Preparation and Assembled Structure of Dipolar Dendrons Based Electron Donor/Acceptor Azobenzene Branching

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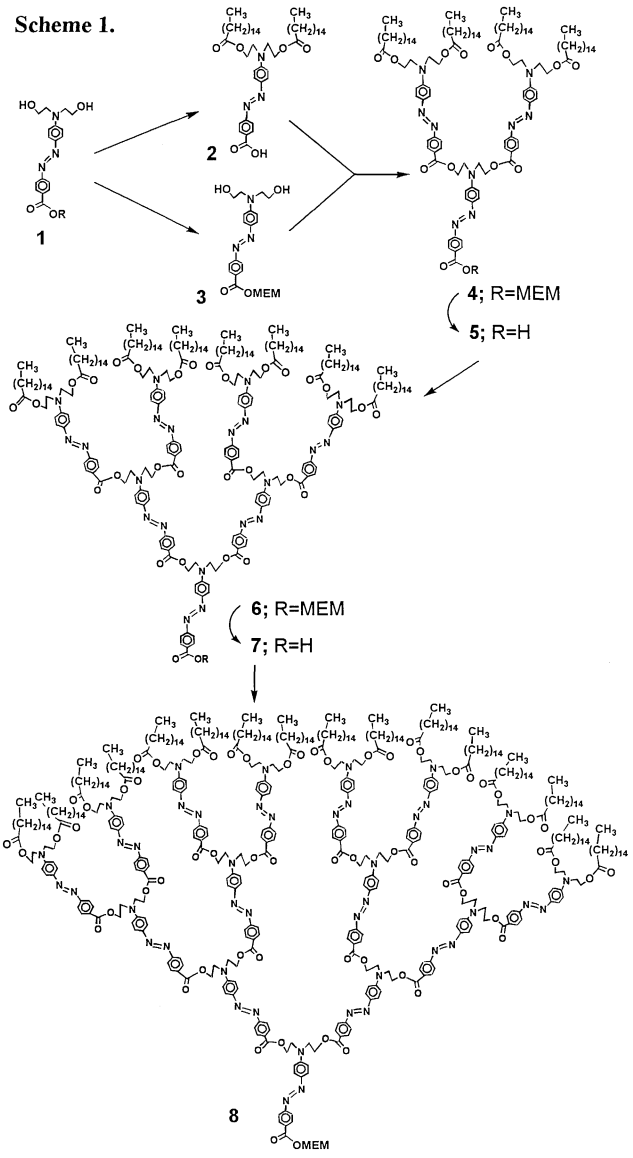
Dipolar dendrons constructed of electron donor/acceptor azobenzene branches and aliphatic exteriors have been synthesized. They formed the polar assemblies in a matrix of fatty acid and showed a significant increase in second-order nonlinear optical activity with an increase in branching.

Because of the need for more efficient functionality in molecular assembled materials, extensive work has been carried out on developing topologically complex materials. For oligomeric or polymeric materials, interest in the synthesis of hyperbranched molecules, such as dendrons or dendrimers, has recently been growing. This is because of their characteristic shape, regular molecular weight and size, and compactness.[1] Although considerable progress in the preparation of spherically modified dendrimers with functional branches has been made in recent years, preparing uniaxial structures constructed of the electron donor/acceptor repeating unit in order to fabricate polar oligomeric or polymeric materials that can be used for future optoelectronic and electronic applications is still challenging. In this report, we describe the stepwise synthesis of the dipolar dendrons based upon electron donor/acceptor azobenzene branches and the preparation of their assembled structures. An important goal of this study is to characterize the polar properties of dendrons in terms of the second-order nonlinear optical activity, especially second harmonic generation (SHG). An essential requirement for the second-order nonlinear optical activity is the noncentrosymmetric arrangement of the constituent dipole moment.[2] The polar assemblies of dendrons were prepared using the Langmuir-Blodgett (LB) film transfer technique, resulting in their molecular asymmetric orientation without a center of inversion.

All the new compounds have been synthesized as shown in Scheme 1. The starting compound is the 4-carboxy-4'-[bis(2-hydroxyethyl)amino]azobenzene chromophore, **1**, whose π-electrons are coupled with electron donor amino and acceptor carbonyl groups. Compound **2**, which was in our case the first generation, was obtained by the reaction of **1** with hexadecanoyl chloride in the presence of pyridine in THF in 92% yield. The hydrophobic chains in compound **2** will be an exterior unit in the final dendrons. The methoxyethoxymethyl (MEM) unit was used to protect a carboxyl group of **1**, where the reaction of **1** and MEM chloride in the presence of triethylamine in THF gave **3** in 80%. The key step in the generation growth is an esterification reaction, which is optimized by using a coupling reagent of dicyclohexylcarbodiimide and a catalyst of 4-dimethylamino-pyridine in dichloromethane at room temperature.[3] Typically, the coupling of **3** with 2.2 equivalents of **2** gave dendron **4**, generation 2, in 81% yield (TOFMS m/z 1997, calcd for $[M+H]^+$ 1995.0). The subsequent cleavage of the MEM ester was accomplished with 2-4% HCl in THF at below 5 °C to give the acid **5** in 85% yield (TOFMS m/z 1907, calcd for $[M+H]^+$ 1906.9). Repeating the above two steps using the same reagents generates the growth of dendrons. The reaction of **5** and **3** gave dendron **6**, generation 3, in 83% yield (TOFMS m/z 4199, calcd for $[M+H]^+$ 4194.1), and subsequently the corresponding acid **7** in 58% yield (TOFMS m/z 4112, calcd for $[M+H]^+$ 4106.0). Similarly dendron **8**, generation 4, was obtained after coupling of **7** and **3** in 46% yield (TOFMS m/z 8596, calcd for $[M+H]^+$ 8592.4). The compounds synthesized were purified by column chromatography or HPLC and were

Scheme 1.



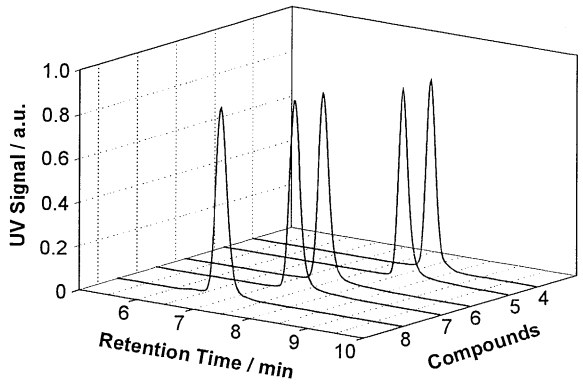


Figure 1. SEC traces of the compounds **4-8** in THF.

thoroughly characterized by ^{1}H and ^{13}C NMR spectroscopy. The most important characterization in dendron synthesis is the monodisperse purity and the correct molecular weight of the products. Figure 1 shows a series of size exclusion chromatography (SEC) traces for compounds **4-8**. Each compound shows a sharp and monodisperse peak, from which they were found to be >99.5% pure. Although SEC showed high purity levels of the dendrons, it is a measure of the hydrodynamic volume and not of the molecular weight. Thus, the exact molecular weight of the dendrons was measured by MALDI TOFMS spectroscopy. All experimental m/z values (see in the synthesis) were identical to the correct molecular weights as expected for the structures. All the compounds have the maximum absorption centered at 430 nm due to the π-π^* transition of the azobenzene unit in chloroform solution.

The dendrons synthesized above have an amphiphilic structure, where alkyl chains are located at the exterior position and azobenzene repeats are alternated in branches. Therefore, fabrication of the molecular assembled films could be implemented using the LB film transfer technique. In order to prepare stable films and arrange the molecular packing, dendrons were mixed with an excess of arachidic acid in chloroform solution, and then spread on a water subphase in the Langmuir trough. The single layer films were transferred onto glass substrate at a constant surface pressure of 20 mN/m. The absorption band due to the azobenzene unit in the assembled films was slightly shifted to the shorter wavelength compared with the pure films. Transmission SHG measurements were carried out in the standard p-polarized geometry using the 1064 nm output of a dye laser pumped by a Q-switched Nd-YAG laser. Pulse energies of < 1.0 mJ were used for stable SHG measurements on the films. Figure 2 shows the typical p-polarized SHG in the film of **8** (dendron/arachidic acid = 1/10) at rotating angles. The fringe resulted from the phase difference between two SHG waves generated at either side of the films on the substrate. The complementary constructive and destructive interference indicates that the SHG is fully coherent, which is characteristic of the thin film with a uniform polar order or molecular orientation. The behavior is analogous to the conventional SHG active LB films.[4] If we consider general assumptions and calculations for evaluating the second-order nonlinear coefficients of the LB films,[4,5] d_{ijk} values can be estimated to be d_{zzz}=15-27 pm/V and d_{zxx}=8-15 pm/V for the films of **2**, **4**, **6**, and **8**. Since SHG from the diluted chromopholic film is generally scaled with the square of the molecular density, experimental SHG should be normalized

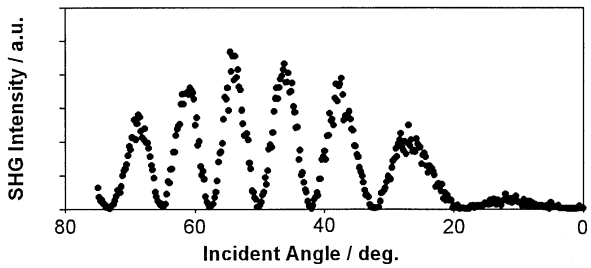


Figure 2. SHG as a function of the incident angles for the film of **8** (dendron/arachidic acid = 1/10).

Table 1. SHG results for the films of **2**, **4**, **6**, and **8**

Compounds	Normalized I/I_{quartz} ($\times 10^{-4}$)[a]	
	in pure film	in assembled film[b]
2	0.01	0.2
4	0.6	5.3
6	6.0	11.8
8	1.7	63.7

[a] SHG intensity is relative to a quartz reference (d_{11}=0.32 pm/V).
[b] Films are diluted with arachidic acid (dendron/arachidic acid=1/1-10).

to 100% coverage concentration when comparing SHG activity or polar order of each dendron.[6] Table 1 summarizes the normalized SHG intensities of dendrons relative to the SHG intensity of a quartz reference. The experimental SHG intensities were normalized by dividing by the square of fractional densities of the dendrons in the films. For all the dendrons, SHG activity in the diluted films of arachidic acid was found to be superior to that in the pure films, suggesting that the well organization ability of arachidic acid significantly improves the molecular orientation and packing arrangement by means of the alkyl chain. The significant enhancement of SHG in the film of **8** is noteworthy, where the strongest SHG intensity was observed. Since normalized SHG activity is directly linked to the polar parameter of the dendrons, which includes second-order molecular hyperpolarizability, molecular orientation, and local field factors, the SHG result indicates that the polar order of dendrons becomes large as the generation becomes large. The observations agree with the expectation that the structure of the dendrons synthesized is uniaxally dipolar, and that there is a particular merit in this structure for the generation of SHG.

References and Notes

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