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Synthesis of New 1,1′-Binaphthyl-Based Chiral Phenylenevinylene Dendrimers

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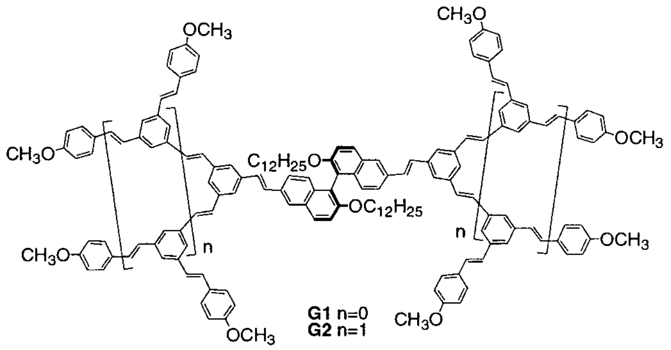
ABSTRACT



Dendrimeric *meta*-substituted phenylenevinylene moieties have been incorporated on a chiral binaphthyl core, providing new chiral and photoluminescent molecules.

Dendrimers have become a subject of intense research in recent years as a result of their unique structures and properties.[1] Among them, optically active dendrimers[2] can be used to carry out asymmetric processes. They respond differently toward the left and right circularly polarized lights and are potentially useful as chiral sensors to recognize the enantiomers of chiral molecules. It is noteworthy that the chirality is almost always introduced by using stereocenters. So far, only a few examples are known in which axial chirality is reported.[3] Dendrimeric structures have been tested as efficient light harvesting antennae[4] and suitable compounds for application in optoelectronics.[5] Pu et al. have recently used 1,1′-bi-2-naphthol derivatives to construct novel

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(1) For recent reviews see: (a) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (b) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193. (c) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (d) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681. (e) Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353. (f) Newcome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Macromolecules: Concepts, Syntheses, Perspectives*; VCH: Weinheim, Germany, 1996. (g) Gorman, C. *Adv. Mater.* **1998**, *10*, 295.

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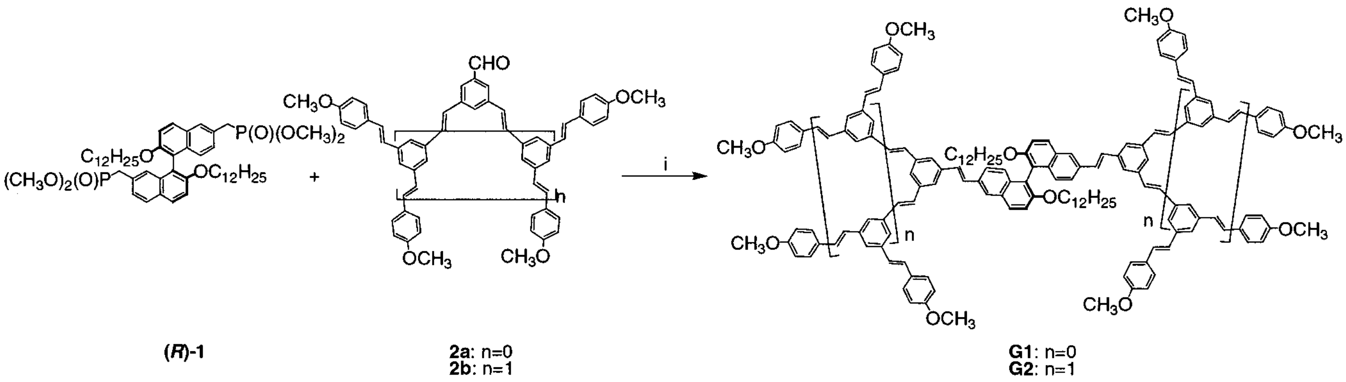
Scheme 1. Synthesis of Binaphthyl Derivatives Coontaining Conjugated Dendritic Wedges[a]



[a] Reagents and conditions: (i) ^{t}BuOK, THF, rt.

rigid and cross-conjugated optically active dendrimers with phenylacetylene-based dendrons.[3b] They demonstrate that there is a very efficient energy migration from the cross-conjugated dendrons to the center core, leading to greatly enhanced fluorescences at higher generations. This is the first example of an efficient energy migration conducted in an optically pure dendritic system, which is potentially useful in developing an enantioselective fluorescence sensor.

On the other hand, *p*-phenylenevinylene oligomers are one of the most studied systems,[6] and blue electroluminescence has been demonstrated in poly(*p*-phenylene vinylene) derivatives.[7] Blue-luminescent organic materials are very limited.[8]

In this goal we report here the synthesis, chiroptical, spectroscopic, and electrochemical features of dendrimers **G1** and **G2**, which have been prepared in good yields by Horner−Wadsworth−Emmons reaction of a 1,1′-binaphthyl derivative, ***(R)*-1**,[9] and the appropriate dendrons, **2a** and **2b**, in KBu^{t}O−THF (Scheme 1).[10] Compounds **2a** and **2b** were synthesized following a methodology previously reported by some of us.[11] The long hydrocarbon chains at the core have been incorporated to ensure the solubility of the target molecules. Both of them were obtained as unique all-*trans* isomers, as determined by ^{1}H NMR spectroscopy.

Since these new dendrimers were synthesized from enantiomerically pure (*R*)-binaphthyl derivatives, chiral compounds were obtained with optical rotations ($[\alpha]_D$) of −299° ($c = 1 \times 10^{-3}$, $CHCl_3$) for **G1** and −110° ($c = 1 \times 10^{-3}$, $CHCl_3$) for **G2**.

The results of UV−vis and fluorescence measurements of **G1** and **G2** in methylene dichloride at room temperature are shown in Figure 1. Because of the *meta* arrangement of the dendrons linked, it was expected that the observed absorption spectra would consist of a superposition of the absorptions due to the stilbene dendrons and the binaphthyl core. Thus, the maximum at 329.5 nm for **G1** ($c = 1 \times 10^{-6}$ M) is associated with the stilbene units in the dendron, and the shoulder at 340.5 nm is associated with the core. When the spectrum was registered at a 10-times lower concentration ($c = 1 \times 10^{-7}$ M), two resolved bands were observed instead. When recording spectra of different samples at a range of concentrations between 10^{-5} and 10^{-8} M, changes in shape, shift, and chromicity of the bands were also detected. Although at this moment we do not have a satisfactory explanation for these effects, a concentration-dependent aggregation could be assumed. Changes at the ultraviolet and fluorescence spectra of stilbenoid units indicative of association has been widely observed.[5c,12] The absorption spectrum of **G2** is similar to that of **G1**. A band with a maximum at 326.5 nm ($c = 1 \times 10^{-6}$ M) and a shoulder at 340.5 nm were observed (when $c = 1 \times 10^{-7}$ M two separated bands appeared again). The fluorescence spectra have typical bands for stilbenoid compounds at 409

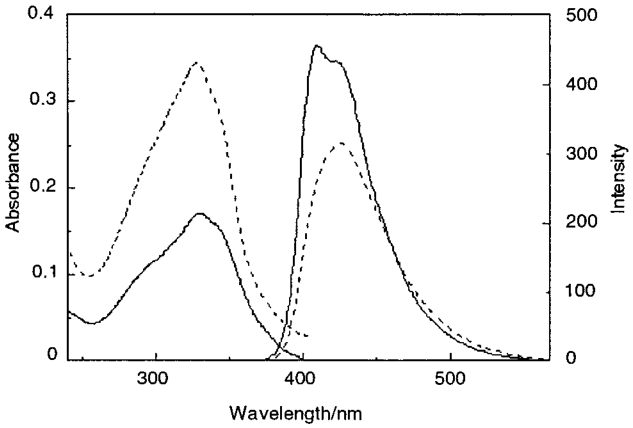


Figure 1. UV−vis absorption ($c = 1 \times 10^{-6}$ M) and fluorescence spectra ($c = 1 \times 10^{-7}$ M) of **G1** (full line) and **G2** (dashed line) in CH_2Cl_2 at room temperature. The excitation wavelength is 329.5 nm for **G1** and 326.5 nm for **G2**.

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(**G1**) and 425 (**G2**) nm together with a shoulder at 425 nm (observed only for **G1**). Although it has been claimed for stilbene dendrons that the absence of any shorter wavelength emission for excitation in the range 300−400 nm shows that energy transfer to the core is very efficient,[5b] these results do not permit us unequivocally to assume that fact for this kind of compound.[13] Anyway, both molecules are new chiral blue-emitting phenylenevinylene-based dendrimers that are highly fluorescent.

The electrochemical properties of the new dendrimers were studied by cyclic voltammetry (CV) at room temperature in dichloromethane as solvent, glassy carbon as working electrode, and SCE as reference electrode. The CV of dendrimers **G1** and **G2** show the presence of an irreversible oxidation wave at 1.38 and 1.31 V, respectively, and a second oxidation wave is observed for **G2** at 1.73 V. These first oxidation potentials should correspond to the oxidation of each independent dendrimeric moiety in **G1** and **G2**, since for comparison, **2a** exhibits an oxidation potential at 1.38 V and an oxidation wave at 1.51 V was found for the parent bisdodecyloxybinaphthyl as reference.

In summary, we have synthesized new soluble conjugated chiral luminescent dendrimers with electron-donor character that are appealing systems for the preparation of optoelectronic devices.

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[10] **General Procedure for the Horner−Wadsworth−Emmons Reaction.** To a stirred solution of the diphosphonate ***(R)*-1** (0.1 mmol) and the corresponding dendritic aldehyde **2a,b** (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 then stirred at room temperature. After 5 h, it was quenched with water, neutralized with 1 N HCl, extracted with CH_2Cl_2 (x3), and dried ($MgSO_4$). After filtration and evaporation of the solvent, the crude product was washed with CH_3Cl/EtOH, and the insoluble dendrimer was isolated by filtration. **G-1:** yield 95%. ^1H NMR ($CDCl_3$): δ 0.85 (t, 6H, $J = 6.9$ Hz, 2 × CH_3), 0.87−1.50 (m, 40H, 20 × CH_2), 3.84 (s, 12H, 4 × OCH_3), 3.90−4.10 (m, 4H, 2 × OCH_2), 6.92 (A of ABq, 8H, $J = 8.7$ Hz, arom.), 7.01 (A of ABq, 4H, $J = 16.2$ Hz, 4 × CH═), 7.16 (B of ABq, 4H, $J = 16.2$ Hz, 4 × CH═), 7.12−7.36 (m, 8H, core and 4 × CH═), 7.42 (d, 2H, $J = 9.0$ Hz, core), 7.49 (B of ABq, 8H, $J = 8.7$ Hz, arom.), 7.50−7−53 (m, 6H, arom.), 7.92 (d, 2H, $J = 1.2$ Hz, core), 7.95 (d, 2H, $J = 9.0$ Hz, core). ^{13}C NMR and DEPT ($CDCl_3$): 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 (OCH_2), 55.3 (OCH_3), 32.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (two signals, 2 CH_2), 29.4 (two signals, 2 CH_2), 29.2 (CH_2), 25.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3). HRMS *m*/*e* calcd for $C_{96}H_{106}O_6$ 1354.7989; found 1354.7998. **G-2:** yield: 70%. ^1H NMR ($CDCl_3$): δ 0.85 (t, 6H, $J = 6.6$ Hz, 2 × CH_3), 0.90−1.50 (m, 40H, 20 × CH_2), 3.82 (s, 24H, 8 × OCH_3), 3.88−4.06 (m, 4H, 2 × OCH_2), 6.91 (A of ABq, 16H, $J = 8.7$ Hz, arom.), 7.00 (A of ABq, 8H, $J = 16.2$ Hz, 8 × CH═), 7.15 (B of ABq, 8H, $J = 16.2$ Hz, 8 × CH═), 7.15−7.40 (m, 16H, core and 12 × CH═), 7.42 (d, 2H, $J = 9.0$ Hz, core), 7.48 (B of ABq, 16H, $J = 8.7$ Hz, arom.), 7.44−7−60 (m, 18H, arom.), 7.90−7.96 (m, 4H, core). ^{13}C NMR ($CDCl_3$): 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 (OCH_2), 55.3 (OCH_3), 32.0, 29.8, 29.7, 29.6, 29.4 (two signals), 29.2, 29.1, 25.7, 22.7, 14.2 (CH_3). HRMS *m*/*e* calcd for $C_{164}H_{162}O_{10}$ 2291.2168; found 2291.2237.

[11] Structures of type **2** show fluorescence spectra with bands at 396−414 nm.

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