cl_2: (a) **G1** ($c = 3.0 \times 10^{-6}$ M); (b) **G″1** ($c = 5.0 \times 10^{-6}$ M).

terms of optical properties, the meta-substitution pattern causes all chromophores to be independent, and all of the compounds exhibit absorption wavelengths in the UV or visible region and emit light with large Stokes shifts and moderate quantum yields. Finally, excitation of dendrimers **G″1** and **G1** results in emission from the extended 2,5-distyrylthiophene units regardless of the λ_{exc} value. This fluorescence behavior, together with the shorter lifetimes observed in comparison to those of **G0** and **G′0**, suggests an energy transfer from the less conjugated branches. Thus, the methodology reported here opens up new possibilities for the preparation of hybrid dendritic architectures bearing both thienylenevinylene and phenylenevinylene units in a variety of practical applications.

■ EXPERIMENTAL SECTION

General Considerations. In air- and moisture-sensitive reactions all glassware was flame-dried and cooled under Ar. Unless stated otherwise, NMR spectra were acquired at 25 °C. Chemical shifts are given in ppm relative to TMS using signals of the residual protons of the deuterated solvent or carbon nuclei of DMSO or $CHCl_3$ (^{1}H and ^{13}C) as the internal standard or H_3PO_4 (^{31}P) as the external standard. IR spectra were recorded on an FT-IR spectrophotometer equipped with an ATR accessory. UV/vis and fluorescence spectra were recorded using standard 1 cm quartz cells. Compounds were excited at their absorption maxima to record the emission spectra (uncorrected); however, different wavelengths at which compounds and standards absorbed significantly were used to determine fluorescence quantum yields. Stokes shifts were calculated considering the absolute maxima of the absorption spectra. ESI and MALDI-TOF mass spectra were registered in positive detection mode. Polypropylene glycols, polyethylene glycols, or polyethylene glycol monomethyl ethers were used for internal calibration in HRMS. 5-Hexylthiophene-2-carboxaldehyde (**1**),[58] 1,3,5-tris(diethoxyphosphorylmethyl)benzene (**2**),[53] methyl 3,5-bis(diethoxyphosphorylmethyl)benzoate (**3**),[59] and 5-(1,3-dioxolan-2-yl)thiophene-2-carboxaldehyde (**8**)[60] were prepared according to literature procedures.

(E,E,E)-1,3,5-Tris[2-(5-hexylthiophen-2-yl)vinyl]benzene (Dendrimer G0). Solid K^{t}BuO (401 mg, 3.57 mmol) was added in small portions to a solution of 5-hexylthiophene-2-carboxaldehyde (**1**; 242 mg, 1.23 mmol) and 1,3,5-tris(diethoxyphosphorylmethyl)-benzene (**2**; 210 mg, 0.398 mmol) in dry THF (25 mL) at −40 °C under argon. After 1 h, the mixture was warmed to room temperature for 2 h. H_2O was added, and the mixture was neutralized with 1 M HCl. The product was extracted with AcOEt, and the organic layer was washed with H_2O and then dried over $MgSO_4$. The solution was filtered and the solvent evaporated under reduced pressure to give a brown solid, which was washed with cold ethanol to afford **G0** (257 mg, 98%) as a yellow solid. Mp: 64−66 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, 9H, J = 6.5 Hz), 1.29−1.42 (m, 18H), 1.69 (m, 6H), 2.79 (t, 6H, J = 7.0 Hz), 6.67 (d, 3H, J = 3.5 Hz), 6.79 (d, 3H, J =

16.0 Hz), 6.89 (d, 3H, J = 3.5 Hz), 7.21 (d, 3H, J = 16.0 Hz), 7.37 (s, 3H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 31.6 (CH_2), 122.7 (CH), 122.9 (CH), 124.6 (CH), 126.4 (CH), 126.7 (CH), 137.9 (C), 140.4 (C), 145.7 (C). IR (ATR) ν 2924, 1620, 1583, 1464, 1454, 947, 939 cm^{-1}. Anal. Calcd for $C_{42}H_{54}S_3$: C, 77.01; H, 8.31; S, 14.68. Found: C, 76.79; H, 8.34; S, 14.35. MALDI-TOF (dithranol): m/z 654.4 [M]$^+$. HRMS (ESI): m/z calcd for $C_{42}H_{55}S_3$ 655.3466, found 655.3485 [M + H]$^+$.

(E,E)-3,5-Bis[2-(5-hexylthiophen-2-yl)vinyl]benzoic Acid (4). Solid K^{t}BuO (1.66 g, 14.8 mmol) was added in small portions to a solution of 5-hexylthiophene-2-carboxaldehyde (**1**; 1.00 g, 5.10 mmol) and methyl 3,5-bis(diethoxyphosphorylmethyl)benzoate (**3**; 1.07 g, 2.45 mmol) in dry THF (25 mL) at −40 °C under argon. After 1 h, the mixture was warmed to room temperature for 2 h. A solution of 1 M KOH was added, and the reaction mixture was heated under reflux for 3 h. The mixture was cooled to room temperature and was neutralized with 1 M HCl. The product was extracted with AcOEt. The organic layer was washed with H_2O and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude product was washed with MeOH to give **4** as a beige solid (1.15 g, 92%). Mp: 123−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, J = 7.0 Hz), 1.22−1.42 (m, 12H), 1.69 (m, 4H), 2.80 (t, 4H, J = 7.5 Hz), 6.68 (d, 2H, J = 3.5 Hz), 6.81 (d, 2H, J = 16.0 Hz), 6.91 (d, 2H, J = 3.5 Hz), 7.27 (d, 2H, J = 16.0 Hz), 7.67 (s, 1H), 8.02 (s, 2H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 31.6 (CH_2), 123.8 (CH), 124.7 (CH), 125.5 (CH), 126.2 (CH), 127.0 (CH), 128.7 (CH), 130.0 (C), 138.1 (C), 140.0 (C), 146.2 (C), 171.6 (C). IR (ATR): ν 2922, 1693 (C=O), 1587, 1454, 1418, 1304, 1265, 1240, 945 cm^{-1}. Anal. Calcd for $C_{31}H_{38}O_2S_2$: C, 73.47; H, 7.56; S, 12.65. Found: C, 73.16; H, 7.89; S, 12.39. MALDI-TOF (dithranol): m/z 506.3 [M]$^+$. HRMS (ESI:) m/z calcd for $C_{31}H_{39}O_2S_2$ 507.2392, found m/z 507.2403 [M + H]$^+$.

(E,E)-3,5-Bis[2-(5-hexylthiophen-2-yl)vinyl]benzyl Alcohol (5). LiAlH$_4$ (4.4 mL, 1 M in THF) was added dropwise, at 0 °C under argon, to a solution of acid **4** (1.00 g, 1.97 mmol) in THF (50 mL). The reaction was kept at 0 °C for 1 h and warmed to room temperature for 2 h. The reaction mixture was quenched with H_2O and neutralized with 1 M HCl. The product was extracted with Et$_2$O, and the organic layer was dried over $MgSO_4$. After filtration and evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (SiO$_2$, hexane/AcOEt 8/2 to 1/1) to give **5** (870 mg, 88%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, 6H, J = 7.0 Hz), 1.22−1.40 (m, 12H), 1.68 (m, 4H), 2.80 (t, 4H, J = 7.5 Hz), 4.71 (s, 2H), 6.67 (d, 2H, J = 3.5 Hz), 6.81 (d, 2H, J = 16.5 Hz), 6.88 (d, 2H, J = 3.5 Hz), 7.21 (d, 2H, J = 16.0 Hz), 7.32 (s, 2H), 7.42 (s, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 31.6 (CH_2), 65.3 (CH_2), 122.8 (CH), 123.4 (CH), 123.5 (CH), 124.6 (CH), 126.4 (CH), 126.5 (CH), 137.9 (C), 140.3 (C), 141.6 (C), 145.8 (C). IR (ATR): ν 3333 (broad, OH), 2924, 1622,

1591, 1454, 1035, 945, 789 cm^{-1}. Anal. Calcd for C$_{31}$H$_{40}$OS$_2$: C, 75.56; H, 8.18; S, 13.01. Found: C, 75.17; H, 8.49; S, 12.69. MALDI-TOF (dithranol): m/z 492.3 [M]$^+$. HRMS (ESI): m/z calcd for C$_{31}$H$_{41}$OS$_2$ 493.2599, found 493.2588 [M + H]$^+$.

(E,E)-3,5-Bis[2-(5-hexylthiophen-2-yl)vinyl]benzyl Iodide (6). Iodine (545 mg, 2.15 mmol), imidazole (59 mg, 0.87 mmol), and a solution of alcohol **5** (212 mg, 0.43 mmol) in CH$_2$Cl$_2$ (12 mL) were successively added to a solution of triphenylphosphine (564 mg, 2.15 mmol) at 0 °C under argon, allowing 10 min periods between each addition. The mixture was stirred for 12 h, and the reaction was quenched by addition of H$_2$O (30 mL). The product was extracted with CH$_2$Cl$_2$ (20 mL). The organic layer was successively washed with NaHCO$_3$ (5% aqueous solution, 3 × 30 mL) and NaHSO$_3$ (0.1% aqueous solution, 3 × 30 mL), dried over MgSO$_4$, filtered, and evaporated under reduced pressure. The resulting solid was crystallized from MeOH to give **6** as a beige solid (146 mg, 56%). Mp: 67−69 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.84−0.92 (m, 6H), 1.22−1.44 (m, 12H), 1.67 (m, 4H), 2.79 (t, 4H, J = 7.5 Hz), 4.44 (s, 2H), 6.67 (d, 2H, J = 3.5 Hz), 6.76 (d, 2H, J = 16.5 Hz), 6.88 (d, 2H, J = 3.5 Hz), 7.19 (d, 2H, J = 16.5 Hz), 7.30 (s, 2H), 7.36 (s, 1H). ^{13}C NMR and DEPT (125 MHz, CDCl$_3$): δ 5.4 (CH$_2$I), 14.1 (CH$_3$), 22.6 (CH$_2$), 28.8 (CH$_2$), 30.4 (CH$_2$), 31.5 (CH$_2$), 31.6 (CH$_2$), 123.1 (CH), 123.5 (CH), 124.6 (CH), 125.2 (CH), 126.1 (CH), 126.6 (CH), 138.2 (C), 139.9 (C), 140.2 (C), 145.9 (C). IR (ATR): ν 2924, 1622, 1587, 1151, 1031, 945, 786 cm^{-1}. Anal. Calcd for C$_{31}$H$_{39}$IS$_2$: C, 61.78; H, 6.52; S, 10.64. Found: C, 61.83; H, 6.70; S, 10.35. MALDI-TOF (dithranol): m/z 601.2 [M − H]$^+$, 475.2 [M − I]$^+$. HRMS (ESI): m/z calcd for C$_{31}$H$_{40}$IS$_2$ 603.1616, found m/z 603.1631 [M + H]$^+$.

Diethyl (E,E)-3,5-Bis[2-(5-hexylthiophen-2-yl)vinyl]-benzylphosphonate (7). This compound was prepared by an Arbuzov reaction of compound **6** (926 mg, 1.54 mmol) with triethyl phosphite (3.00 g, 18.0 mmol) following a standard methodology.[16,17] The brown oil obtained in quantitative yield was of sufficient purity (determined by ^{1}H NMR spectroscopy) and was used in the next step without further purification. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.89 (t, 6H, J = 7.0 Hz), 1.26 (t, 6H, J = 6.5 Hz), 1.22−1.40 (m, 12H), 1.68 (m, 4H), 2.79 (t, 4H, J = 7.5 Hz), 3.15 (d, 2H, J = 22.0 Hz), 3.98−4.08 (m, 4H), 6.66 (d, 2H, J = 3.5 Hz), 6.73 (d, 2H, J = 15.5 Hz), 6.88 (d, 2H, J = 3.5 Hz), 7.19 (d, 2H, J = 16.0 Hz), 7.25 (s, 2H), 7.38 (s, 1H). ^{13}C NMR and DEPT (125 MHz, CDCl$_3$): δ 14.1 (CH$_3$), 16.4 (d, J = 6.0 Hz, CH$_3$), 22.6 (CH$_2$), 28.8 (CH$_2$), 30.4 (CH$_2$), 31.5 (CH$_2$), 31.6 (CH$_2$), 33.7 (d, J = 137.2 Hz, CH$_2$P), 62.2 (d, J = 6.0 Hz, CH$_2$), 122.7 (d, J = 3.9 Hz, CH), 122.8 (CH), 124.6 (CH), 126.4 (CH) 126.4 (CH), 126.5 (CH), 132.3 (d, J = 8.1 Hz, C), 137.8 (d, J = 3.0 Hz, C), 140.3 (C), 145.7 (C). ^{31}P NMR (162 MHz, CDCl$_3$): δ 27.0. IR (ATR): ν 2926, 1624, 1589, 1454, 1248, 1053, 1024, 945, 789 cm^{-1}. MALDI-TOF (dithranol): m/z 612.4 [M]$^+$, 635.4 [M + Na]$^+$, 651.4 [M + K]$^+$. HRMS (ESI): m/z calcd for C$_{35}$H$_{50}$O$_3$PS$_2$ 613.2939, found 613.2922 [M + H]$^+$.

(E,E,E)-5-{3,5-Bis[2-(5-hexylthiophen-2-yl)vinyl]styryl}-thiophene-2-carboxaldehyde (9). Solid K^{t}BuO (863 mg, 7.69 mmol) was added in small portions to a solution of 5-(1,3-dioxolan-2-yl)thiophene-2-carboxaldehyde (**8**; 472 mg, 1.05 mmol) and phosphonate **7** (1.57 g, 1.00 mmol) in dry THF (30 mL) at −40 °C under argon. After 1 h at 0 °C the mixture was warmed to room temperature for 4 h. A solution of 1 M HCl was then added, and the reaction mixture was stirred overnight in order to remove the acetal group. The product was extracted with AcOEt. The organic layer was washed with saturated NaHCO$_3$ and H$_2$O and dried over MgSO$_4$. After filtration and evaporation of the solvent, the crude product was washed with MeOH to give **9** as a beige solid in quantitative yield. Mp: 74−76 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.90 (t, 6H, J = 6.5 Hz), 1.18−1.42 (m, 12H), 1.69 (m, 4H), 2.80 (t, 4H, J = 7.5 Hz), 6.68 (d, 2H, J = 3.5 Hz), 6.79 (d, 2H, J = 16.0 Hz), 6.90 (d, 2H, J = 3.5 Hz), 7.13 (d, 1H, J = 16.0 Hz), 7.17 (d, 1H, J = 3.5 Hz), 7.22 (d, 2H, J = 16.0 Hz), 7.25 (d, 1H, J = 16.0 Hz), 7.40 (s, 2H), 7.43 (s, 1H), 7.67 (d, 1H, J = 3.5 Hz), 9.86 (s, 1H). ^{13}C NMR and DEPT (125 MHz, CDCl$_3$): δ 14.1 (CH$_3$), 22.6 (CH$_2$), 28.8 (CH$_2$), 30.4 (CH$_2$), 31.5 (CH$_2$), 31.6 (CH$_2$), 121.2 (CH), 123.1 (CH), 123.4 (CH), 124.2 (CH), 124.7 (CH), 126.1 (CH), 126.7 (CH), 132.6 (CH), 136.5 (C),

137.2 (CH), 138.1 (C), 140.2 (C), 141.6 (C), 145.9 (C), 152.3 (C), 182.6 (CH═O). IR (ATR): ν 2922, 1661 (C═O), 1583, 1447, 1221, 1041, 945 cm^{-1}. Anal. Calcd for C$_{37}$H$_{42}$OS$_3$: C, 74.20; H, 7.07; S, 16.06. Found: C, 73.90; H, 7.31; S, 15.72. MALDI-TOF (dithranol): m/z 598.3 [M]$^+$. HRMS (ESI): m/z calcd for C$_{37}$H$_{43}$OS$_3$ 599.2476, found 599.2486 [M + H]$^+$.

Dendrimer G1. This compound was prepared from K^{t}BuO (46 mg, 0.410 mmol), aldehyde **9** (83 mg, 0.139 mmol), and 1,3,5-tris(diethoxyphosphorylmethyl)benzene (**2**; 24 mg, 0.045 mmol) using the same procedure described for **G0**. The brown solid obtained was washed with cold ethanol to afford **G1** (70 mg, 83%) as an orange solid. Mp: >300 °C. ^{1}H NMR (500 MHz, DMSO-d_6 + CDCl$_3$): δ 0.90 (broad s, 18H), 1.18−1.40 (m, 36H), 1.67 (m, 12H), 2.79 (m, 12H), 6.70−7.56 (m, 54H). ^{13}C NMR and DEPT (125 MHz, DMSO-d_6 + CDCl$_3$, 60 °C): δ 13.3 (CH$_3$), 22.7 (CH$_2$), 27.8 (CH$_2$), 29.5 (CH$_2$), 30.6 (CH$_2$), 30.7 (CH$_2$), 122.0 (CH), 122.5 (CH), 122.6 (CH), 124.2 (CH), 125.8 (CH), 126.0 (CH), 127.0 (CH), 127.3 (CH), 127.5 (CH), 137.0 (C), 137.3 (C), 139.5 (C), 141.2 (C), 141.3 (C), 144.8 (C). IR (ATR): ν 2924, 1583, 1454, 1220, 943 cm^{-1}. MALDI-TOF (dithranol): m/z 1862.1 [M + H]$^+$. HRMS (MALDI-TOF, DCTB): m/z calcd for C$_{120}$H$_{132}$S$_9$ 1860.7816, found 1860.7822 [M]$^+$.

(E,E,E)-1,3,5-Tris[2-(thiophen-2-yl)vinyl]benzene (Dendrimer G′0). This compound was prepared from K^{t}BuO (462 mg, 4.13 mmol), 2-thiophenecarboxaldehyde (159 mg, 1.42 mmol), and 1,3,5-tris(diethoxyphosphorylmethyl)benzene (**2**; 242 mg, 0.458 mmol) using the same procedure as for **G0**. The brown solid obtained was washed with cold ethanol to afford **G′0** (160 mg, 87%) as a yellow solid. Mp: 243−245 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.94 (d, 3H, J = 16.0 Hz), 7.02 (dd, 3H, J = 3.5 and 5.5 Hz), 7.11 (d, 3H, J = 3.5 Hz), 7.21 (d, 3H, J = 5.5 Hz), 7.31 (d, 3H, J = 16.0 Hz), 7.45 (s, 3H). ^{13}C NMR and DEPT (125 MHz, CDCl$_3$): δ 122.4 (CH), 123.4 (CH), 124.6 (CH), 126.4 (CH), 127.7 (CH), 127.8 (CH), 137.7 (C), 142.7 (C). IR (ATR): ν 1584, 1418, 1198, 957, 943, 698 cm^{-1}. Anal. Calcd for C$_{24}$H$_{18}$S$_3$: C, 71.60; H, 4.51; S, 23.89. Found: C, 71.26; H, 4.56; S, 23.56. MALDI-TOF (dithranol): m/z 401.8 [M]$^+$.

(E,E,E,E,E)-2,5-Bis{3,5-bis[2-(5-hexylthiophen-2-yl)vinyl]-styryl}thiophene (Dendrimer G″1). This compound was prepared at −60 °C from K^{t}BuO (67 mg, 0.600 mmol), 2,5-thiophenedicarboxaldehyde (13 mg, 0.095 mmol), and phosphonate **7** (122 mg, 0.199 mmol) using a procedure similar to that described for **G0**. The brown solid obtained was purified by column chromatography (SiO$_2$, hexane) to give **G″1** (40 mg, 40%) as a yellow viscous oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.90 (t, 12H, J = 6.5 Hz), 1.28−1.41 (m, 24H), 1.70 (m, 8H), 2.81 (t, 8H, J = 7.5 Hz), 6.68 (d, 4H, J = 3.5 Hz), 6.82 (d, 4H, J = 16.0 Hz), 6.91 (d, 4H, J = 3.5 Hz), 6.93 (d, 2H, J = 16.0 Hz), 7.00 (s, 2H), 7.24 (d, 4H, J = 16.0 Hz), 7.25 (d, 2H, J = 16.0 Hz), 7.41 (s, 6H). ^{13}C NMR and DEPT (125 MHz, CDCl$_3$): δ 14.1 (CH$_3$), 22.6 (CH$_2$), 28.8 (CH$_2$), 30.4 (CH$_2$), 31.5 (CH$_2$), 31.6 (CH$_2$), 122.3 (CH), 122.8 (CH), 123.1 (CH), 123.2 (CH), 124.6 (CH), 126.5 (CH), 1126.5 (CH), 127.3 (CH), 128.2 (CH), 137.5 (C), 137.9 (C), 140.3 (C), 142.0 (C), 145.8 (C). IR (ATR): ν 2922, 1622, 1583, 1454, 1034, 943, 817, 787 cm^{-1}. MALDI-TOF (DCTB or dithranol): m/z 1056.5 [M]$^+$. HRMS (MALDI-TOF, DCTB): m/z calcd for C$_{68}$H$_{80}$S$_5$ 1056.4863, found 1056.4841 [M]$^+$.

Acid 10. This compound was prepared from K^{t}BuO (235 mg, 2.09 mmol), aldehyde **9** (429 mg, 0.716 mmol), and methyl 3,5-bis(diethoxyphosphorylmethyl)benzoate (**3**; 152 mg, 0.349 mmol) using the same procedure described for **4**. The crude product was washed with EtOH to give the acid **10** (330 mg, 72%) as a beige solid. Mp: 145−148 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 75 °C): δ 0.88 (t, 12H, J = 6.5 Hz), 1.22−1.42 (m, 24H), 1.65 (m, 8H), 2.80 (t, 8H, J = 7.5 Hz), 6.78 (d, 4H, J = 3.0 Hz), 6.84 (d, 4H, J = 15.5 Hz), 6.98 (d, 2H, J = 16.0 Hz), 7.03 (d, 4H, J = 3.5 Hz), 7.05 (d, 2H, J = 16.0 Hz), 7.20 (d, 2H, J = 4.0 Hz), 7.25 (d, 2H, J = 4.0 Hz), 7.47 (d, 4H, J = 16.0 Hz), 7.54 (d, 2H, J = 16.0 Hz), 7.58 (d, 2H, J = 16.0 Hz), 7.61 (s, 2H), 7.62 (s, 4H), 8.01 (s, 2H), 8.04 (s, 1H). ^{13}C NMR and DEPT (125 MHz, DMSO-d_6, 75 °C): δ 13.4 (CH$_3$), 21.6 (CH$_2$), 27.7 (CH$_2$), 29.3 (CH$_2$), 30.5 (CH$_2$), 30.6 (CH$_2$), 122.3 (CH), 122.7 (CH), 122.8 (CH), 122.9 (CH), 123.1 (CH), 124.8 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 126.7 (CH), 127.4 (CH), 127.5 (CH), 127.8

(CH), 128.0 (CH), 131.9 (C), 137.1 (C), 137.3 (C), 137.4 (C), 139.6 (C), 141.0 (C), 141.7 (C), 144.8 (C), 166.7 (COOH). IR (ATR): ν 2922, 1684 (C=O), 1584, 1456, 1240, 1036, 943, 787, 677 cm^{-1}. MALDI-TOF (DCTB or dithranol): m/z 1310.4 [M]$^+$. HRMS (MALDI-TOF, DCTB): m/z calcd for $C_{83}H_{90}O_2S_6$ 1310.5265, found 1310.5226 [M]$^+$.

Alcohol 11. This compound was prepared from LiAlH$_4$ (0.350 mL, 1 M in THF) and acid **10** (207 mg, 0.158 mmol) using the same procedure as for **4**. The crude product was washed with EtOH to give the alcohol **11** (171 mg, 83%) as a dark red solid. Mp: >300 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.90 (t, 12H, J = 7.0 Hz), 1.25−1.45 (m, 24H), 1.69 (m, 8H), 2.80 (t, 8H, J = 7.5 Hz), 4.72 (s, 2H), 6.68 (d, 4H, J = 3.0 Hz), 6.79 (d, 4H, J = 15.5 Hz), 6.89 (d, 4H, J = 15.5 Hz), 6.90 (d, 4H, J = 3.5 Hz), 6.98 (s, 4H), 7.21 (d, 4H, J = 16.0 Hz), 7.22 (d, 2H, J = 16.5 Hz), 7.23 (d, 2H, J = 16.5 Hz), 7.34 (broad s, 2H), 7.37 (broad s, 6H), 7.44 (broad s, 1H). ^{13}C NMR and DEPT (125 MHz, CDCl$_3$): δ 14.1 (CH$_3$), 22.6 (CH$_2$), 28.8 (CH$_2$), 30.4 (CH$_2$), 31.5 (CH$_2$), 31.6 (CH$_2$), 65.2 (CH$_2$OH), 122.2 (CH), 122.5 (CH), 122.8 (CH), 123.1 (CH), 123.2 (CH), 123.8 (CH), 123.9 (CH), 124.6 (CH), 126.5 (CH), 126.6 (CH), 127.3 (CH), 127.4 (CH), 127.9 (CH), 128.3 (CH), 137.5 (C), 137.7 (C), 137.9 (C), 140.3 (C), 141.7 (C), 141.8 (C), 142.1 (C), 145.8 (C). IR (ATR): ν 3437 (broad, OH), 2922, 1622, 1583, 1454, 1033, 941 cm^{-1}. MALDI-TOF (dithranol): m/z 1297.0 [M]$^+$. HRMS (MALDI-TOF, DCTB): m/z calcd for $C_{83}H_{92}OS_6$ 1296.5471 found 1296.5483 [M]$^+$.

Phosphonate 12. SOBr$_2$ (170 μL, 2.16 mmol) and DMF (170 μL, 2.16 mmol) were added to a solution of alcohol **11** (140 mg, 0.108 mmol) in dry THF (20 mL) at −40 °C under argon. After the mixture was stirred overnight at this temperature, the solvent was evaporated under reduced pressure and the crude product was reacted with triethyl phosphite (2 mL), following the standard methodology.[16,17] The phosphonate **12** was obtained as an oil and was used in the next step without further purification. ^{1}H NMR (500 MHz, CD$_3$OD + CDCl$_3$): δ 0.87 (broad t, 12H, J = 7.0 Hz), 1.20−1.40 (m, 24H), 1.66 (m, 8H), 2.77 (broad t, 8H, J = 7.0 Hz), 4.01 (broad s, 2H), 6.65 (broad s), 6.73 (d, 4H, J = 16.5 Hz) 6.78−7.00 (broad m), 7.08−7.42 (broad m). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.1, 16.4 (broad), 22.6, 28.8, 30.4, 31.5, 31.6, 33.9 (broad d, J = 137.8 Hz), 62.3 (broad), 122.3, 122.8, 123.0, 124.6, 126.5, 127.3, 128.5, 132.1, 137.9, 138.0, 140.3, 145.8. ^{31}P NMR (162 MHz, CDCl$_3$): δ 26.9. MALDI-TOF (DCTB or dithranol): m/z 1416.6 [M]$^+$. HRMS (MALDI-TOF, DCTB): m/z calcd for $C_{87}H_{101}O_3PS_6$ 1416.5812, found 1416.5837 [M]$^+$.

Aldehyde 13. This compound was prepared from 5-(1,3-dioxolan-2-yl)thiophene-2-carboxaldehyde (**8**; 11.5 mg, 0.063 mmol) and phosphonate **12** (89 mg, 0.063 mmol) using the same procedure as for **9**. The crude product was purified by column chromatography (SiO$_2$, hexane) to give **13** (23 mg, 26%) as a yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.90 (broad s, 12H), 1.25−1.41 (m, 24H), 1.68 (broad s, 8H), 2.81 (broad t, 8H, J = 7.5 Hz), 6.69 (broad d, 4H, J = 3.5 Hz), 6.82 (d, 4H, J = 16.0 Hz), 6.92 (broad d, 4H, J = 3.5 Hz), 6.95 (broad s), 7.00−7.05 (broad m), 7.17−7.33 (broad m), 7.23 (broad s), 7.42 (broad s), 7.49 (broad s), 7.52−7.55 (broad m), 7.68−7.72 (broad m), 9.86 (broad s, 1H). IR (ATR): ν 1693 (C=O), 1454, 1261, 1094, 1030, 800 cm^{-1}. MALDI-TOF (DCTB or dithranol): m/z 1402.6 [M]$^+$. HRMS (MALDI-TOF, DCTB): m/z calcd for $C_{89}H_{94}OS_7$ 1402.5350, found 1402.5354 [M]$^+$.

ASSOCIATED CONTENT

S **Supporting Information**

Figures giving ^{1}H NMR and ^{13}C NMR spectra for all compounds and fluorescence decay profiles for dendrimers **G0**, **G′0**, **G″1**, and **G1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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