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Synthesis of Photo- and Electroactive Stilbenoid Dendrimers Carrying Dibutylamino Peripheral Groups

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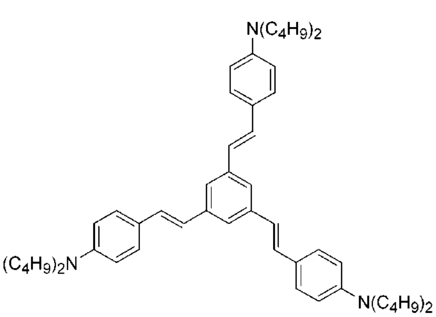
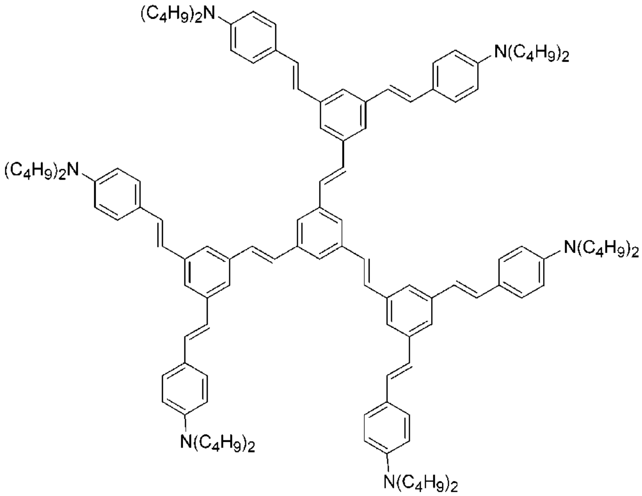
ABSTRACT





A novel convergent synthetic route for the preparation of functionalized and fluorescent stilbenoid dendrons built on the 1,3,5-benzene core and endowed with a periphery of dibutylamino groups has been developed. Long alkyl chains have been incorporated on the peripheral amino moieties to increase the solubility of the final products. Good donor ability of the new dendrimers has been observed by cyclic voltammetry measurements as a result of the presence of the peripheral dibutylaniline moieties.

On the basis of their unique properties, monodisperse dendritic materials emerged as attractive candidates for photonic applications. For example, dendritic macromolecules have been blended into organic light emitting diodes (OLEDs) as either (i) hole[1] transporting components or (ii) electron[2] transporting components or even as (iii) single-component emitters.[3] Shirota and co-workers developed a concept of π-electron starburst molecules such as triarylamine-based dendritic molecules. The latter have been successfully employed as hole transport layers in OLEDs.[4] On the other hand, the interesting photophysical and photochemical[5] properties of stilbenoids evoked the incorporation of stilbenoid chromophores into dendrimers. Only very

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[1] Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677.
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[4] Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.
[5] (a) Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399. (b) Lewis, F. D.; Kalgutkar, R. S.; Yang, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 12045.

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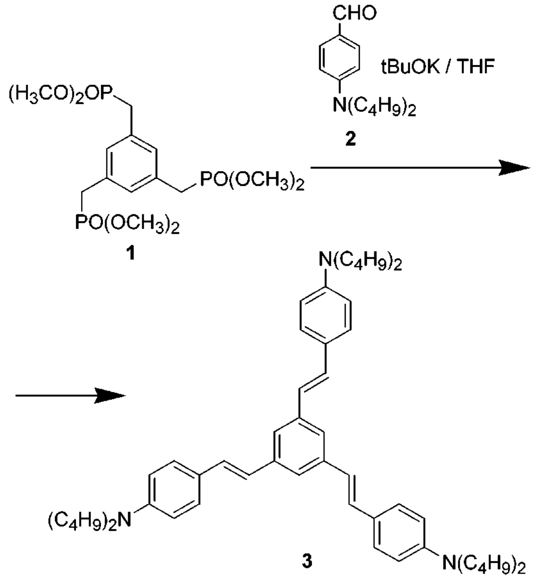
recently, several synthetic routes have been developed to achieve this target.[6]

In this Letter we wish to report a new convergent synthetic route toward dendrimeric compounds that combines a stilbenoid skeleton and an array of electron-donating dibutylamine groups bearing solubilizing alkyl chains on the peripheral positions.

The first generation dendrimer (**3**) was obtained in 30% yield following the Wittig−Horner reaction between triphosphonate (**1**) and 4-(*N*,*N*-dibutylaminobenzaldehyde (**2**) in dry tetrahydrofuran, using potassium *tert*-butoxide as base (Scheme 1).

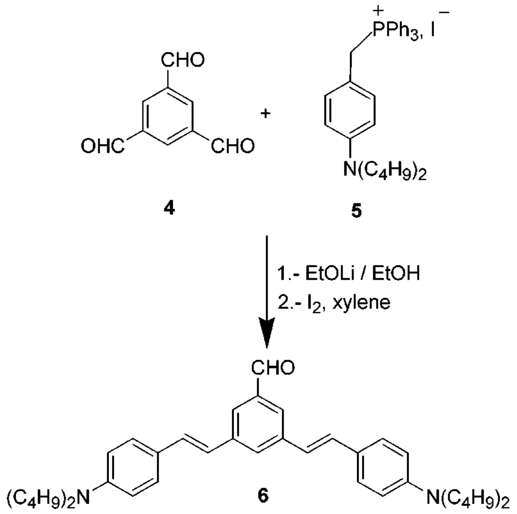
Scheme 1. Synthesis of First-Generation Dendrimer **3**



To grow subsequent generations of dendrimeric ensembles, through a convergent synthetic route, necessitated the design of stilbenoid AB_2 building block **6** by following three different strategies (Schemes 2 and 3).

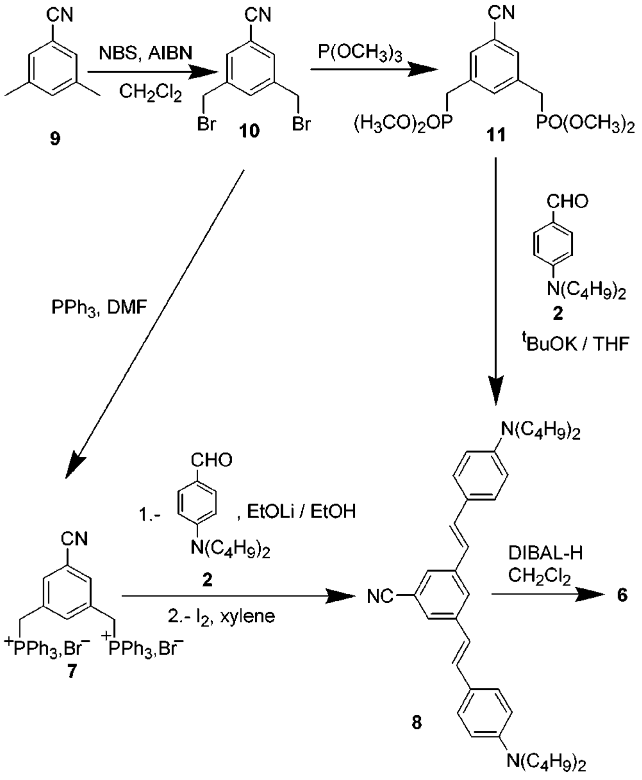
The first strategy involves the Wittig reaction between 1,3,5-triformylbenzene[7] (**4**) and 4-(*N*,*N*,-dibutylaminobenzyl)-triphenylphosphonium iodide[8] (**5**) in dry ethanol, using lithium ethoxide as base, under stoichiometric control. This afforded **6** as a mixture of three possible configurational isomers. In a second step, iodine-catalyzed thermal isomerization of the mixture led to the all-*trans* isomer **6** in 65% yield (Scheme 2).

Scheme 2. Synthesis of Stilbenoid AB_2 Building Block **6**



An alternative route involves the preparation of intermediates **8** and **11** as precursors to synthesize higher generation dendrimers. Bromination of 3,5-dimethylbenzonitrile[9] (**9**) under radical conditions gave the 3,5-bis(bromomethyl)-benzonitrile[10] (**10**) as a white solid. Subsequent treatment of **10** with triphenylphosphine in dimethylformamide allowed us to obtain the 3,5-bis(triphenylphosphoniummethyl)-benzonitrile (**7**) in 70% yield. On the other hand, reaction

Scheme 3. Alternative Syntheses of Stilbenoid AB_2 Building Block **6**



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(6) (a) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079. (b) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 643. (c) Meier, H.; Lehmann, M.; Kolb, U. *Chem. Eur. J.* **2000**, *6*, 2462. (d) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1999**, *32*, 5985. (e) Díez-Barra, E.; García-Martínez, J. C.; Rodríguez López, J.; Gómez, R.; Segura, J. L.; Martín, N. *Org. Lett.* **2000**, *2*, 3651. (f) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Bässler, H. *Adv. Mater.* **2001**, *13*, 258.

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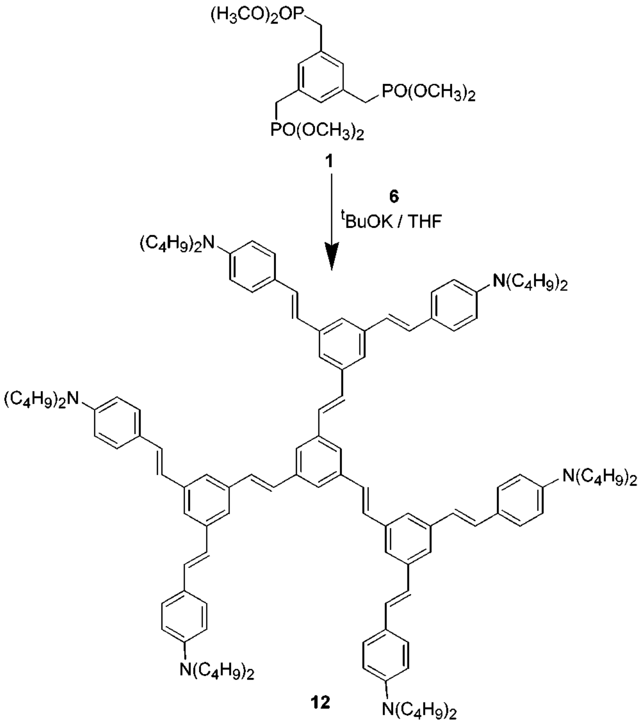
of **10** with excess trimethyl phosphite led to the corresponding bis(phosphonate) **11** in 84% yield as a white solid. Wittig reaction between **7** and 4-(*N*,*N*-dibutylamino)benzaldehyde (**2**) in dry ethanol, using lithium ethoxide as base, afforded **8** as a mixture of isomers. Again, iodine-catalyzed thermal isomerization of the mixture afforded **8** as an all-*trans* isomer.

In the third strategy the direct synthesis of the all-*trans* **8** was pursued, and 67% yield was accomplished by the Wittig−Horner reaction between bis(phosphonate) **11** and aldehyde **2** in dry THF at 0 °C, using potassium *tert*-butoxide as base. Treatment of a dichloromethane solution of **8** with a stoichiometric amount of DIBAL-H (1.0 M) afforded the pure all-*trans* isomer **6** in 73% yield.

Wittig−Horner reaction between tris(phosphonate) **1** and aldehyde **6** in dry THF at 0 °C, using potassium *tert*-butoxide as base, afforded the second-generation dendrimer **12** as a yellow compound in a 40% yield (Scheme 4). The presence of the peripheral dibutylamino groups provides enhanced solubility of this compound, and therefore appropriate spectroscopic[11] and electrochemical characterization could be carried out.

Scheme 4. Syntheses of Second-Generation Dendrimer **12**



An overall advantage of the convergent route presented in this communication is the use of a nitrile group in the readily available AB_2 starting material **9**. Importantly, this functionality remains unaffected during the subsequent workup and could be easily converted, in the final step, to the reactive aldehyde group. It is worth to point out that, in our hands, previously reported synthetic routes toward stilbenoid dendrimers[12] have failed to obtain higher generations of dendrimers containing peripheral dibutylamino groups. This is due to the basic requirement of oxidizing a benzylic alcohol to the corresponding aldehyde as a key step to obtain the intermediate dendrons. However, the strong electron-donor character of the dibutylaniline groups limits the stability of these compounds under oxidation conditions as a result of the possibility of electron transfer processes. In the present approach, this intrinsic problem has been efficiently overcome by using nitrile functionalities. The latter can be readily converted into the corresponding aldehydes upon selective reduction conditions, thus avoiding the oxidation process.

The new dendrimers show in dichloromethane ground-state absorption maxima at 373 and 379 nm for the second and first generation, respectively (see Figure 1). A marked red shift is noted in these transitions, relative to the absorption of distyrylbenzene (λ_{max} = 360 nm),[13] caused by the dialkylamino substituted stilbene units. Moreover, the second-generation dendrimer shows an additional 337 nm shoulder, stemming from the core stilbenoid system, which lacks the

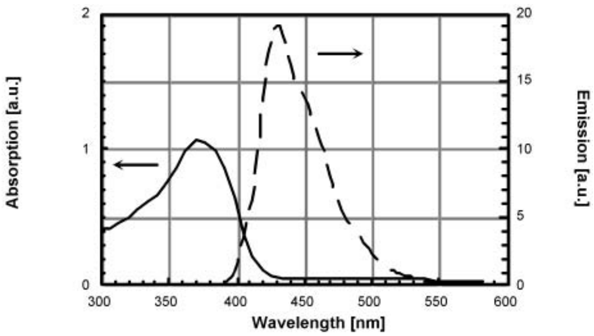


Figure 1. Absorption (solid line) and emission (dashed line) spectra (λ_{exc} 380 nm) of dendrimer **12**.

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[11] Dendrimers were characterized on the basis of the FTIR and ^1H and ^{13}C NMR analyses for which satisfactory results were obtained. Synthetic procedure for **12**: Under argon atmosphere, 1 mmol of trisphosphonate **1** and 3 mmol of aldehyde **6** were disolved in dry THF at 0 °C. Afterwards, 3 mmol of potassium *tert*-butoxide was added portionswise, and the reaction was allowed to stand for 10 min. After this time, first methanol and then water were added. The layers were separated and extracted with chloroform. The combined organic layers were washed with water, dried over magnesium sulfate, and then evaporated to yield a solid that was purified by chromatography. Yield: 40%. Selected data for **12**: FT-IR (KBr) ν 2955, 2926, 2854, 1607, 1585, 1518, 1367, 1221, 959 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.60 (s, 3H), 7.43 (s, 3H), 7.37 (d, 12H, J = 8.6 Hz), 7.21 (s, 3H), 7.09 (d, 9H, J_{trans} = 16.2 Hz), 6.87 (d, 9H, J_{trans} = 16.2 Hz), 6.59 (d, 12H, J = 8.6 Hz), 3.23 (t, 24H), 1.53 (m, 24H), 1.39−1.21 (m, 24H), 0.90 (t, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 144.76, 135.83, 135.09, 134.62, 134.60, 126.39, 126.18, 121.42, 120.95, 120.46, 120.44, 120.38, 119.50, 108.55, 47.73, 26.62, 17.29, 13.87.

[12] Díez-Barra, E.; García-Martínez, J.; Rodríguez-López, J. *Tetrahedron Lett.* **1999**, *40*, 8181. See also: Díez-Barra, E.; García-Martínez, J. C.; Merino, S.; Del Rey, R.; Rodriguez-López, J.; Sánchez-Verdú, P.; Tejada, J. *J. Org. Chem.*, in press.

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conjugation with the peripheral *p*-dialkylaminostyryl groups because of the chosen *meta* linkage.

Cyclic voltammetry measurements, conducted with **3** and **12** in dichloromethane, reveal an irreversible oxidation wave at +0.59 V for both compounds. For the second-generation dendrimer a second irreversible oxidation wave is observed at +1.46 V. This suggests that, in contrast to stilbenoid dendrimers containing a nitrogen core,[6f] where the first oxidation step is directed to the core, in these new dendrimers, the first oxidation occurs at the periphery, that is, the dialkylaminostilbene units. The second oxidation, which was solely seen for **12**, is then assigned to the core (i.e., stilbenoid unit). In agreement with these findings, the parent *p*-(*N*,*N*-dibutylamino)stilbene used as reference exhibits an irreversible oxidation wave at +0.65 V under the same experimental conditions.

In analogy to the basic constituent of **3** and **12**, namely, a conjugated stilbene unit, both dendrimers are strong fluorophores. Their singlet-excited states exhibit, mirror-imaged to the ground-state absorption, a long-lived emission (**3**, $\tau = 2.19$ ns; **12**, $\tau = 2.1$ ns) at 430 nm, produced in high quantum yields (**3**, $\Phi = 0.55$; **12**, $\Phi = 0.55$), measured relative to a 9,10 diphenyl anthracene ($\Phi = 1$) (see Figures 1 and 2). It should be noted that these values differ, nevertheless, from those seen for stilbenes ($\tau = 0.075$ ns; $\Phi = 0.036$), in which "*cis*−*trans*" isomerization dominates (>95%) the deactivation of the singlet excited state. Therefore, with the scope to suppress this contribution we added *p*-(*N*,*N*-dibutylamino)stilbene to the emission assay, in which one of the two arenes is substituted at the *para* position with a bulky dibutylamino substituent. Indeed, the high fluorescence quantum yield ($\Phi = 0.22$) and the fluorescence lifetime ($\tau = 0.11$ ns), as measured at the 425 maximum, further support the features associated with the fluorescence of dendrimers **3** and **12**.

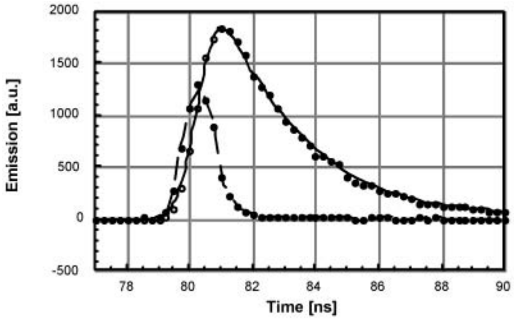

Figure 2. Fluorescence decay profiles for dendrimer **12** ($\sim 2.0 \times 10^{-5}$ M) in deoxygenated toluene (solid line). In addition, the lamp scatter is shown (dashed line).

As far as transient absorption characteristics of this new class of dendrimers are concerned, short laser excitation (20 ps; 355 nm) generates a broadly absorbing singlet−singlet excited-state absorption, which centers around 650 nm (not shown). The singlet lifetimes, which were determined by fitting the singlet−singlet decay to a monoexponential rate law, are 2.25 ns (**3**) and 2.06 ns (**12**). In other words they are in excellent agreement with the emissive component of the singlet excited state.

In conclusion, we have presented a new convergent synthetic strategy en route to stilbenoid dendrimers carrying a periphery of dibutylamino substituents. The synthesis of the stilbenoid AB_2 building blocks **6** and **11** paves the way for the convergent synthesis of higher generation dendrimeric systems. Furthermore, as a result of the good donor ability exhibited by these systems and the enhanced solubility provided by the presence of peripheral dibutylamino groups, the AB_2 system **6** can be an appealing molecule to study the charge-transport and processability properties of materials for OLEDs and photovoltaic devices.

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