

Intermolecular Coupling Enhancement of the Molecular Hyperpolarizability in Multichromophoric Dipolar Dendrons

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Abstract: Nonlinear optical dendritic macromolecules, called *azobenzene dendrons*, were synthesized, and their conformational properties and molecular nonlinear optical properties were clarified by second-order nonlinear optical measurement. The synthesized molecules were modified by introducing 1–15 numbers of azobenzene branching units as the nonlinear optical chromophore and by placing aliphatic chains at the end of the dendritic chains. In these topologically complex molecules, each chromophore contributed coherently to the macroscopic nonlinear optical activity. The first-order molecular hyperpolarizability of the azobenzene dendron having 15 chromophoric units was measured to be 3010×10^{-30} esu using the hyper-Rayleigh scattering method. This level of molecular hyperpolarizability was much higher than that for an azobenzene monomer (150×10^{-30} esu). The polarized nonlinear optical measurement provided structural information on the dendrons and indicated that each chromophore was oriented noncentrosymmetrically along the molecular axis to become a cone shape rather than a spreading or spherical shape. This structure gave rise to a large electronically dipolar macromolecule system, in which each chromophoric unit coherently contributed to the second harmonic generation.

Introduction

The fabrication of organic nonlinear optical (NLO) materials for second harmonic generation (SHG) applications has received considerable attention due to their demonstrated large second-order nonlinear susceptibility.¹ For a useful nonlinear optical material, the NLO chromophores must have large molecular hyperpolarizability and must crystallize into a noncentrosymmetric structure, resulting in nonvanishing second-order susceptibility. The synthetic approaches are being extended to topologically complex materials, such as polymers, by chemically linking the NLO chromophores to the polymeric backbone.² A suitable molecular design for an NLO polymer should make it possible to achieve a large molecular hyperpolarizability and to fine-tune the NLO properties to target applications.³ A major challenge in these approaches is the construction of a noncentrosymmetric chromophore orientation in macromolecular system having a nonvanishing second-order susceptibility.⁴

Dendritic macromolecules, called *dendrons* or *dendrimers*, are a new category of hyper-structured materials.⁵ Their widely

branching polymeric chains and high degree of control over regular molecular weight through stepwise synthesis have led to three-dimensional structures that are roughly spherical or

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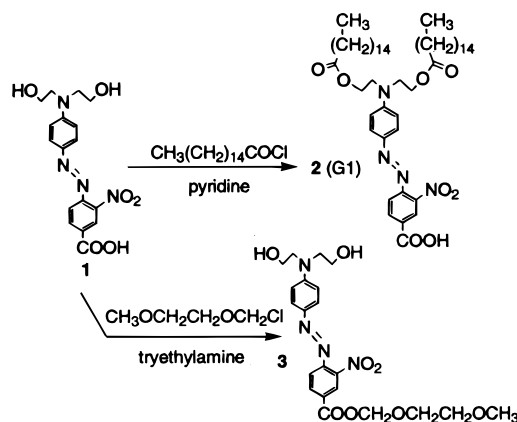
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globular.⁶ A variety of dendritic macromolecules have been studied to determine their characteristic chemical and physical properties.⁷ However, there are few reports describing a dendritic macromolecule having an electronically dipolar structure, which is essential for SHG. We previously found that using a rod-shaped chromophore as the branching unit enabled dendrons to be assembled into Langmuir–Blodgett monolayer films and that these films exhibited a large second-order susceptibility.⁸ In these molecularly assembled thin films, SHG activity was attributed to their microscopic second-order nonlinear susceptibility due to the molecular orientation and packing structure.

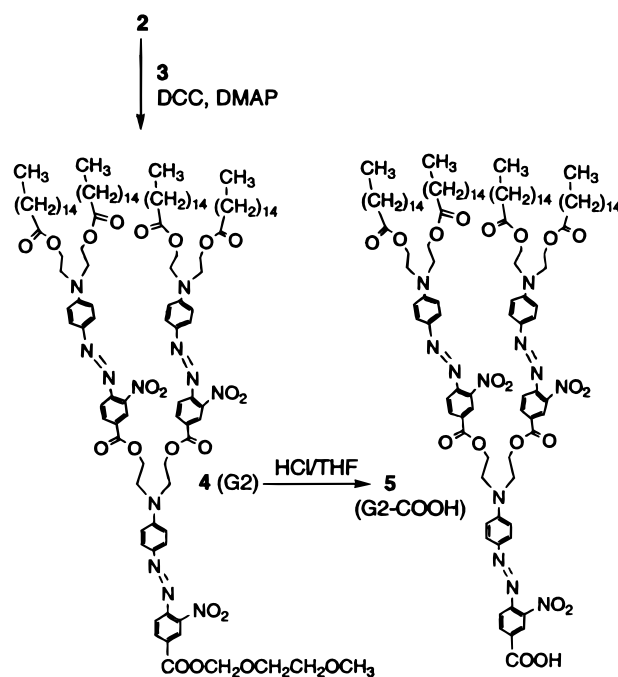
This paper describes our experimental approach to the design and synthesis of dipolar dendrons for NLO application and their molecular structure. Synthesized dendrons consist of three distinct chemical units: the main NLO functional branch unit (azobenzene chromophore), the aliphatic functionality at the end of the dendritic chain (hexadecanoic acid), and the focal unit (a methoxyethoxymethyl group). The synthesized azobenzene chromophore has an electron donor and acceptor system, and exhibits a high second-order nonlinear optical activity.

An important goal of this study is to characterize the noncentrosymmetric chromophore arrangement of the synthesized azobenzene dendrons and the effect of these dendrons on macroscopic second-order susceptibility. The NLO activity of the dendrons was characterized by their molecular hyperpolarizabilities. The hyper-Rayleigh scattering (HRS) method is a reliable technique for measuring the molecular hyperpolarizability of NLO chromophores as is the more commonly used electric field-induced second-harmonic generation (EFISH) method.^{9–12} Both methods require an isotropic solution. The specific advantage of the HRS method over the EFISH method is that it does not need an external electric field. Therefore, the HRS method is capable of more direct measurement of the NLO polymers, particularly their molecular conformation and geometric property at the macroscopic level, which originate from their dynamic processes. Furthermore, depolarization HRS measurement provides the individual tensor components of the

Scheme 1



Scheme 2



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molecular hyperpolarizability.¹³ Thus, this method is ideally suited for describing the macroscopic structural features of topologically complex materials, such as dendrimers and dendrons, and their molecular noncentrosymmetry or symmetry.

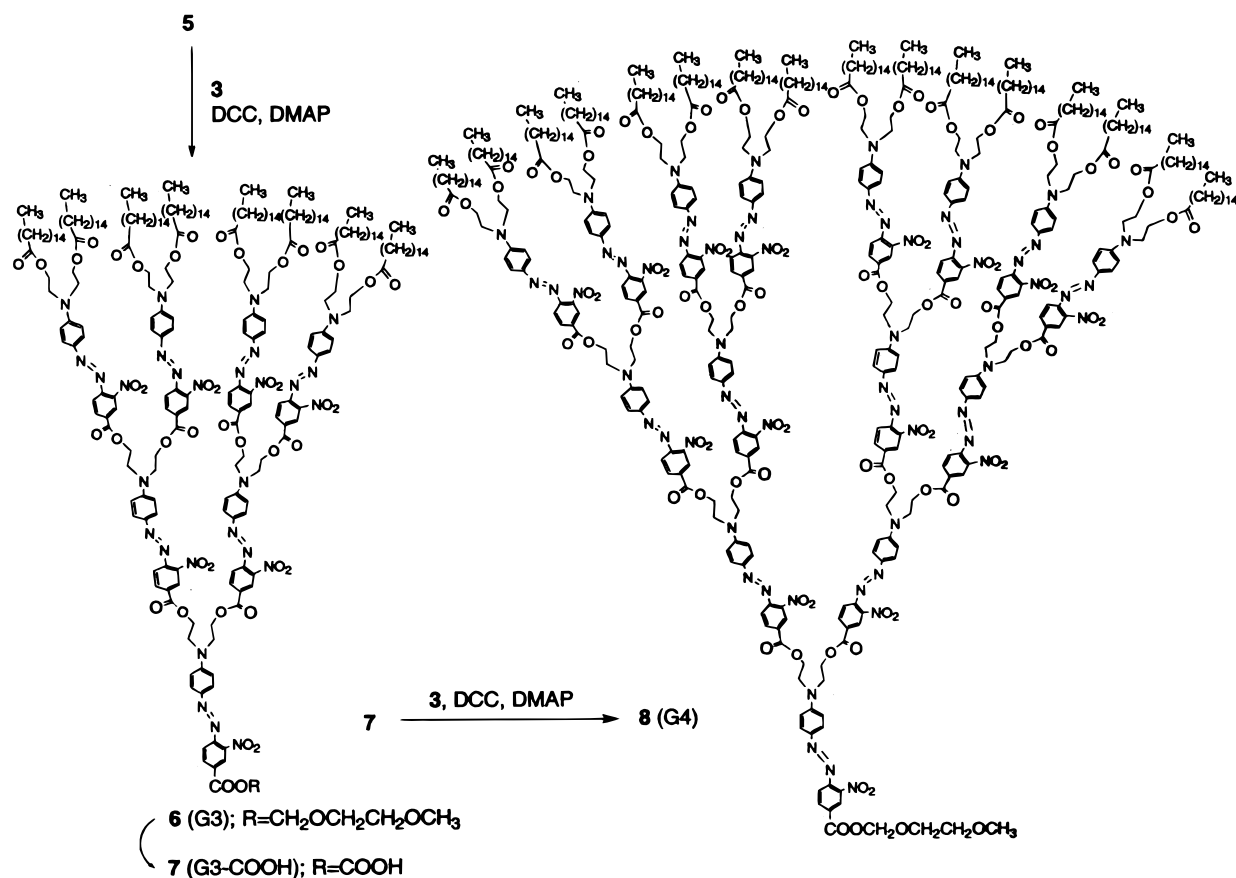
Results and Discussion

Synthesis and Characterization. The NLO functional unit we synthesized is an azobenzene chromophore (**1**), with a π -electronic structure coupled with electron donor and acceptor groups (Scheme 1). The chromophore was obtained after the diazo-coupling reaction of 4-amino-3-nitrobenzoic acid and *N*-phenyldiethanolamine under acidic conditions. A carboxyl group was used as the focal point and diol as the branching point. Because the electron-withdrawing effect of the carboxyl group is weak, a nitro group was added to the azobenzene at an ortho position to optimize the molecular hyperpolarizability of the chromophore.

We used two compounds as starting monomers. Compound **2**, in our case the first-generation dendron (G1), was obtained by the reaction of **1** with hexadecanoyl chloride in the presence

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Scheme 3



of a pyridine base in 95% yield. Compound **3** was a diol monomer modified with a methoxyethoxymethyl (MEM) unit to protect the carboxyl group from any side reaction. The reaction of **1** and MEM chloride in the presence of triethylamine produced **3** in 78% yield.

Using these monomers, dendrons were synthesized via an AB₂-type coupling reaction, and resulting in a head-to-tail orientation of the chromophoric units along the molecular axis. The coupling reaction was optimized by using dicyclohexylcarbodiimide (DCC) and (dimethylamino)pyridine (DMAP) in a dichloromethane solution (Scheme 2).¹⁴ Typically, the reaction of diol (**3**) with 2.1 equiv of the acid (**2**) gave a dendron (**G2**, **4**) in 98% yield. The MEM protection was subsequently removed in a 2–5% hydrochloric acid/THF solution at below 5 °C, giving the acid (**G2-COOH**, **5**) in 88% yield. Repeating these two steps (coupling and activating) using the same reagents generated dendron growth. The reaction of **5** and **3** gave a dendron (**G3**, **6**) in 97% yield and, subsequently, a corresponding acid (**G3-COOH**, **7**) in 71% yield. Finally, we synthesized a dendron (**G4**, **8**) in 79% yield. All of the products were purified using column chromatography, where the large *R_f* difference in the silica gel between compounds with MEM ester and those with acid allowed for easy purification.

The structure of the products was thoroughly characterized by ¹H and ¹³C NMR spectroscopy. The NMR spectrum features for dendrons **4**, **6**, and **8** and acids **5** and **7** were similar, while resonant peaks broadened slightly as their molecular weights increased. The removal of the MEM protection group was also characterized by ¹H and ¹³C NMR spectroscopy, where resonances due to the MEM group in **4** and **6** completely disappeared in **5** and **7**.

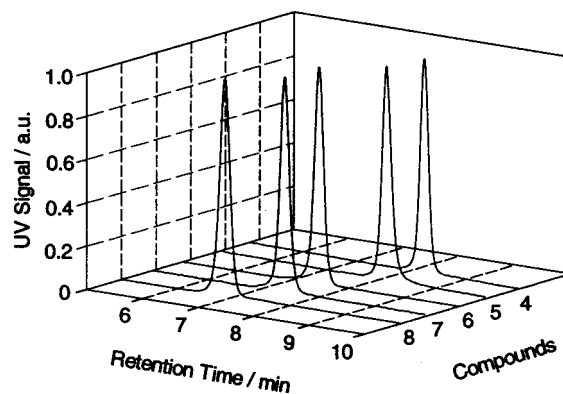


Figure 1. SEC traces of compounds 4–8.

Another important characteristics of dendron synthesis are the high purity and monodispersed molecular weight of the products. The purity of products **4**–**8** was measured using size-exclusion chromatography (SEC) (Figure 1). Each product had a narrow peak, from which the purity was determined to be 99.5%, and the distribution of the molecular weight was $M_n/M_w < 1.01$ relative to the monodispersed polystyrene standard (Table 1). Although SEC analysis showed that the synthesized dendrons had high purity levels, the dendrons had significant errors in M_n and M_w , as expected for their molecular weight. This result is not surprising because SEC is a measure of the hydrodynamic volume of solutes and not of their molecular weight.

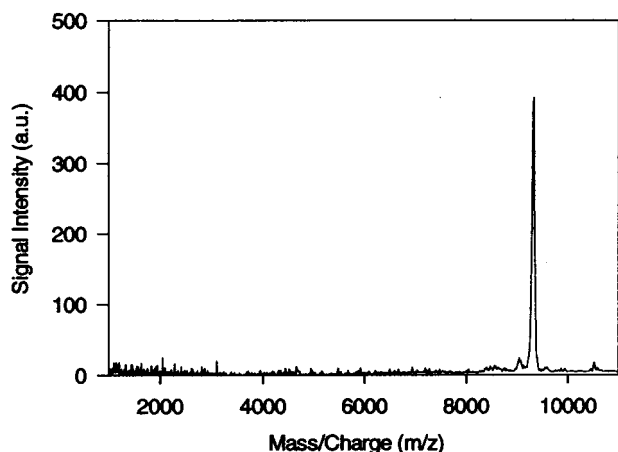
The exact molecular weights were measured using matrix-assisted laser-desorption–ionization time-of-flight (MALDI-TOF) mass spectroscopy. The typical mass spectrum measured for dendron **G4** showed the expected $[M + Na]^+$ ion at $m/z =$

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Table 1. Molecular Weights of Synthesized Azobenzene Dendrons

compd	M_w^a	M_w/M_n	m/z^b	m/z (calcd)
4	3479	1.01	2138	2129.9 ^c
5	3357	1.01	2049	2041.8 ^c
6	7158	1.01	4543	4530.8 ^d
7	7188	1.01	4439	4442.6 ^d
8	13190	1.01	9311	9288.7 ^d

^a Values estimated by SEC (polystyrene standards, eluent as tetrahydrofuran). ^b Measured by MALDI-TOF mass spectroscopy. ^c Calculated for $[M + H]^+$. ^d Calculated for $[M + Na]^+$.

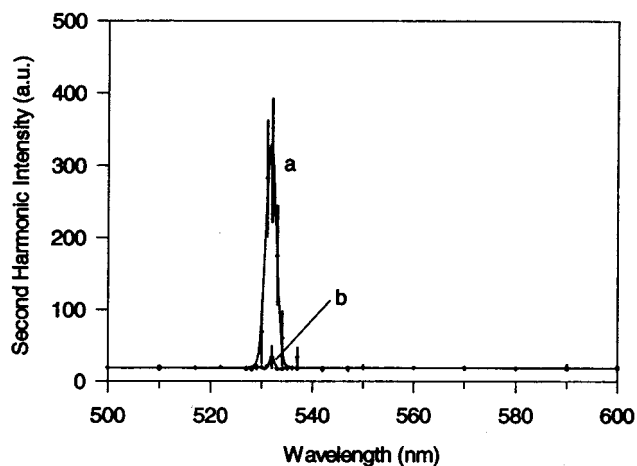
**Figure 2.** MALDI-TOF mass spectrum of dendron G4.**Table 2.** Optical and Nonlinear Optical Properties of Azobenzene Dendrons

dendron	n_c	λ_{max}^a (nm)	$\beta_{zzz}^2/\beta_{xxx}^2$ ^a	β (10^{-30} esu)	β_0 (10^{-30} esu)	$n_c f$
G1	1	455	4.6	673	150	(1.0)
G2	3	458	4.9	2380	500	3.36
G3	7	460	4.5	6760	1430	9.32
G4	15	460	4.5	14640	3010	20.2

^a Absorption spectra and HRS were measured in chloroform solution.

9311 as the most intense signal (Figure 2). The m/z values of the dendrons are summarized in Table 1. All the experimental results were in good agreement with the expected molecular weights for the structure. The removal of MEM group was clearly evident from the MALDI-TOF mass results, where the decrease in the m/z value of ~ 90 from G2 **4** to G2-COOH **5** and from G3 **6** to G3-COOH **7**, corresponded to the removal of a MEM unit. NMR, SEC, and MALDI-TOF analyses confirmed that the purity of the synthesized dendrons was extremely high.

Optical and Nonlinear Optical Properties. The UV/visible spectra of the synthesized dendrons in chloroform solution showed a strong absorption band between 455 and 460 nm, with a long absorption tail due to the $\pi-\pi^*$ transition of the azobenzene chromophores. The absorption maximum shifted slightly to longer wavelengths as the generation of dendrons increased (Table 2). In our HRS measurements, two incident photons at the fundamental frequency, ω , with a wavelength of 1064 nm generated a photon at the second harmonic frequency, 2ω , with a wavelength of 532 nm. One might argue that the fluorescence originating from two-photon absorption would hamper HRS measurement.¹⁵ We therefore analyzed the scattering spectrum from a sample solution to show that the

**Figure 3.** Nonlinear scattering spectra for a chloroform solution of dendron G4 (curve a) and a neat chloroform solution (curve b).

fluorescence does not contribute to the HRS signal (Figure 3). The intense peak at 532 nm in the scattering spectra from a chloroform solution of G4 (curve a) was the HRS signal due to second harmonic generation, and there was no fluorescence in the other wavelength regions. The signal intensity level in the background wavelengths was identical to that measured for the neat chloroform solution (curve b). Thus, we could be sure that the dendrons exhibited no fluorescence and that the detected signal was caused only by the second-harmonic scattered light.

In HRS measurement, the detected signal intensity at 2ω is given by¹⁰

$$I_{j,2\omega} = G \langle B_{jzz}^2 \rangle I_0^2 = G \sum_s N_s \langle \beta_{jzz,s}^2 \rangle I_0^2 \quad (1)$$

where $I_{j,2\omega}$ is the intensity of the light at 2ω polarized in j direction, $j=x$ or z in laboratory coordinates,^{16,17} G is the scattering geometry and instrumental factor, $\langle B \rangle$ is the averaged macroscopic second-order susceptibility, and I_0 is the intensity of the fundamental light at ω . N_s is the number density of species s with molecular hyperpolarizability $\beta_{jzz,s}$. Depolarization measurement with the analyzer perpendicular or parallel to the laser polarization gives the ratio of $I_{z,2\omega}$ to $I_{x,2\omega}$.¹³ The HRS intensity ratio of $I_{z,2\omega}/I_{x,2\omega}$ is identical to the tensor component ratio of $\beta_{zzz}^2/\beta_{xxx}^2$.

The depolarized HRS signal intensities from a chloroform solution of G4 were measured as a function of the fundamental light intensity (Figure 4). For both polarizations, the quadratic dependence of $I_{z,2\omega}$ and $I_{x,2\omega}$ with respect to the fundamental intensity of I_0 fit well with the factor of the quadratic coefficient, $G \langle B_{jzz}^2 \rangle$, as expected in eq 1. From these two polarizations, the ratio of $\beta_{zzz}^2/\beta_{xxx}^2$ was estimated to be 4.5. The order of $\beta_{zzz}^2/\beta_{xxx}^2$ on the macroscopic scale is theoretically 5.0 for a linearly conjugated molecule with one dominant β component,¹³ while it becomes smaller for macromolecules depending on the macroscopic molecule's size and shape and on the orientation correlation length.¹⁶ The experimentally obtained $\beta_{zzz}^2/\beta_{xxx}^2$ was identical to that obtained for the thin rod model, suggesting that each of the chromophoric units in the dendron was arranged noncentrosymmetrically. This peculiar property was in contrast with the general tendency of a dendritic macromolecule to be spherical or globular with spreading branches. Other studies have

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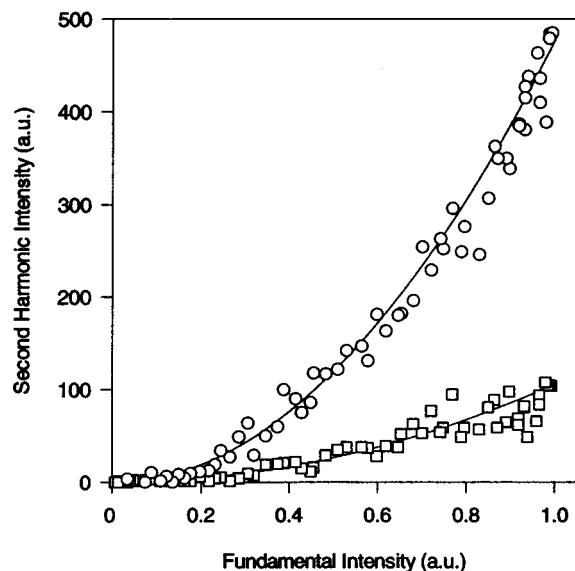


Figure 4. Polarized HRS signal intensities as a function of the fundamental laser intensities for a chloroform solution of dendron G4. Detected polarizations were parallel (○) and perpendicular (□) to the polarization of the fundamental laser.

shown that the $\beta_{zzz}^2/\beta_{xzz}^2$ is small for molecules having high symmetry^{18,19} or spherically functionalized dendrimers.²⁰

For a two-component system, e.g., solute chromophores in solvent, the quadratic macroscopic second-order susceptibility, $\langle B^2 \rangle$, in HRS measurement is proportional to the number of chromophores and to the square of its molecular hyperpolarizability:

$$G\langle B_{jzz}^2 \rangle = GF_{\omega}^4 F_{2\omega}^2 [N_{\text{solvent}} \beta_{jzz,\text{solvent}}^2 + N_{\text{chromophore}} \beta_{jzz,\text{chromophore}}^2 \times 10^{-\epsilon(2\omega)Nl}] \quad (2)$$

where F is the local field factor at the optical frequency, $\epsilon(2\omega)$ is the molar absorption coefficient at 532 nm, and l is the effective optical path length. To estimate the molecular hyperpolarizability of the dendrons, we used the molecular cluster, or assembly model, in which the effective molecular hyperpolarizability of these molecular systems is summed over the contribution of each chromophore.²¹ The molecular hyperpolarizabilities of the dendrons and chromophores in the HRS measurement are expressed as $\beta_{\text{dendron}} = n_c f \beta_{\text{chromophore}}$, where n_c is the number of chromophoric units, and f is the local field factor due to the screening electric field generated from neighboring molecules.

Figure 5 shows the plots of the experimental quadratic coefficient, $G\langle B^2 \rangle$, against the number density of chromophoric units for dendrons G1–G4. A nonpolarized HRS signal was measured assuming one dominant β component for the azobenzene chromophore parallel to the molecular axis. All of the plots could be well fitted to the nonlinear dependence of $G\langle B^2 \rangle$ on $N_{\text{chromophore}}$, as expressed by eq 2. The constant $G\langle B^2 \rangle$ value at $N = 0$ (intercept) resulted from the second-order susceptibility of the neat chloroform. Using the known value of $\beta = -0.49 \times 10^{-30}$ esu for chloroform,²² we calculated the β values of

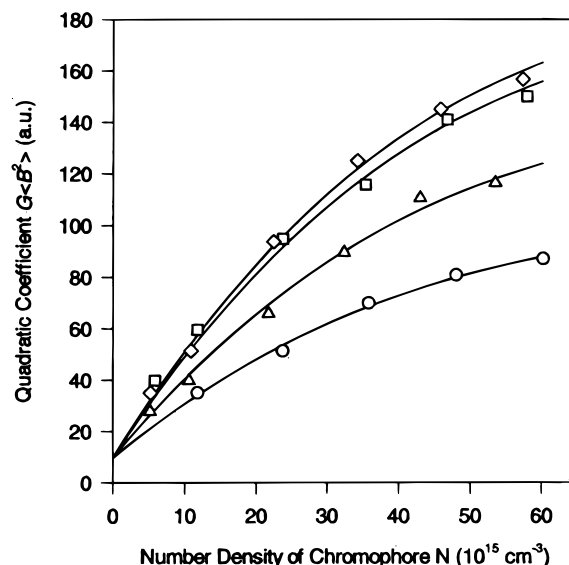


Figure 5. Quadratic coefficients of dendrons as a function of the number density of the chromophores in chloroform solution: (○) G1, (△) G2, (□) G3, and (◇) G4.

Table 3. Optical and Nonlinear Optical Properties of Azobenzene Dendrons in Cyclohexanone and Dioxane

dendron	cyclohexanone			dioxane		
	λ_{max}	β_0 (10^{-30} esu)	$n_c f$	λ_{max}	β_0 (10^{-30} esu)	$n_c f$
G1	471	229	(1.0)	454	125	(1.0)
G2	475	636	2.78	460	358	2.86
G3	475	1756	7.67	461	1009	8.07
G4	475	3857	16.8	462	2203	17.6

the dendrons according to eq 2 (Table 2). The azobenzene dendrons had a low absorption edge at 2ω , and thus their β values were resonantly enhanced and overestimated by different amounts. For appropriate comparison of the molecular hyperpolarizabilities, we corrected the resonance enhancement of the azobenzene dendrons in our analysis of the HRS measurements. The nonresonant hyperpolarizabilities, β_0 , of the dendrons were estimated by means of a two-level model expression.^{3,23} The β_0 value of the dendrons increased with the number of chromophoric branching units. More importantly, enhancement of β_0 for each chromophore was clearly evident in the dendritic structure. For dendrons G2–G4, the enhancement factor of the molecular hyperpolarizability can be expressed as $n_c f$, with $f > 1.0$. On passing from dendrons G1 to G2, to G3, and to G4, the effective enhancements were 12, 33, and 35% larger, respectively, than the value estimated when simply adding monomer β_0 values. This effective increase was due to the macroscopic structural properties of the dendrons: the chromophoric units in the dendrons had an intermolecular noncentrosymmetric orientation, as discussed in the polarized HRS measurement. In such a molecular structure, each chromophoric unit coherently contributes to the second harmonic generation.

The molecular hyperpolarizability of dendrons showed a significant dependence on solvent polarity (Table 3). When going from a nonpolar solvent, dioxane (dielectric constant, $\epsilon = 2.2$), or chloroform ($\epsilon = 4.8$), to a polar one, cyclohexanone ($\epsilon = 18.3$), the molecular hyperpolarizability of dendrons became larger. This chromophore–solvent effect can be at-

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(23) Within the two-level model,³ the nonresonant molecular hyperpolarizability can be estimated as $\beta_0/\beta_{2\omega} = (\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)/\omega_0^4$, where $\beta_{2\omega}$ is the value measured at 2ω with the fundamental laser at ω .

tributed to the *intramolecular* chemical nature of the chromophores in the ground state as well as in the excited state, where second-order susceptibility is taken to be the sum of two contributions, $\beta = \beta_{\text{ct}} + \beta_{\text{add}}$.²⁴ Here, β_{ct} is the intramolecular charge-transfer contribution arising from the interaction of donor and acceptor units through a conjugated π -electron network, and β_{add} is the additive portion, accounting for the interaction between the individual donor and acceptor units and the conjugated π -electron backbone. Because the second-order activity in a high β chromophore is intrinsically related to the charge-transfer correction term rather than to the additive term, the increase in the molecular hyperpolarizability of dendrons in a polar solvent was well correlated with the solvent-induced shift of the charge-transfer absorption maximum. In cyclohexanone, the dendrons showed a large red-shift in the absorption maximum compared with those in chloroform and dioxane, and their β_0 values were larger.

This solvent dependency resulted points to an *intermolecular* mechanism governing the β enhancement effect and to a structural feature of dendrons behaving as the assembled molecular system. It has been demonstrated theoretically that noncovalently bonded chromophoric interactions enhance or reduce the effective molecular hyperpolarizability in molecular clusters due to their modified electronic structure and the local field effect within the molecular system.^{25–27} The calculated electronic spectra of these molecular clusters, as well as their polarized dipoles, showed a shift in the transition band compared with those of monomeric chromophores. By using a theoretical molecular cluster model, the molecular hyperpolarizability for simple two-chromophores assembly were estimated as^{26,27}

$$\beta_{ijk}^{(n)} = \sum_n \beta_{ijk}^{(n)}$$

Here, $\beta_{ijk}^{(n)}$ is the molecular hyperpolarizability of the n th molecular dipole ($n = 1, 2$) under dipole–dipole interaction and is expressed as the tensor sum of the corresponding monomer polarizabilities, $\beta_{ijk}^{(n)} = \beta_{ijk}^{(0)} + F_l^{(n)} \gamma_{ijkl}^{(0)}$, where the polarizabilities are first-order hyperpolarizabilities, β , and second-order hyperpolarizabilities, γ , and $F_l^{(n)}$ is the l th vectorial component of the induced field by n th chromophore dipole.

By using this model, we clarified the effects of intermolecular electronic interactions on the molecular hyperpolarizabilities of dendrons, including the interaction field experienced by the neighboring chromophoric units. In the absorption spectra of the dendrons, the π – π^* transition of the azobenzene units became slightly red-shifted as the generation increased (Tables 2 and 3). This indicates that dendrons have small stabilizing dipole–dipole interactions between neighboring chromophoric units, involving slightly distorted charge distributions and minimal contributions from the orbitals of the other subunits. In the molecular cluster model, there are various types of short-range intermolecular interaction, i.e., charge-transfer, exchange, polarization, and electrostatic intermolecular interactions. Because the predominant source of the molecular hyperpolarizability is the charge-transfer, which is relevant to the molecular dipole, β enhancement of the dendrons is generated due to the

dipole–dipole electronic coupling of the chromophoric units. It should be pointed out that the HRS technique yielded a vectorial total of various β tensor components, which are originated not only from the molecular axis direction but also from the other molecular planes.^{19,28} Therefore, measured β values for dendrons G2–G4 included induced components of all β tensors by chromophores dipole–dipole coupling interactions. This is in contrast with the conventional oriented-gas model approximation for monomeric chromophore, G1; in this case, the β_{zzz} tensor component dominates the negligibly small other β tensors. Additionally, the bonded chromophore–chromophore interaction along the molecular axis should be taken in account for β enhancement when considering the electron donor and acceptor repeating structure of dendrons.

Comparing β enhancement of dendrons, better enhancement was obtained in chloroform than in dioxane and cyclohexanone. By assuming the chromophore–solvent effect on the molecular hyperpolarizability is independent of the generation of dendrons, β enhancement is thought to be due to the assembled structure of the dendrons at the microscopic level, where there presumably exists van der Waals and electrostatic intermolecular attractive interactions. Synthesized dendrons were well dissolved in both polar and nonpolar solvents because they had a bipolar chemical nature consisting of the polar chromophoric unit and aliphatic chain end unit. The aliphatic unit should have a favorable affinity with nonpolar solvent but not with polar solvent, whereas the chromophoric unit should have the opposite affinity. Dendrons should therefore have a minor dispersion of the molecular conformation against various solvent polarities, and such microscopic conformational properties should affect their nonlinear optical activities.

Conclusions

We have shown that nonlinear optical chromophores can be incorporated into a dendritic structure through repeated stepwise reactions. Size-exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy measurements showed that the products had a high purity and monodispersed molecular weights. Hyper-Rayleigh scattering (HRS) measurement showed that synthesized dendrons had a cone-shaped conformation, thus achieving a noncentrosymmetric macromolecular structure at macroscopic dimensions with no need for an external electric field. This conformational property is presumably due to intermolecular attractive interactions. We found a novel advantage of using the dendritic macromolecules for nonlinear optical (NLO) materials, where NLO chromophoric units were easy to organize into a macroscopic molecular assembly compared to simple monomeric chromophores. This property should lead to bulk polar-order within thin films and optical fiber materials. Although our compounds had non-NLO active units of aliphatic chains, this study pointed out important technological merit that the NLO parameter β/M_w can be enhanced in this dendritic molecular system as it has been in NLO crystalline materials.

Experimental Section

General Methods. All of the solvents and reagents were of reagent quality, purchased commercially, and were used without further purification. Dehydrated grade tetrahydrofuran (THF) and dichloromethane were used as dried solvents (Wako Chemicals). Thin layer chromatography was performed on 0.2 mm silica plastic-coated sheets with F254 indicator (Merck). Chromatography was performed on Merck 40–63 μm silica gel. NMR spectra were recorded on a JEOL 300 MHz JNM-LA 300 spectrometer. Size-exclusion chromatography (SEC) was performed on a Waters Styragel HR3 column (MW range 500–30,-

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000) coupled with a Waters 600 pump system and a 486 tunable absorption detector. Molecular weights calculated from SEC were based on using polystyrene standard (Shodex) as calibrates. Mass spectra were measured by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) on a Shimadzu/KRATOS MALDI IV tDE spectrometer. UV/visible absorption spectra were measured on a Hitachi U-4000 spectrometer.

Hyper-Rayleigh Scattering (HRS). Our experimental HRS apparatus is essentially similar to that described by Clays and Persoons.^{10,11} The only modification was the use of a grating monochromator and a wide wavelength range photomultiplier tube to analyze the scattering optical spectrum and collect the HRS signal. The fundamental beam from a Nd:YAG laser (New Wave Research Mini Lase II-10, 1064 nm, 10 Hz, 8 ns) was focused into a 3 cm long cell containing 5 mL of a sample solution. The incident power and polarization were adjusted by a half-wave plate in combination with a Glan-Taylor polarizer. The maximum incident power behind the cell was 1.2 mJ/pulse. The HRS signal was collected perpendicular to the fundamental beam by a condenser system and detected with a photomultiplier tube (Hamamatsu R636-10) after passing it through an infrared cut filter and a monochromator (Jasco M10). For the depolarization measurement, a polarizer plate was placed before the monochromator. The signals from the photomultiplier tube were processed with a gated integrator and a box car averager (Stanford Research System SR250 and SR 280).

4-Carboxy-2-nitro-4-[bis(2-hydroxyethyl)amino]azobenzene (1). 4-Amino-3-nitrobenzoic acid (4.55 g, 25 mmol) was dissolved in 18% hydrochloride solution (15 mL) and diazotized with sodium nitrite (1.76 g in 2.5 mL of water, 25 mmol) at 1–3 °C. The mixture was then added dropwise to *N*-phenyldiethanolamine (4.5 g, 25 mmol) in a concentrated hydrochloride solution (12 mL) at 0–3 °C. The mixture was stirred for another 1 h, and saturated sodium acetate solution was then added to neutralize the mixture. The precipitate was collected and washed several times with water. The crude product was purified by recrystallization from ethanol to give compound **1** (6.97 g, 75% yield). ¹H NMR (DMSO-*d*₆) δ 3.60 (m, 8H, *J* = 3.60 Hz, CH₂CH₂OH), 4.86 (br s, 2H, OH), 6.90 (d, 2H, *J* = 9.3 Hz, *o*-ArH to NCH₂), 7.73 (d, 2H, *J* = 9.6 Hz, *m*-ArH to NCH₂), 7.77 (d, 1H, *J* = 8.7 Hz, *o*-ArH to COOH), 8.22 (d, 1H, *J* = 8.7 Hz, *m*-ArH to COOH), 8.39 (d, 1H, *o*-ArH to NO₂); ¹³C NMR (DMSO-*d*₆) δ 53.38 (CH₂CH₂OH), 58.19 (CH₂CH₂OH), 111.88 (*o*-ArC to NCH₂), 118.72 (*m*-ArC to COOH), 124.74 (*o*-ArC to COOH and NO₂), 126.52 (*m*-ArC to NCH₂), 130.80 (*o*-ArC to COOH), 133.53 (ArC next to COOH), 142.80 (ArC next to NCH₂), 146.59 (ArC next to NO₂), 147.31 (*p*-ArC to NCH₂), 152.87 (*p*-ArC next to COOH), 165.87 (COOH). Anal. Calcd for C₁₇H₁₈N₄O₆: C, 54.5; H, 4.9; N, 15.0. Found: C, 55.2; H, 4.9; N, 15.1.

Compound 2 (G1). To a solution of compound **1** (3.74 g, 10 mmol) and hexadecanoyl chloride (6.05 g, 22 mmol) in THF (50 mL) was added pyridine (2.4 g, 30 mmol). The mixture was stirred for 2 h at room temperature and then heated at 70 °C for 1 h. The resulting precipitate was collected and purified by recrystallization from a chloroform and methanol mixture. The yield of compound **2** was 8.1 g (95%). ¹H NMR (CDCl₃) δ 0.85 (t, 6H, *J* = 7.2 Hz, CH₃), 1.22 (m, 48H, (CH₂)₁₂CH₃), 1.57 (m, 4H, CH₂CH₂COO), 2.28 (t, 4H, *J* = 7.5 Hz, CH₂CH₂COO), 3.73 (t, 4H, *J* = 6.0 Hz, CH₂N), 4.29 (t, 4H, *J* = 6.0 Hz, CH₂CH₂N), 6.84 (d, 2H, *J* = 9.6 Hz, *o*-ArH to NCH₂), 7.77 (d, 1H, *J* = 8.7 Hz, *m*-ArH to COOH), 7.87 (d, 2H, *J* = 9.3 Hz, *m*-ArH to NCH₂), 8.29 (d, 1H, *J* = 6.6 Hz, *m*-ArH to COOH), 8.55 (d, 1H, *J* = 1.8 Hz, *o*-ArH to COOH and NO₂); ¹³C NMR (CDCl₃) δ 14.10 (CH₃), 22.68 (CH₂CH₃), 24.82 (CH₂CH₂CH₃), 29.13–29.69 (m, (CH₂)₁₀-CH₂CH₂CH₃), 31.93 (CH₂CH₂COO), 34.16 (CH₂COO), 49.66 (CH₂N), 60.81 (CH₂CH₂N), 111.84 (*m*-ArC to NCH₂), 118.88 (*o*-ArC to COOH), 125.99 (*o*-ArC to COOH and NO₂), 126.94 (*m*-ArC to NCH₂), 129.18 (*o*-ArC to COOH), 134.01 (ArC next to COOH), 144.64 (ArC next to NCH₂), 147.01 (ArC next to NO₂), 148.92 (*p*-ArC to NCH₂), 151.75 (*p*-ArC to COOH), 168.99 (COOH), 173.72 (COOCH₂). Anal. Calcd for C₄₉H₇₈N₄O₈: C, 69.1; H, 9.2; N, 6.6. Found: C 69.4, H, 9.0; N, 6.5.

Diol Monomer 3. To a solution of compound **1** (1.87 g, 5 mmol) and triethylamine (0.76 g, 5 mmol) in THF (30 mL), 2-methoxyethoxymethyl chloride (0.61 g, 4.9 mmol) in THF (5 mL) was added at 3–5 °C. The mixture was stirred for 3 h at room temperature. After

removal of the solvent, the crude product was purified by silica gel chromatography eluted with dichloromethane/isopropyl alcohol (IPA) (10:2). The yield of **3** was 1.8 g (78%). ¹H NMR (CDCl₃) δ 3.36 (s, 3H, CH₃), 3.58 (t, 2H, *J* = 4.5, CH₂OCH₃), 3.72 (t, 2H, *J* = 5.1, CH₂N), 3.88–3.95 (m, 6H, CH₂OH and CH₂CH₂OCH₃), 5.61 (s, 2H, COOCH₂), 6.77 (d, 2H, *J* = 9.3 Hz, *o*-ArH to NCH₂), 7.72 (d, 1H, *J* = 8.7 Hz, *m*-ArH to COOMEM), 7.80 (d, 2H, *J* = 9.6 Hz, *m*-ArH to NCH₂), 8.23 (d, 1H, *J* = 6.6 Hz, *o*-ArH to COOMEM), 8.48 (d, 1H, *J* = 1.5 Hz, *o*-ArH to COOMEM and NO₂); ¹³C NMR (CDCl₃) δ 55.32 (CH₃), 59.02 (CH₂N), 60.29 (CH₂CH₂N), 67.95 (CH₂CH₂OCH₃), 71.49 (CH₂-OCH₃), 90.69 (COOCH₂), 113.39 (*o*-ArC to NCH₂), 118.68 (*m*-ArC to COOMEM), 125.66 (*m*-ArC to NCH₂), 127.27 (*o*-ArC to COOMEM and NO₂), 129.74 (*o*-ArC to COOMEM), 133.92 (ArC next to COOMEM), 138.42 (ArC next to NCH₂), 144.15 (ArC next to NO₂), 146.06 (*p*-ArC to NCH₂), 147.96 (*p*-ArC to COOMEM), 163.82 (COOMEM). Anal. Calcd for C₂₁H₂₆N₄O₈: C, 54.5; H, 5.7; N, 12.1. Found: C, 55.3, H, 5.6; N, 12.5.

Azobenzene Dendron (G2, 4) and General Procedure for Ester Formation. To a solution of **2** (4.26 g, 5 mmol) in dry dichloromethane (50 mL) was added **3** (1.11 g, 2.4 mmol), followed by 4-(dimethylamino)pyridine (DMAP) (0.67 g, 5.5 mmol). Dicyclohexylcarbodiimide (DCC) (5.5 mmol) in THF (5 mL) was added and stirred at room temperature under nitrogen until the reaction was complete. The reaction mixture was filtered to remove the precipitated dicyclohexylurea and was evaporated to dryness under reduced pressure. The crude product was purified by silica gel chromatography eluted with dichloromethane/ethyl acetate (10/1) to give **4** (G2). The yield of **4** was 4.5 g (98%). ¹H NMR (CDCl₃) δ 0.85 (t, 12H, *J* = 7.2 Hz, CH₃), 1.22 (m, 96H, (CH₂)₁₂-CH₃), 1.57 (m, 8H, *J* = 7.2 Hz, CH₂CH₂COO), 2.28 (t, 8H, *J* = 8.1 Hz, CH₂CH₂COO), 3.37 (s, 3H, CH₃O), 3.37 (t, 2H, *J* = 4.2 Hz, CH₂-OCH₃), 3.72 (t, 8H, *J* = 6.0, CH₂N in G1), 3.90 (t, 4H, *J* = 4.2 Hz, CH₂CH₂OCH₃), 3.96 (t, 4H, *J* = 5.7 Hz, CH₂N in G2), 4.28 (t, 8H, *J* = 6.6 Hz, CH₂CH₂N in G1), 4.62 (t, 4H, *J* = 6.0 Hz, CH₂CH₂N in G2), 5.60 (s, 2H, COOCH₂O), 6.82 (d, 4H, *J* = 8.7, *o*-ArH to NCH₂ in G1), 6.96 (d, 2H, *J* = 8.7 Hz, *o*-ArH to NCH₂ in G2), 7.72 (d, 3H, *J* = 9.0 Hz, *m*-ArH to COO in G1 and G2), 7.84 (d, 4H, *J* = 9.6 Hz, *m*-ArH to NCH₂ in G1), 7.89 (d, 2H, *J* = 8.7, *m*-ArH to NCH₂ in G2), 8.17 (d, 2H, *J* = 9.0 Hz, *o*-ArH to COO in G1), 8.23 (d, 1H, *J* = 8.7 Hz, *o*-ArH to COOMEM), 8.41 (d, 2H, *J* = 2.4 Hz, *o*-ArH to COO and NO₂ in G1), 8.48 (d, 1H, *J* = 1.5 Hz, *o*-ArH to COOMEM and NO₂); ¹³C NMR δ 14.06 (CH₃CH₃), 22.65 (CH₂CH₃), 24.79 (CH₂CH₂-CH₃), 29.10–29.66 ((CH₂)₁₀CH₂CH₂CH₃), 31.89 (CH₂CH₂COO), 34.10 (CH₂COO), 49.66 (CH₂N in G1 and G2), 59.07 (CH₃O), 60.78 (CH₂-CH₂N in G1), 62.23 (CH₂CH₂N in G2), 70.03 (CH₂CH₂OCH₃), 71.47 (CH₂OCH₃), 90.65 (COOCH₂O), 111.74 (*o*-ArC to NCH₂ in G1), 112.10 (*o*-ArC to NCH₂ in G2), 118.87 (*o*-ArC to COO in G1 and G2), 125.40 (*m*-ArC to CH₂N in G1 and G2), 126.84 (ArC next to COO in G1 and G2), 129.41 (*m*-ArC to COO in G1), 129.97 (*m*-ArC to COO in G2), 133.49 (ArC next to NO₂ in G1), 133.75 (ArC next to NO₂ in G2), 144.58 (*p*-ArC to NCH₂ in G1 and G2), 146.88 (*o*-ArC to COO in G1 and G2), 148.53 (ArC next to NCH₂ in G1 and G2), 151.38 (*p*-ArC to COO in G1 and G2), 163.82 (COOMEM), 164.28 (COOCH₂CH₂), 173.59 (CH₂COO). MALDI-TOF calcd for C₁₁₉H₁₇₈N₁₂O₂₂ *m/z* 2129.9 [M + H]⁺, found *m/z* 2138. Anal. Calcd for C₁₁₉H₁₇₈N₁₂O₂₂: C, 67.1; H, 8.4; N, 7.9. Found: C, 68.1, H, 8.4; N, 7.9.

Azobenzene Dendron (G2-COOH, 5) and General Procedure for the Removal of the MEM-Protecting Group. To a solution of **4** (1.0 g, 0.47 mmol) in THF (50 mL) was added HCl/THF (1:1) (1 mL), and the mixture was stirred at 3–5 °C under nitrogen. After removal of the MEM group was completed, the reaction mixture was poured into water (100 mL) and extracted with dichloromethane. The extracts were dried with anhydrous magnesium sulfate and evaporated to dryness under reduced pressure. The crude product was purified by silica gel chromatography eluted with dichloromethane/IPA (10/1) to give **5**. The yield of **5** was 0.85 g (88%). ¹H NMR (CDCl₃) δ 0.854 (t, 12H, *J* = 7.2 Hz, CH₃), 1.22 (m, 96H, (CH₂)₁₂CH₃), 1.58 (m, 8H, *J* = 7.2 Hz, CH₂CH₂COO), 2.30 (t, 8H, *J* = 8.1 Hz, CH₂CH₂COO), 3.73 (t, 8H, *J* = 4.2, CH₂N in G1), 3.95 (br t, 4H, CH₂N in G2), 4.29 (t, 8H, *J* = 5.1 Hz, CH₂CH₂N in G1), 4.64 (br t, 4H, CH₂CH₂N in G2), 6.79 (d, 4H, *J* = 8.1, *o*-ArH to NCH₂ in G1), 6.94 (d, 2H, *J* = 9.0 Hz, *o*-ArH to

NCH₂ in G2), 7.63 (d, 1H, *J* = 8.1 Hz, *m*-ArH to COOH), 7.65 (d, 2H, *J* = 8.1, *m*-ArH to COO in G1), 7.74 (d, 2H, *J* = 8.9 Hz, *m*-ArH to NCH₂ in G2), 7.77 (d, 4H, *J* = 8.7, *m*-ArH to NCH₂ in G1), 8.07 (d, 3H, *J* = 9.0 Hz, *o*-ArH to COO in G1 and G2), 8.33 (d, 2H, *J* = 1.5 Hz, *o*-ArH to COO and NO₂ in G1), 8.39 (d, 1H, *J* = 1.5 Hz, *o*-ArH to COOH and NO₂); ¹³C NMR δ 14.10 (CH₃CH₂), 22.68 (CH₂-CH₃), 24.82 (CH₂CH₂CH₃), 29.13–29.69 ((CH₂)₁₀CH₂CH₂CH₃), 31.93 (CH₂CH₂COO), 34.16 (CH₂COO), 49.76 (CH₂N in G1 and G2), 61.01 (CH₂CH₂N in G1), 62.36 (CH₂CH₂N in G2), 111.71 (*o*-ArC to NCH₂ in G1), 112.99 (*o*-ArC to NCH₂ in G2), 118.65 (*o*-ArC to COO in G1 and G2), 125.58 (*m*-ArC to CH₂N in G1 and G2), 126.76 (ArC next to COO in G1 and G2), 129.39 (*m*-ArC to COO in G1 and G2), 133.52 (ArC next to NO₂ in G1), 133.98 (ArC next to NO₂ in G2), 144.81 (*p*-ArC to NCH₂ in G1 and G2), 146.81 (*o*-ArC to COO in G1 and G2), 148.49 (ArC next to NCH₂ in G1 and G2), 151.73 (*p*-ArC to COO in G1 and G2), 164.28 (Ph-COOCH₂), 166.55 (COOH), 173.99 (CH₂-COO). MALDI-TOF calcd for C₁₁₅H₁₇₀N₁₂O₂₀ *m/z* 2129.9 [M + H]⁺, found *m/z* 2138. Anal. Calcd for C₁₁₅H₁₇₀N₁₂O₂₀: C, 67.7; H, 8.4; N, 8.2. Found: C, 68.5, H, 8.4; N, 8.1.

Azobenzene Dendron (G3, 6). This compound was prepared from **5** (1.4 g, 0.68 mmol), **3** (0.14 g, 0.31 mmol), DCC (0.17 g, 0.82 mmol), and DMAP (0.084 g, 0.68 mmol) and was purified by chromatography eluted with dichloromethane/ethyl acetate (10/1) to give **6** (G3). The yield of **6** was 1.36 g (97%). ¹H NMR (CDCl₃) δ 0.85 (t, 24H, *J* = 7.2 Hz, CH₃), 1.23 (m, 192H, (CH₂)₁₂CH₃), 1.56 (m, 16H, *J* = 7.2 Hz, CH₂CH₂COO), 2.27 (t, 16H, *J* = 7.5 Hz, CH₂CH₂-COO), 3.36 (s, 3H, CH₃O), 3.57 (t, 2H, *J* = 4.1 Hz, CH₂OCH₃), 3.72 (t, 16H, *J* = 4.8, CH₂N in G1), 3.89 (t, 2H, *J* = 4.6, CH₂CH₂OCH₃), 3.96 (br t, 12H, CH₂N in G2 and G3), 4.27 (t, 16H, *J* = 5.7 Hz, CH₂-CH₂N in G1), 4.62 (br t, 12H, CH₂CH₂N in G2 and G3), 5.60 (s, 2H, COOCH₂O), 6.82 (d, 8H, *J* = 8.7, *o*-ArH to NCH₂ in G1), 6.96 (d, 6H, *J* = 8.7 Hz, *o*-ArH to NCH₂ in G2), 7.69–7.73 (m, 7H, *m*-ArH to COO in G1–3), 7.83–7.89 (m, 14H, *m*-ArH to NCH₂ in G1–3), 8.14–8.19 (m, 7H, *o*-ArH to COO in G1–3), 8.41–8.43 (m, 6H, *o*-ArH to COO and NO₂ in G1 and G2), 8.48 (d, 1H, *J* = 1.5 Hz, *o*-ArH to COOMEM and NO₂); ¹³C NMR δ 14.00 (CH₃CH₂), 22.62 (CH₂CH₃), 24.82 (CH₂CH₂CH₃), 29.10–29.62 ((CH₂)₁₀CH₂CH₂CH₃), 31.86 (CH₂-CH₂COO), 34.10 (CH₂COO), 49.79 (CH₂N in G1–3), 58.97 (CH₃O), 60.81 (CH₂CH₂N in G1), 62.33 (CH₂CH₂N in G2 and G3), 70.06 (CH₂-CH₂OCH₃), 71.57 (CH₂OCH₃), 90.65 (COOCH₂O), 111.87 (*o*-ArC to NCH₂ in G1), 112.17 (*o*-ArC to NCH₂ in G2 and G3), 118.91 (*o*-ArC to COO in G1–3), 125.33 (*m*-ArC to CH₂N in G1–3), 126.81 (ArC next to COO in G1–3), 129.57 (*m*-ArC to COO in G1), 130.13 (*m*-ArC to COO in G2 and G3), 133.49 (ArC next to NO₂ in G1–3), 144.71 (*p*-ArC to NCH₂ in G1–3), 146.98 (*o*-ArC to COO in G1–3), 148.10 (ArC next to NCH₂ in G1–G3), 151.48 (*p*-ArC to COO in G1 and G2), 163.79 (COOMEM), 164.25 (Ph-COOCH₂), 173.46 (CH₂COO). MALDI-TOF calcd for C₂₅₁H₃₆₂N₂₈O₄₆ *m/z* 4530.8 [M + Na]⁺, found *m/z* 4543. Anal. Calcd for C₂₅₁H₃₆₂N₂₈O₄₆: C, 66.9; H, 8.1; N, 8.7. Found: C, 66.5, H, 8.1; N, 8.7.

Azobenzene Dendron (G3-COOH, 7). This compound was prepared from **6** (1.0 g, 0.22 mmol) and HCl/THF (1 mL), and purified by chromatography eluted with dichloromethane/IPA (10/1) to give **7**. The yield of **7** was 0.70 g (71%). ¹H NMR (CDCl₃) δ 0.86 (t, 24H, *J* = 7.2 Hz, CH₃), 1.23 (m, 192H, (CH₂)₁₂CH₃), 1.58 (m, 16H, *J* = 6.6

Hz, CH₂CH₂COO), 2.28 (t, 16H, *J* = 7.2 Hz, CH₂CH₂COO), 3.71 (t, 16H, *J* = 5.7, CH₂N in G1), 3.95 (br t, 12H, CH₂N in G2 and G3), 4.28 (t, 16H, *J* = 6.6 Hz, CH₂CH₂N in G1), 4.62 (br t, 12H, CH₂-CH₂N in G2 and G3), 6.82 (d, 8H, *J* = 8.7, *o*-ArH to NCH₂ in G1), 6.92 (d, 6H, *J* = 8.7 Hz, *o*-ArH to NCH₂ in G2), 7.64–7.72 (m, 7H, *m*-ArH to COO in G1–3), 7.78–7.85 (m, 14H, *m*-ArH to NCH₂ in G1–3), 8.06–8.11 (m, 3H, *o*-ArH to COO in G2 and G3), 8.17 (d, 4H, *J* = 8.1 Hz, *o*-ArH to COO in G1), 8.35 (d, 2H, *J* = 2.1, *o*-ArH to COO and NO₂ in G2), 8.41–8.42 (m, 5H, *o*-ArH to COO and NO₂ in G1 and G3); ¹³C NMR δ 14.00 (CH₃CH₂), 22.62 (CH₂CH₃), 24.85 (CH₂CH₂CH₃), 29.13–29.62 ((CH₂)₁₀CH₂CH₂CH₃), 31.89 (CH₂CH₂-COO), 34.13 (CH₂COO), 49.83 (CH₂N in G1–3), 60.88 (CH₂CH₂N in G1), 62.39 (CH₂CH₂N in G2 and G3), 111.91 (*o*-ArC to NCH₂), 118.95 (*o*-ArC to COO in G1–3), 125.36 (*m*-ArC to CH₂N in G1–3), 126.84 (ArC next to COO in G1–3), 129.61 (*m*-ArC to COO), 133.42 (ArC next to NO₂ in G1–3), 144.77 (*p*-ArC to NCH₂ in G1–3), 146.85 (*o*-ArC to COO in G1–3), 148.49 (ArC next to NCH₂ in G1–G3), 151.45 (*p*-ArC to COO in G1 and G2), 164.25 (Ph-COOCH₂), 166.62 (COOH), 173.53 (CH₂COO). MALDI-TOF calcd for C₂₄₇H₃₅₄N₂₈O₄₄ *m/z* 4442.6 [M + Na]⁺, found *m/z* 4439. Anal. Calcd for C₂₄₇H₃₅₄N₂₈O₄₄: C, 67.1; H, 8.1; N, 8.9. Found: C, 65.3, H, 7.9; N, 9.0.

Azobenzene Dendron (G4, 8). This compound was prepared from **7** (0.3 g, 0.068 mmol), **3** (0.014 g, 0.031 mmol), DCC (0.021 g, 0.10 mmol), and DMAP (0.0084 g, 0.068 mmol), and purified by chromatography eluted with dichloromethane/ethyl acetate (10/1) to give **8** (G4). The yield of **8** was 0.23 g (79%). ¹H NMR (CDCl₃) δ 0.85 (t, 48H, *J* = 7.2 Hz, CH₃), 1.23 (m, 384H, (CH₂)₁₂CH₃), 1.57 (m, 32H, *J* = 6.6 Hz, CH₂CH₂COO), 2.27 (t, 32H, *J* = 7.2 Hz, CH₂CH₂COO), 3.35 (s, 3H, CH₃O), 3.57 (t, 2H, *J* = 4.5 Hz, CH₂OCH₃), 3.71 (t, 32H, *J* = 5.7, CH₂N in G1), 3.89 (t, 2H, *J* = 4.5, CH₂CH₂OCH₃), 3.96 (br t, 28H, CH₂N in G2 and G3), 4.27 (t, 32H, *J* = 5.7 Hz, CH₂CH₂N in G1), 4.61 (br t, 28H, CH₂CH₂N in G2 and G3), 5.58 (s, 2H, COOCH₂O), 6.81 (d, 16H, *J* = 9.6, *o*-ArH to NCH₂ in G1), 6.94 (d, 6H, *J* = 8.7 Hz, *o*-ArH to NCH₂ in G2), 7.66–7.73 (m, 15H, *m*-ArH to COO in G1–3), 7.82–7.89 (m, 30H, *m*-ArH to NCH₂ in G1–3), 8.11–8.19 (m, 15H, *o*-ArH to COO in G1–3), 8.40–8.42 (m, 14H, *o*-ArH to COO and NO₂ in G1 and G2), 8.46 (d, 1H, *J* = 1.2 Hz, *o*-ArH to COOMEM and NO₂); ¹³C NMR δ 14.00 (CH₃CH₂), 22.62 (CH₂CH₃), 24.82 (CH₂CH₂CH₃), 29.10–29.62 ((CH₂)₁₀CH₂CH₂CH₃), 31.86 (CH₂CH₂COO), 34.10 (CH₂COO), 49.79 (CH₂N in G1–3), 58.97 (CH₃O), 60.81 (CH₂CH₂N in G1), 62.33 (CH₂CH₂N in G2 and G3), 70.06 (CH₂CH₂OCH₃), 71.57 (CH₂OCH₃), 90.65 (COOCH₂O), 111.87 (*o*-ArC to NCH₂ in G1), 112.17 (*o*-ArC to NCH₂ in G2 and G3), 118.91 (*o*-ArC to COO in G1–3), 125.33 (*m*-ArC to CH₂N in G1–3), 126.81 (ArC next to COO in G1–3), 129.57 (*m*-ArC to COO in G1), 130.13 (*m*-ArC to COO in G2 and G3), 133.49 (ArC next to NO₂ in G1–3), 144.71 (*p*-ArC to NCH₂ in G1–3), 146.98 (*o*-ArC to COO in G1–3), 148.10 (ArC next to NCH₂ in G1–G3), 151.48 (*p*-ArC to COO in G1 and G2), 163.79 (COOMEM), 164.25 (Ph-COOCH₂), 173.46 (CH₂COO). MALDI-TOF calcd for C₅₁₅H₇₃₀N₆₀O₉₄ *m/z* 9288.7 [M + Na]⁺, found *m/z* 9311. Anal. Calcd for C₅₁₅H₇₃₀N₆₀O₉₄: C, 66.8; H, 7.9; N, 9.1. Found: C, 66.1, H, 8.1; N, 9.5.

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