

Synthesis and Photoluminescent Properties of 1,1'-Binaphthyl-Based Chiral Phenylenevinylene Dendrimers

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New chiral, soluble binaphthyl derivatives that incorporate stilbenoid dendrons at the 6,6'-positions have been prepared. The synthesis of the new enantiopure dendrimers was performed in a convergent manner by Horner–Wadsworth–Emmons (HWE) reaction of the appropriately functionalized 1,1'-binaphthyl derivative (**R**)-**1** and the appropriate dendrons (**R**)_{2n}G_n-CHO. Different electroactive units were incorporated in the peripheral positions of the dendrons in order to tune both the optical and electrochemical behavior of these systems. Fluorescence measurements on the chiral dendrimers reveal a strong emission with maxima between 409 and 508 nm depending upon the substitution pattern. Finally, the redox properties of the dendrimers were determined by cyclic voltammetry, showing the influence of the functional groups at the peripheral positions of the dendrimer on the redox behavior of these systems.

Introduction

Synthetic macromolecules that contain π -conjugated systems have attracted a great deal of attention owing to their potential to act as photosynthetic antennas, as molecular wires for electron and energy transfer, and also as materials in organic photo- and electroluminescent devices. In this regard, linear-chain polymers are the systems most often prepared with these aims in mind. However, such materials do suffer from some limitations such as broad molecular weight distribution, poorly defined morphologies, and uncontrolled intra- and inter-chain interactions.¹ Convergent and divergent synthetic methodologies for the synthesis of dendrimers provide a high degree of control in terms of the molecular size, shape, and location of functional groups, leading to almost total control over the molecular architecture.^{1,2} Thus, dendrimers have become suitable materials to overcome the drawbacks of linear-chain polymers, and

dendritic structures have been shown to act as light-harvesting antennas³ and to be appropriate compounds for optoelectronics applications.⁴

Chiral dendrimers⁵ represent another important target due to their possible applications in asymmetric catalysis, in sensor technology, and for chemical separations. The majority of the chiral dendrimers reported to date have been prepared using dendrons or cores with stereogenic centers. On the other hand, only a few examples are known in which axial chirality is reported and all of these compounds are based on 1,1'-binaphthyl derivatives.

1,1'-Binaphthol is a useful core unit because its versatility and well-established chemistry permits the preparation of a wide range of different molecular structures. Thus, nucleophilic aromatic substitution,⁶ Heck,⁷ Suzuki,⁸

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Sonogashira,⁹ Wittig,¹⁰ Horner–Wadsworth–Emmons,¹¹ and Williamson¹² reactions have been used for the synthesis of 1,1'-binaphthyl derivatives. Bazan et al. have recently reported the synthesis of 6,6'-bis(polyphenylenevinylene)-substituted 1,1'-binaphthol derivatives and have shown the importance of the molecular topology of the binaphthyl framework for the design of noncrystallizable organic chromophores.⁷ Pu et al. have used 1,1'-bi-2-naphthol derivatives to construct novel rigid and cross-conjugated optically active dendrimers with phenylacetylene-based dendrons. They also demonstrated that a very efficient energy migration occurs from the cross-conjugated dendrons to the central core, leading to greatly enhanced fluorescence at higher generations. This is the first example of an efficient energy migration conducted in an optically pure dendritic system.⁹ The same authors recently reported the usefulness of these dendrimers as enantioselective fluorescence sensors for the recognition of chiral amino alcohols.⁸

Blue-luminescent polymers are usually prepared by three main strategies: (i) a random interruption of the conjugation along the chain by copolymerization with nonconjugated monomers, (ii) the presence of a backbone twist caused by steric interactions as in the case of widely studied poly-*p*-phenylenes (PPP), polyfluorenes, polytetrahydropyrenes, poly-2,8-indenofluorene, and ladder-type PPP,¹³ and (iii) the use of cross-conjugation. The first approach affords polymers that suffer from the drawback that emission usually occurs from the more conjugated segments only. The second set of materials, on the other hand, have very little potential for fine-tuning. Only cross-conjugation gives rise to an efficient and predictable method to interrupt the conjugation in the system.¹⁴ Thus, dendritic polyphenylenevinyls, also called stilbenoid dendrimers, are interesting and attractive targets.¹⁵

In a previous communication¹¹ we reported a Horner–Wadsworth–Emmons approach to new soluble cross-conjugated chiral luminescent dendrimers bearing methoxy groups on the periphery. We report here the synthesis, characterization, chiroptical properties, UV–vis and

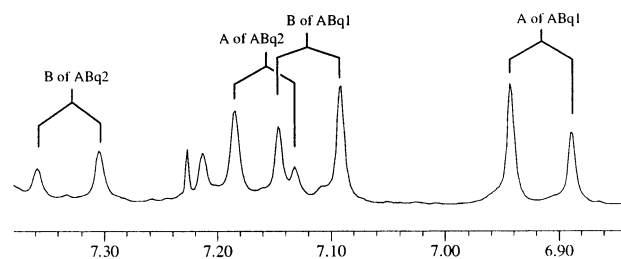


FIGURE 1. The double bond signals in the ¹H NMR spectrum of (NBu₂)₄G1-Bn. Two AB quartets can be observed with $J \approx 16$ Hz. ABq2 corresponds to the double bond linking the binaphthyl core.

fluorescence measurements, and electrochemical behavior of new dendrimers based on 1,1'-binaphthol with cross-conjugated arms and electron-donor and electron-acceptor groups at the periphery.

Results and Discussion

Synthesis and Characterization of Chiral Dendrimers. The synthesis of dendrimers (R)_{4n}G_n-Bn was achieved in a convergent manner by Horner–Wadsworth–Emmons (HWE) reaction of the 1,1'-binaphthyl derivative (R)-1¹⁶ and the appropriate dendrons (R)_{2n}G_n-CHO^{15a} in K^tBuO/THF (Scheme 1).

All new compounds were characterized using various analytical techniques. MS and NMR experiments proved very useful to confirm the structures of the compounds (see Experimental Section and Supporting Information). The NMR spectra indicate that these dendrimers maintain a C₂ symmetry in solution. The selectivity of the HWE reaction is sufficiently high to generate all-*trans* isomers within the limits of NMR detection. This stereochemistry for the double bonds was unequivocally established for the first generation dendrimers (OCH₃)₄G1-Bn and (NBu₂)₄G1-Bn on the basis of the coupling constant of the vinylic protons in the ¹H NMR spectra ($J \approx 16$ Hz), where the AB quartet for the double bond linking the binaphthyl core and the dendron could be distinguished (Figure 1). In the rest of compounds there is some overlapping of signals that precludes the unambiguous determination of the coupling constant; however, there is no reason to obtain a different selectivity.

Assessment of the overall purity of these molecules proved difficult. The ¹H NMR spectra of these dendrimers are well-resolved and do not reveal impurities, but the high number of lines in the 0.8–1.5 and 7–8 ppm zones could obscure the presence of small amounts of other compounds.

LSIMS mass spectroscopic analyses of (OCH₃)₄G1-Bn and (OCH₃)₈G2-Bn gave the expected molecular ions. The MALDI-TOF spectra of (NBu₂)₄G1-Bn, (NBu₂)₈G2-Bn, (CF₃)₄G1-Bn, and (CF₃)₈G2-Bn showed peaks matching the calculated values for the expected molecular weights. However, the mass spectrum of (CF₃)₈G2-Bn showed evidence of some degree of contamination. Further purification of this compound was achieved by

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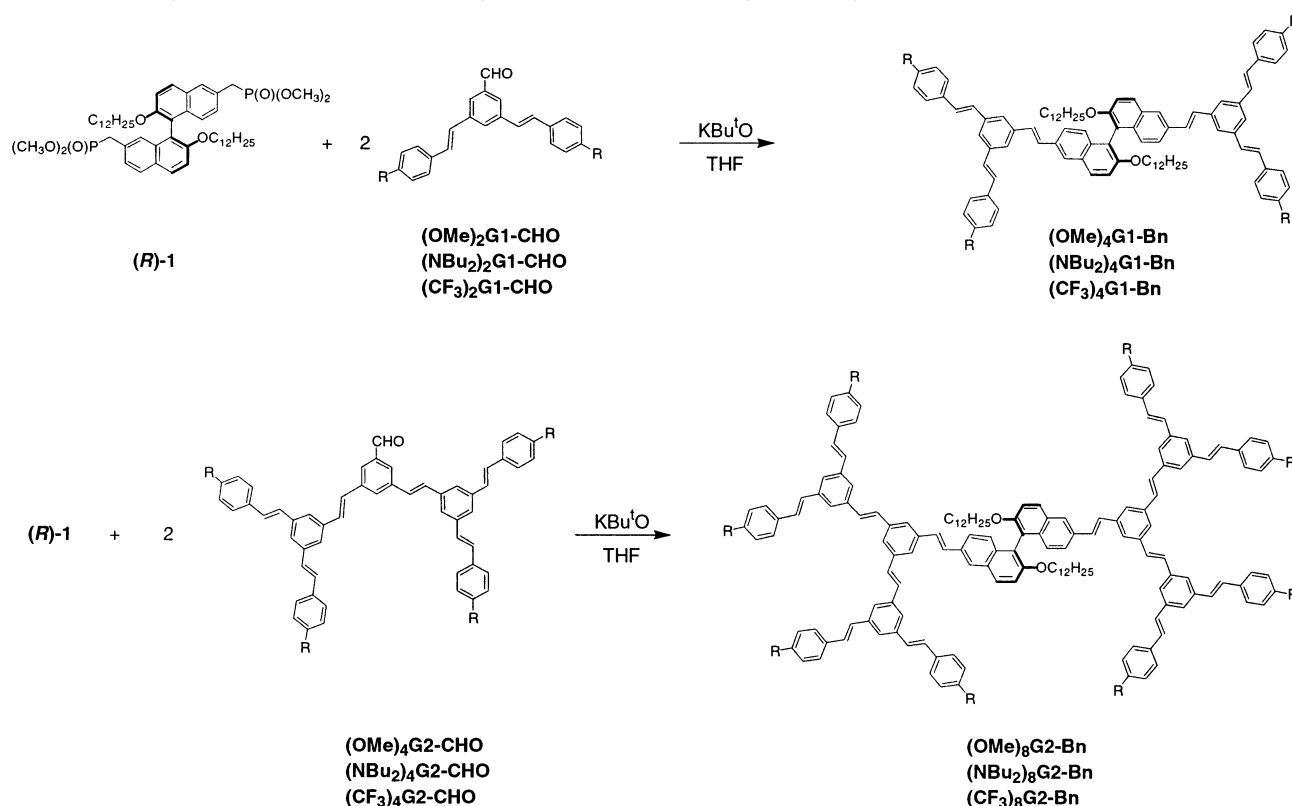
SCHEME 1. Synthesis of 1,1'-Binaphthyl-Based Chiral Phenylenevinylene Dendrimers $R_{4n}G_n$ -Bn

TABLE 1. UV-vis, Photoluminescence (PL), Optical Rotation, and Electrochemical Data

compound	UV-vis ^a λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)	PL ^b λ_{\max} , nm (λ_{exc} , nm)	Φ_f^c	$[\alpha]_D^d$	$[M]_D$	E_{ox}^1 ^e	E_{ox}^2 ^e	$E_{\text{ox}}^{e,f}$	E_{red}^e
(OMe) ₄ G1-Bn	329.5 (171500)	409 (329.5)	0.71	-193	-2615	1.09	1.45	1.25	
(OMe) ₈ G2-Bn	326.5 (336600)	425 (326.5)	0.34	-65	-1489	1.09	1.47	1.25	
(NBu ₂) ₄ G1-Bn	367.5 (208600)	496 (360.5)	0.20	-223	-3888	0.65	1.22		
(NBu ₂) ₈ G2-Bn	363.0 (324900)	508 (360.5)	0.13	-66.5	-2041	0.63	1.59	1.18	
(CF ₃) ₄ G1-Bn	317.5 (143100)	444 (317.5)	0.29	-184	-2772	1.12	1.73	1.35	-0.91
(CF ₃) ₈ G2-Bn	316.5 (391800)	431 (316.5)	0.10	-22.5	-584	1.08	1.72		-0.97

^a All spectra were recorded in CH₂Cl₂ at room temperature at $c = 3 \times 10^{-6}$ M, except for (OCH₃)₄G1-Bn and (OCH₃)₈G2-Bn where $c = 1 \times 10^{-6}$ M. ^b All spectra were recorded in CH₂Cl₂ at room temperature at $c = 3 \times 10^{-7}$ M, except for (OCH₃)₄G1-Bn and (OCH₃)₈G2-Bn where $c = 1 \times 10^{-7}$ M. ^c Fluorescence quantum yield in dichloromethane determined relative to quinine sulfate dissolved in 1 N H₂SO₄. ^d Recorded in CH₂Cl₂ at $c = 1 \times 10^{-3}$ M, except for (OCH₃)₈G2-Bn and (CF₃)₈G2-Bn where $c = 4 \times 10^{-4}$ M. ^e Scan rate: 100 mV·s⁻¹ in dry CH₂Cl₂ (0.1 M *n*-Bu₄NClO₄) using SCE as reference and GCE as working electrodes. ^f This oxidation wave can only be observed after multiple scans.

column chromatography, although a significant amount of product was also lost during this process. The mass spectrum subsequently showed a much purer product, although a peak at m/z 1006.2 was evident, which could correspond to the carboxylic acid (CF₃)₄G1-COOH derived from oxidation of the starting material. A similar situation has been previously observed by us in a case where some second generation dendrons were treated under HWE conditions and the substrate had a higher degree of steric hindrance around the reactive site.^{15a}

Optical Spectroscopic Studies of the Chiral Dendrimers. The UV-vis absorption and PL spectra of dendrimers (R)_{4n}G_n-Bn were recorded in CH₂Cl₂ at room temperature (Figure 2). The data obtained are summarized in Table 1. Owing to the *meta* arrangement through which the dendrons are linked, it was expected that the absorption spectra would consist of a simple superposition of the absorptions due to the stilbene dendrons and the binaphthyl core. Indeed, strong bands

with maxima at 317–367 nm, associated with the stilbene units, are observed. In some cases small shoulders at ca. 340 nm can be observed, and these are associated with the core. The absorptions become much stronger as the dendritic generation grows owing to the exponential increase in the number of light-absorbing phenylenevinylene units. These molecules are almost colorless, with the exception of the dialkylamino derivatives. When the spectra were recorded at lower concentrations (10⁻⁷–10⁻⁸ M range), two resolved bands were often observed instead of a single absorption as well as changes in the shift and chromicity of the bands (higher ϵ). A satisfactory explanation for these effects is unclear at the moment and will require further investigations. Several authors have pointed out that a concentration-dependent aggregation provokes changes in the UV-vis and fluorescence spectra of stilbenoid units.^{15f,17} The absorption maxima show only very small blue-shifts upon increasing the generation. This is expected since the *meta* linkage of the stilbene

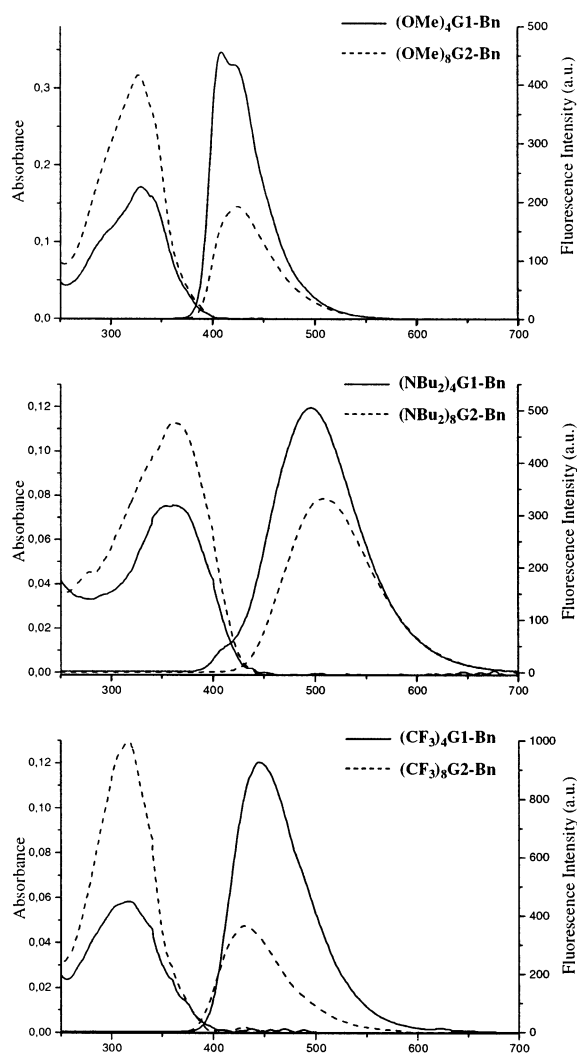


FIGURE 2. Absorption and fluorescence emission spectra of dendrimers $(R)_4G1-Bn$ (—) and $(R)_8G2-Bn$ (---) in CH_2Cl_2 at room temperature. The fluorescence spectra are normalized to a constant absorbance.

units should cause little change in conjugation as the dendrimer grows. The small blue-shift may be explained in terms of a decrease in the planarity of the conjugated backbone. Low energy absorption bands were not observed, a situation in agreement with the lack of conjugation between the dodecyloxynaphthalene and the stilbene units. Through-bond or through-space interactions between the two moieties do not take place in the ground state.

The dendrimers emit strong blue light under UV irradiation, showing typical bands for the stilbenoid compounds reported previously by us.^{15a,b} The fluorescence quantum yields, Φ_f , were determined by using a solution of quinine sulfate in 1 N H_2SO_4 as the reference standard ($\Phi_s = 0.546$). The intensity of the fluorescence from compounds $(R)_8G2-Bn$, the higher generation dendrimers, is substantially lower than that from their

corresponding counterparts $(R)_4G1-Bn$. Similar behavior has been previously observed for other structurally rigid dendrons^{3f,18} and has been accounted for by the many modes used to dissipate the excitation energy in larger dendrons, a property that enhances the nonradiative decay. The through-space interaction between the fluorescent units become more significant with increasing molecular size, providing additional fluorescence quenching pathways.

It has been claimed that stilbene dendrons are efficient energy transmitters.^{4f} Similar emissions in the range 400–500 nm for stilbene moieties and core do not allow us to unequivocally assume that such a property is present in all of our 1,1'-binaphthyl dendrimers, although these systems may be envisioned as appropriate candidates for energy transfer processes. In any case, all of the molecules described here are new chiral blue-emitting phenylenevinylene-based dendrimers that are highly fluorescent.

Chiroptical Properties. The optical rotation data for the studied chiral dendrimers are summarized in Table 1.

Chen¹⁹ and Meijer¹² studied the effect of dendritic branches at the 2,2'-positions of the 1,1'-binaphthyls on the optical rotation of the chiral binaphthyl-core-based dendrimers and observed a change in the molar optical rotation upon passing from lower to higher generation dendrons. In contrast, Pu and co-workers showed that substitution at the 4,4',6,6'-positions of the binaphthyl core with rigid phenyleneethynylene-based dendrons does not significantly change the 1,1'-binaphthyl dihedral angle—at least from generation zero to generation two.⁹ In our case, we observed in the 1,1'-dendron-substituted binaphthyls that molar optical rotation values for first and second generation dendrimers are significantly different despite the fact that the substitution is in the 6,6'-positions. This finding is in agreement with the observations reported by Pu and co-workers on a family of optically active dendrimers containing a 1,1'-binaphthyl core with cross-conjugated phenylene dendrons at the 4,4'- and 6,6'-positions.⁸ The authors suggest that, in this case, the changes in molar optical rotation with increasing dendron generation might not be solely due to a change in the binaphthyl dihedral angle. In our case also the increased steric interactions between phenylenevinylene units may play an effective role in the molar optical rotation variation.

Electrochemical Behavior. The electrochemical features of the binaphthyl-based phenylene dendrimers were investigated by cyclic voltammetry at room temperature (Table 1). Dichloromethane was used as the solvent, and tetrabutylammonium perchlorate (0.1 M) was employed as the supporting electrolyte in a conventional three-compartment cell, equipped with glassy carbon, SCE, and platinum wire as electrode, reference electrode, and auxiliary electrode, respectively.

The redox behavior of the stilbenoid dendrons shows an anodic shift of the oxidation potentials on going from the trifluoromethane- and methoxy-based systems to the

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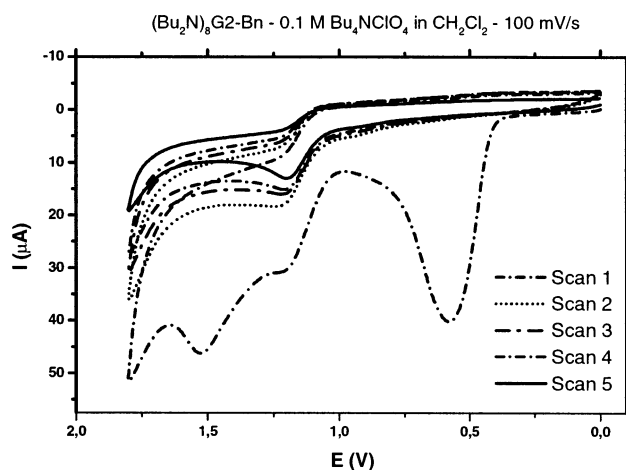


FIGURE 3. Cyclic voltammograms for dendrimer **(NBu₂)₈G2-Bn** at room temperature (solvent CH₂Cl₂, supporting electrolyte 0.1 M Bu₄NClO₄, scan rate 100 mV/s).

more strongly electron-donating dibutylamino-based analogues **(Bu₂N)₄G1-Bn** and **(Bu₂N)₈G2-Bn** ($E_{\text{ox}}^1 \approx 0.6$ V).

As far as the reduction potentials are concerned, only the trifluoromethane-based systems show an electrochemically irreversible wave ($E_{\text{red}}^1 \approx -0.9$ V, $\Delta E \approx 100$ mV) within the window of the solvent. This electrochemical behavior is in agreement with the stronger donating ability of the dibutylamino group and the stronger accepting ability of the trifluoromethane moiety. Thus, the redox behavior of these systems depends on the electronic nature of the functional groups at peripheral positions of the dendrons. As expected, the CV of the CF₃-substituted dendrimer shows the reduction peak at around -0.9 V, thus showing the acceptor ability of these dendrons. Regarding the oxidation potential of the dendritic structures, the first oxidation potential appears at around 0.6 V for the NBu₂-substituted derivatives, 1.09 V for the methoxy derivatives, and around 1.1 V for the CF₃ derivatives. These oxidation potential values could suggest that the *N,N*-dibutylstilbene moiety is responsible for the first oxidation potential observed for **(Bu₂N)₄G1-Bn** and **(Bu₂N)₈G2-Bn**, whereas in the MeO- and CF₃-derivatives the central core involving the naphthalene unit is responsible for the first oxidation potential observed.

A most interesting observation for these optically active dendrimers is that the first two irreversible oxidation potentials, which are observed after one single scan, disappear after multiple scans while a new chemically reversible oxidation wave ($\Delta E \approx 100$ mV) appears between the previously observed waves (see Table 1, Figure 3). This behavior clearly indicates that the dendrimers are electrochemically unstable and, after the first oxidation, give rise to a new electroactive species that exhibits electrochemically reversible behavior. This electrochemical behavior, as well as the characterization of the species formed, requires further electrochemical studies, and these are currently under way in our laboratories. However, the lack of stability of the radical-cations could be a problem for their further use in the preparation of organic LEDs.

Conclusions

In summary, we have developed a general synthetic route for the preparation of optically active stilbenoid dendrimers containing enantiopure binaphthyl cores. In the present study we focused our attention on the possibility of tuning both optical and redox properties by means of chemical modification of the peripheral groups on the dendrimers. Considering the large number of functionalized fluorophores synthesized in recent years with specific electrochemical and photophysical properties, we feel that a remarkable aspect of this contribution is that it represents an effective approach to the synthesis of chiral luminescent materials in which the emission colors, electron affinity, and ionization potentials can be efficiently tailored.

Unfortunately, on the basis of the electrochemical results, this particular group of compounds may not be suitable for LEDs because of redox instability; however, given the good solubility imparted by the long alkyl chains and the strong fluorescence of these systems, they may also be useful as fluorescent sensors for the discrimination of chiral molecules.

Experimental Section

General. The general experimental conditions have been reported previously.^{15a} $[\alpha]_{\text{D}}$ values were determined using a sodium lamp ($\lambda = 589$ nm) at room temperature in a cylindrical cell of 1 dm length and a volume of 1 mL. Cyclic voltammograms were recorded on a potentiostat/galvanostat equipped with electrochemical analysis software and a GCE (glassy carbon) as working electrode, SCE as reference electrode, Bu₄NClO₄ as supporting electrolyte, and dichloromethane as solvent. The mass spectra were obtained by the Universidad Autónoma de Madrid (Servicio Interdepartamental de Investigación, S.I.D.I.) mass spectroscopy facility. Spectra matrices: 3-nitrobenzyl alcohol (HRMS, LSIMS) and dithranol (MALDI-TOF). Poly(ethylene glycol) was used for internal calibration.

Binaphthyl phosphonate derivative **(R)-1**¹⁶ and dendrons **(R)_{2n}G_n-CHO**^{15a} were prepared according to procedures previously reported by us.

General Procedure for Horner–Wadsworth–Emmons Reaction. Method A. All glassware was oven-dried and cooled under Ar. To a stirred solution of the diphosphonate **(R)-1** (0.1 mmol) and the corresponding dendritic aldehyde **(R)_{2n}G_n-CHO** (0.2 mmol) in anhydrous THF (10 mL) under argon was added potassium *tert*-butoxide (0.6 mmol) in small portions. The red mixture was stirred at room temperature for the indicated period of time. The reaction was quenched with water, neutralized with 1 N HCl, extracted with CH₂Cl₂ ($\times 3$), and dried (MgSO₄). After filtration and evaporation of the solvent, the crude product was either washed with CHCl₃/EtOH and the insoluble dendrimer isolated by filtration or purified by column chromatography (silica gel, hexanes/EtAcO mixtures). **Method B.** All operations were identical to those described for Method A except that, after quenching and neutralization, the insoluble compound was isolated by filtration.

(OMe)₄G1-Bn. Method A. Reaction time: 5 h. White solid. Yield: 95%. ¹H NMR (CDCl₃): δ 0.85 (t, 6H, $J = 6.9$ Hz), 0.87–1.50 (m, 40H), 3.84 (s, 12H), 3.90–4.10 (m, 4H), 6.92 (A of ABq, 8H, $J = 8.7$ Hz), 7.01 (A of ABq, 4H, $J = 16.2$ Hz), 7.16 (B of ABq, 4H, $J = 16.2$ Hz), 7.12–7.36 (m, 8H), 7.42 (d, 2H, $J = 9.0$ Hz), 7.49 (B of ABq, 8H, $J = 8.7$ Hz), 7.50–7.53 (m, 6H), 7.92 (d, 2H, $J = 1.2$ Hz), 7.95 (d, 2H, $J = 9.0$ Hz). ¹³C NMR and DEPT (CDCl₃): δ 159.3 (C), 154.9 (C), 138.2 (two signals, 2 C), 133.9 (C), 132.4 (C), 130.1 (C), 129.3 (two signals, 2 C), 128.6 (CH), 127.8 (CH), 127.6 (CH), 126.9 (CH), 126.4 (CH),

125.9 (CH), 123.8 (CH), 123.3 (CH), 120.6 (C), 116.0 (CH), 114.1 (CH), 69.6 (OCH₂), 55.3 (OCH₃), 32.0 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 29.6 (two signals, 2 CH₂), 29.4 (two signals, 2 CH₂), 29.2 (CH₂), 25.7 (CH₂), 22.7 (CH₂), 14.2 (CH₃). HRMS (LSIMS) *m/e* calcd for C₉₆H₁₀₆O₆ 1354.7989, found 1354.7998.

(OMe)₈G2-Bn. Method A. Reaction time: 5 h. White solid. Yield: 70%. ¹H NMR (CDCl₃): δ 0.85 (t, 6H, *J* = 6.6 Hz), 0.90–1.50 (m, 40H), 3.82 (s, 24H), 3.88–4.06 (m, 4H), 6.91 (A of ABq, 16H, *J* = 8.7 Hz), 7.00 (A of ABq, 8H, *J* = 16.2 Hz), 7.15 (B of ABq, 8H, *J* = 16.2 Hz), 7.15–7.40 (m, 16H), 7.42 (d, 2H, *J* = 9.0 Hz), 7.48 (B of ABq, 16H, *J* = 8.7 Hz), 7.44–7.60 (m, 18H), 7.90–7.96 (m, 4H). ¹³C NMR (CDCl₃): δ 159.3, 154.9, 138.2, 138.1, 137.9, 137.8, 133.9, 132.3, 130.0, 129.3, 128.9, 128.6, 127.8, 127.0, 126.3, 124.0, 123.7, 123.4, 120.6, 115.9, 114.1, 69.6, 55.3, 32.0, 29.8, 29.7, 29.6, 29.4 (two signals), 29.2, 29.1, 25.7, 22.7, 14.2. HRMS (LSIMS) *m/e* calcd for C₁₆₄H₁₆₂O₁₀ 2291.2168, found 2291.2237.

(NBu₂)₄G1-Bn. Method A. Reaction time: 15 h. Purified by column chromatography. Yellow oil. Yield: 94%. ¹H NMR (CDCl₃): δ 0.86 (t, 6H, *J* = 6.9 Hz), 0.96 (t, 24H, *J* = 7.5 Hz), 0.9–1.3 (m, 40H), 1.30–1.50 (m, 16H), 1.50–1.68 (m, 16H), 3.29 (t, 16H, *J* = 7.5 Hz), 3.88–4.05 (m, 4H), 6.64 (A of ABq, 8H, *J* = 9.0 Hz), 6.91 (A of ABq, 4H, *J* = 15.9 Hz), 7.12 (B of ABq, 4H, *J* = 16.2 Hz), 7.16 (A of ABq, 2H, *J* = 15.9 Hz), 7.20 (d, 2H, *J* = 8.4 Hz), 7.33 (B of ABq, 2H, *J* = 16.2 Hz), 7.41 (B of ABq, 8H, *J* = 8.7 Hz), 7.47 (broad s, 8H), 7.52 (dd, 2H, *J* = 9.0 Hz, *J* = 1.2 Hz), 7.90–7.97 (m, 4H). ¹³C NMR and DEPT (CDCl₃): δ 154.8 (C), 147.8 (C), 138.8 (C), 137.9 (C), 133.8 (C), 132.6 (C), 129.4 (C), 129.2 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.8 (CH), 126.7 (CH), 125.9 (CH), 124.5 (C), 123.8 (CH), 123.6 (CH), 122.8 (CH), 122.4 (CH), 120.7 (C), 116.0 (CH), 111.6 (CH), 69.7 (OCH₂), 50.8 (NCH₂), 32.0 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 25.7 (CH₂), 22.7 (CH₂), 20.4 (CH₂), 14.1 (CH₃), 14.0 (CH₃). MALDI-TOF (C₁₂₄H₁₆₆N₄O₂) *m/e* 1743.8.

(NBu₂)₈G2-Bn. Method A. Reaction time: 17 h. Purified by column chromatography. Yellow oil. Yield: 84%. ¹H NMR (CDCl₃): δ 0.85 (t, 6H, *J* = 7.2 Hz), 0.96 (t, 48H, *J* = 7.5 Hz), 0.9–1.3 (m, 40H), 1.30–1.50 (m, 32H), 1.50–1.68 (m, 32H), 3.29 (t, 32H), 3.9–4.1 (m, 4H), 6.65 (A of ABq, 16H, *J* = 8.7 Hz), 6.93 (A of ABq, 8H, *J* = 16.2 Hz), 7.14 (B of ABq, 8H, *J* = 16.2 Hz), 7.23–7.66 (m, 34H), 7.43 (B of ABq, 16H, *J* = 8.7 Hz), 7.57 (d, 2H, *J* = 9.0 Hz), 7.94–8.00 (m, 4H). ¹³C NMR (CDCl₃): δ 154.9, 147.8, 138.9, 138.3, 138.1, 137.6, 133.9, 132.4, 129.3, 129.2, 128.4, 127.8, 126.9, 125.8, 124.5, 123.9, 123.7,

123.5, 123.2, 122.5, 120.7, 116.0, 111.6, 69.7, 50.8, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 25.7, 22.7, 20.4, 14.1 (CH₃), 14.0 (CH₃). MALDI-TOF *m/e* 3070.0.

(CF₃)₄G1-Bn. Method A. Reaction time: 5 h 30 min. White solid. Yield: 71%. ¹H NMR (CDCl₃): δ 0.83 (t, 6H, *J* = 7.2 Hz), 0.9–1.5 (m, 40H), 3.90–4.05 (m, 4H), 7.13 (A of ABq, 2H, *J* = 16.2 Hz), 7.19 (s, 8H), 7.23 (d, 2H, *J* = 8.7 Hz), 7.33 (B of ABq, 2H, *J* = 16.2 Hz), 7.43 (d, 2H, *J* = 9.3 Hz), 7.52 (dd, 2H, *J* = 9.0 Hz, *J* = 1.2 Hz), 7.53 (broad s, 2H), 7.58 (d, 4H, *J* = 1.2 Hz), 7.60 (s, 16H), 7.91 (d, 2H, *J* = 1.5 Hz), 7.94 (d, 2H, *J* = 9.3 Hz). ¹³C NMR (CDCl₃): δ 155.0, 140.6, 138.5, 137.4, 134.0, 132.1, 130.7, 130.1[#], 129.9, 129.6[#], 129.6^{*}, 129.4, 129.3, 129.2, [#]128.8[#] ([#]q, *J* = 32 Hz), 127.8, 127.1, 126.6, 126.0^{*}, 125.6 (q, *J* = 4 Hz), 124.6, 124.1, 123.7, ^{*}120.5, 118.8^{*} (^{*}q, *J* = 270 Hz, CF₃), 116.0, 69.6, 32.0, 29.8, 29.7, 29.6, 29.4, 29.2, 25.7, 22.7, 14.1. MALDI-TOF (C₉₆H₉₄F₁₂O₂) *m/e* 1507.2.

(CF₃)₈G2-Bn. Method B. Reaction time: 6 h. White solid. Yield: 63%. ¹H NMR (THF-*d*₆): δ 0.85 (t, 6H, *J* = 6.9 Hz), 1.0–1.5 (m, 40H), 3.95–4.10 (m, 4H), 7.19–7.82 (m, 84H), 7.98–8.04 (m, 4H). ¹³C NMR and DEPT (THF-*d*₆): δ 156.1 (C), 142.3 (C), 139.6 (C), 139.4 (C), 139.1 (C), 138.8 (C), 135.0 (C), 133.4 (C), 132.8 (CH), 131.9 (CH), 130.9^{*}, 130.5[#], 130.5 (CH), 130.2 (CH), 130.2 (CH), 130.1[#], 129.7[#], 129.5 (CH), 129.3[#] ([#]q, *J* = 31.6 Hz, C), 128.7 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.3^{*}, 126.8 (CH), 126.5 (q, *J* = 4 Hz, CH), 125.6 (CH), 125.1 (CH), 124.6 (CH), 124.4 (CH), 123.6^{*}, 121.4 (C), 120.1^{*} (^{*}q, *J* = 270 Hz, CF₃), 116.5 (CH), 70.0 (OCH₂), 32.9 (CH₂), 30.8 (CH₂), 30.7 (CH₂), 30.6 (CH₂), 30.4 (CH₂), 30.4 (CH₂), 30.2 (CH₂), 26.8 (CH₂), 23.6 (CH₂), 14.5 (CH₃). MALDI-TOF (C₁₆₄H₁₃₈F₂₄O₂) *m/e* 2596.8.

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Supporting Information Available: Copies of ¹H NMR and ¹³C NMR spectra for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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