Characterization of Dendrimers for Photonic Applications

O. O. Oyebola\textsuperscript{1,2*} and A. Sieradzan\textsuperscript{2}

\textsuperscript{1}Department of Physics, University of Lagos, Akoka, Nigeria
\textsuperscript{2}Department of Physics and Astronomy, Central Michigan University, Mount Pleasant, ML 48859

ABSTRACT

Nonlinear optical (NLO) materials are well suited for photonic applications as well as the development of optical communication devices. The nonlinear optical response of these materials is a result of the absence of an optical center of symmetry. Such materials usually produce higher orders of optical harmonics. Using dendrimer samples available from a Michigan-based company – Dendritic Nano-Technology (DNT), the ability of dendrimers to produce higher optical harmonics have been studied using spectroscopic techniques. The production of second harmonic signals in these dendrimer species indicates that they do not possess a center of symmetry, and confirms their suitability for nonlinear optical applications.

Keywords: Dendrimers, Photonics, Optical harmonics, Nonlinear optics, Centre of symmetry.

INTRODUCTION

Recent developments in dendrimer technology have led to several novel applications of these materials, and have justified the optimism about their widespread future utilization (Feuerbacher et al, 1998). Fields, which may most strongly benefit from dendrimer use, are optics and photonics.

We used standard spectroscopic techniques to survey optical properties of a group of dendrimers available from Dendritic Nano-Technology (DNT). Of particular interest was the investigation of the ability of these dendrimers to produce higher optical harmonics, to harvest and store the energy of light, and to affect conditions in solutions of organic dyes resulting in more efficient laser action.

Dendrimers are a relatively new class of highly branched macromolecules (Feuerbacher et al, 1998), consisting of a multifunctional central core to which repetitive branches are attached, giving it the tree-like structure (Buhleier et al, 1978). The branches are synthesized from identical building blocks through an iterative sequence of reaction steps, with each reaction step forming a “generation” in the dendrimer’s hierarchical growth, giving the dendrimer a globular structure (Figure 1) with various branching units, internal cavities and closely packed surface groups formed around the initiator core (Buhleier et al, 1978).

![Figure 1: The Dendritic Structure, a highly branched globular structure](image)

*Correspondence: ooyebola@unilag.edu.ng.
They can contain chemically active components and therefore can exhibit particularly interesting properties. This is because cooperation among the units allows the dendrimer to perform specific functions, and also, changes in the properties of such units are used to monitor how dendrimers participate in chemical processes (Tomalia et al., 1984). Several applications and potential applications take advantage of these properties. The possibility of the dendrimer playing host to ‘foreign’ molecules was first observed and reported (Meijer, 1994), by trapping several molecules of Bengal Pose dye in the cavities of water-soluble dendrimer molecules of about 5nm diameter. The so called “dendritic box” is a fifth generation poly (propylene-imine) dendrimer (Meijer, 1994), which has 64 functional groups at the periphery. The trapped molecules are unable to diffuse out of the box, except under prolonged heating. This “dendritic box” is being proposed as a vehicle for drug delivery, especially given the non-toxic nature of dendrimers (Meijer, 1994). In fact, Frenchet’s group at Cornell, while studying the possibility of using dendrimer for chemotherapy, has shown that dendrimer could be eliminated through the kidneys as urine or through feces (Freemantle, 1999), further giving credence to its non-toxic nature.

Current research trends suggest that light will increasingly replace electrons in the deployment of information and communication technology, with broad applications in optical communications, data storage and computer systems (Petkov et al., 2005). To effectively use light in these applications, electronic switching devices such as diodes and transistors must be replaced with their photonic analogs. Such photonic devices require materials whose properties may provide an efficient means of controlling and processing signal-carrying light beams used in photonic technologies (Zavada and Zhang, 1995). Materials with significant quadratic and/or cubic NLO properties are consequently of great importance, especially in the development of compact and efficient solid-state lasers, which emit in the visible spectral region and are of interest for applications ranging from medicinet optical storage, and display techniques (Huber et al., 1999). New materials with such desirable NLO properties are being synthesized, and the various nonlinear optical effects arising from them have been the subject of current research interest (Tomalia et al., 2002). Probably the most popular and most useful of these effects is the production of higher optical harmonics, particularly second and third harmonics.

### SECOND HARMONIC GENERATION THEORY

Nonlinear optics describes the behavior of light in nonlinear media. During the interaction of electromagnetic radiation with matter, the polarization produced in the medium is normally proportional to the electric field of the interacting radiation for small radiation intensities. A nonlinear behavior can result when the intensity of the interacting radiation is strong enough to produce a nonlinear relation between the polarization and the electric field of the interacting radiation. Materials whose properties depend on the intensity of the interacting radiation are called Nonlinear Optical (NLO) materials (Fowles, 1975).

The polarization ($\mathbf{P}$) of a medium interacting with electromagnetic radiation is given by the integral or summation of all the dipole moments ($p_i$) over a unit volume of the medium. When the intensity of the electric field ($\mathbf{E}$) is small, the polarization is proportional to the incident electric field, and the electromagnetic waves associated with the dipole oscillations cannot be distinguished from the original wave. However, with a sufficiently large incident electric field, as is the case with laser light, $\mathbf{P}$ is no longer simply proportional to $\mathbf{E}$. The nonlinearity between $\mathbf{P}$ and $\mathbf{E}$ is now given by the series expansion

$$\mathbf{P} = \varepsilon_0 (\chi_1 \mathbf{E} + \chi_2 \mathbf{E} \cdot \mathbf{E} + \chi_3 \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \ldots)$$

where $\varepsilon_0$ = permittivity of free space

$\chi_i$ = Polarizability tensor or dielectric susceptibility of the medium

$\mathbf{E}$ = Electric field vector of the incident light – a measure of the field strength.

Suppose the incident light beam is represented by:

$$\mathbf{E} = \mathbf{E}_0 \cos \omega t$$

Then

$$\mathbf{P} = \varepsilon_0 (\chi_1 \mathbf{E}_0 \cos \omega t + \chi_2 \mathbf{E}_0 \cdot \mathbf{E}_0 \cos^2 \omega t + \chi_3 \mathbf{E}_0 \cdot \mathbf{E}_0 \cdot \mathbf{E}_0 \cos^3 \omega t + \ldots)$$

Using the fact that:

$$\cos^2 \omega t = \frac{1 + \cos 2\omega t}{2}$$

and

$$\cos^3 \omega t = \frac{3 \cos \omega t + \cos 3\omega t}{4}$$
\[
\vec{P} = E_0 (\chi_1 E_0 \cos \omega t + \frac{\chi_2}{2} (1 + \cos 2 \omega t) \vec{E}_0 \vec{E}_0
+ \frac{\chi_4}{4} (3 \cos \omega t + \cos 3 \omega t) \vec{E}_0 \vec{E}_0 \vec{E}_0 \}
\]

The first term represents the linear optics region where the polarization is just proportional to the electric field vector of the incident light, and produces a harmonic oscillation of fundamental frequency \(\omega\). The second and subsequent terms are the higher order harmonics. Of particular interest to us is the second term of the right hand side of equation 4, which is the nonlinear (quadratic) polarization component responsible for second harmonic generation (SHG). It contains a term of twice the fundamental frequency of the applied optical field, as well as a constant term, which gives rise to a d.c. field across the medium. Since the \(\cos 2 \omega t\) term can appear only in conjunction with a constant term, no SHG is possible in materials possessing optical center of symmetry. This is because the constant term in the SHG indicates a direction-specific field, and for a material possessing center of symmetry, there cannot be a preferred direction, hence SHG cannot occur. Consequently, observance of SHG is a clear evidence of asymmetry in the species exposed to electromagnetic radiation.

The presence of the d.c component in the polarization quadratic term is of a strong practical significance in the study of structure and symmetry of materials. Superficially, practically all dendrimers, especially those from divergent growth, appear to be spherically symmetric (Mukhopadhyay et al, 2009). They look like balls and occasionally are even called “big atoms” (Mukhopadhyay and Ramasesha, 2009). By looking at the dendrimer’s second harmonic response, we should be able to test any hidden asymmetry within the species, even if not at all suggested by its surface appearance. The two signature points of evidence for the presence of 2nd harmonic are:

1. \(\lambda_{out} = \frac{\lambda}{2}\) that is the emergent radiation which has a wavelength two times shorter than the incident beam.
2. \(I_{out} = I_{in}^2\) that is there is a quadratic relation between the intensities of the harmonic signal and the incident light.

MATERIALS AND METHODS

High intensity pulsed laser light from Nd:YAG laser at \(\lambda = 1064\)nm was passed through a dendrimer sample dissolved in methyl alcohol. The shorter-wavelength light (if produced in the sample, is sent through a spectrograph (monochromator) and monitored by a photomultiplier tube as shown in Figure 2. The resulting signal is recorded and analyzed with a Digital Signal Analyzer. The dichroic mirror \(M_1\) reflects the visible light into the spectrograph and transmits the infrared into the dump, while \(M_2\) is only transparent to the visible, thereby blocking any IR light.

The dendrimer samples obtained from DNT and chosen for comparison across generations and structural properties are dissolved in pure methyl alcohol before exposure to laser radiation. To ensure that signals observed are produced solely by the dendrimer species, the pure methyl alcohol solvent is also tested for possible SHG. For proper comparison, samples used are of the same concentration in mg/liter and are irradiated under the same optical arrangement (identical geometry).
Dendrimer species investigated include:
1. DNT 103 dendrimer – a 1,4-diaminobutane-cored second-generation dendrimer having a PAMAM (Poly AmidoAmine) branch and an amine surface. It has 16 surface groups with molecular formula C_{144}H_{292}N_{58}O_{28} and molecular weight of 3284 (Tomalia et al, 1985).
2. G6 PAMAM and G10 PAMAM dendrimers, which also belong to the DNT family but are of much higher generations than the first two (Tomalia et al, 1985).
3. Hyperbranched PAMAM dendrimer, which appears with rather irregular atomic arrangement and is not globular in shape (Tomalia et al, 1985).

All samples are irradiated at several energies of laser pulse (150 mJ, 212 mJ and 300 mJ): second harmonic signals are sought and optimum conditions for SHG established.

RESULTS AND DISCUSSION

SHG signals monitored at 532nm were observed and recorded for the pure alcohol solvent and each of the dendrimer samples, for each energy of laser pulse applied.

As expected, the pure solvent exhibits practically no SHG signal. However, independent of their structure, all dendrimer samples appear to be second harmonic active. The graphs presented in Figure 3 show the strongest SHG signal (at 532nm) for the highest intensity of laser pulse used. In all the samples, the quadratic relation between signal amplitude and laser intensity is evident. In simple mathematical terms, for all nonlinear processes, the signal amplitude (A) is related to the laser pulse intensity (I) by:

\[ A = I^\alpha \]  \hspace{1cm} 5

\[ \log_{10} A = \alpha \log_{10} I \]  \hspace{1cm} 6

which is of the form

\[ Y = mX + C \]  \hspace{1cm} 7

where \( m = \alpha \) is the slope of the log-log graph and also the index of \( I \) in equation 5.

Equation 5 is a quadratic relation when \( \alpha=2 \). The plot of SHG signal amplitude vs. the square of laser intensity shown on the right hand side of Figure 3(a) for the DNT-103 dendrimer confirms this quadratic relation, with a linear fit of near unity correlation.

Figure 2: Experimental setup for investigating Second Harmonic Generation (SHG)
coefficient ($R^2 \approx 0.9957$). Observed relations may not be entirely quadratic, as the relation between signal amplitude and intensity is not purely of the form $Y = X^2$. Hence the simple log-log analysis given in equations 5 to 7 only confirms the present of a dominant quadratic relation. The log-log graphs of signal amplitude vs. pulse intensity in the other two dendrimer samples further demonstrates this dominant quadratic relation, with straight lines having approximate slope values of $\alpha \approx 2$ and linear correlation coefficients $R^2 \approx 0.9907$ and $R^2 \approx 0.9997$ respectively [Figures 3(b) and 3(c)].

The signal intensity peaking at wavelength of 532 nm is another clear evidence of the production of second harmonic signals.

Figure 3(a): (LHS) SHG in G2 DNT-103 dendrimer observed at 532 nm; (RHS) Quadratic relation between signal amplitude and laser intensity.

Figure 3(b): (LHS) SHG in G6 PAMAM dendrimer observed at 532 nm; (RHS) Log-log graph of SHG signal and pulse intensity.

Figure 3(c): (LHS) SHG in Hyperbranched PAMAM dendrimer observed at 532 nm; (RHS) Log-log graph of SHG signal and pulse intensity.
CONCLUSION

Our results show significant presence of second harmonic signals in all the dendrimer samples tested, irrespective of their physical structure or generation. This indicates that contrary to their seeming symmetric physical appearance, dendrimers are indeed asymmetric, that is they do not possess a center of symmetry. Even the hyper-branched species, which look obviously asymmetric, sometimes show weaker SHG signals than the much more “regular-looking” counterparts formed from divergent growth. The asymmetric nature or the lack of a center of symmetry in dendrimers is a significant nonlinear optical property, which makes them suitable as candidates for producing photonic devices.

REFERENCES


Gunter Huber, Tim Kellner, Hanno M. Kretschmann, Thomas Sandrock, Hanno Scheibe, (1999), Compact diode pumped cw solid-state lasers in the visiblespectral region *Optical Materials* 11, 205-216


