

Letters

Second-Order Nonlinear Optical Properties of Highly Symmetric Chiral Thin Films

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Received February 20, 2001

We demonstrate second-harmonic generation in highly symmetric thin films of chiral molecules. The films were prepared by spin-coating, and no external force (such as electric field poling) was used to induce noncentrosymmetry. The films have a nonpolar D_n symmetry with second-order susceptibility values of 2–9 pm/V. Furthermore, the samples are stable at elevated temperatures.

1. Introduction

The development of organic materials for second-order nonlinear optics has traditionally focused on noncentrosymmetric, one-dimensional charge-transfer molecules.¹ For practical applications, these molecules have to be incorporated into a noncentrosymmetric macroscopic medium. The most widely used method to induce macroscopic noncentrosymmetry has been electric field poling of nonlinear optical polymers.² A polymer containing (quasi one-dimensional) nonlinear optical chromophores is spin-coated onto a solid substrate to yield high-quality thin films. Subsequently, the polymer film is heated above its glass transition temperature and a strong static electric field is applied to orient the chromophores in the polymer matrix. Then, the polymer film is cooled below T_g , in the presence of the field, to freeze in the orientation. The poling procedure results in polar ordering of the one-dimensional molecules along the film normal, yielding films with a $C_{\infty v}$ symmetry. Such poled samples are thermodynamically

unstable, and eventually they return to their original isotropic centrosymmetric state.² Furthermore, poling can be quite complex and time-consuming. However, polar order is not required for second-order nonlinear optical processes. Chirality can significantly relax the requirement of polar ordering.³ Hence, even highly symmetric ensembles of chiral molecules can exhibit second-order nonlinear optical properties. The advantage of such structures is that no external force is needed to induce noncentrosymmetry. The earliest example was sum-frequency generation in isotropic solutions of chiral sugar molecules.⁴ Subsequently, electro-optic effects were predicted to occur in chiral isotropic media.⁵ However, second-harmonic generation (SHG) is not allowed in isotropic chiral media. The highest symmetry that allows SHG is the nonpolar D_{∞} symmetry.³ But to the best of our knowledge, efficient SHG in such a medium has never been observed. In this paper, we demonstrate second-harmonic generation in thin films of chiral helicenebisquinone derivatives with noncentrosymmetric D_{∞} and D_2

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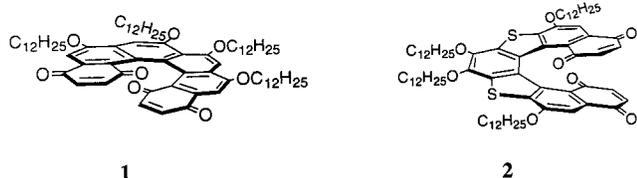


Figure 1. Chemical structures of the helicenebisquinone derivatives.

symmetries. Furthermore, no artificial technique (such as poling) was used to induce the noncentrosymmetry in the films.

2. Experimental Procedures

The materials used were the chiral helicenebisquinone derivatives **1** and **2** (Figure 1).⁶ The nonracemic form of these materials self-aggregates into corkscrew-shaped assemblies, both in concentrated alkane solutions and in the pure material.⁷ In thin films the corkscrew-shaped assemblies further organize into thin lamellae.⁸ Recently, it has been shown that when such films are produced by the Langmuir–Blodgett procedure, they exhibit extraordinary nonlinear optical properties.⁹ In thicker films (several tens of microns) obtained by cooling nonracemic **1** and **2** from an isotropic melt, the corkscrew-shaped assemblies organize into macroscopic fibers that are clearly visible under an optical microscope. Because they therefore scatter too much light, they are not useful for optical applications.⁶

We have spin-coated nonracemic **1** and **2** from concentrated chloroform solutions onto hydrophobic glass slides, yielding films with thicknesses from 0.1 to 0.6 μm . Slightly thicker films (up to 1.2 μm) were prepared by heating small amounts of solid **1** and **2** between two glass slides above the melting point, followed by cooling to room temperature. The resulting films are of remarkable optical quality. No macroscopic fibers are visible. Presumably the fibers cannot form because the films are too thin. UV–vis absorption spectra are almost identical to the spectra of LB films measured previously. They clearly show that the helicene molecules are aggregated into corkscrew-shaped assemblies.⁸

The second-harmonic generation experiments were done by irradiating the samples at a 45° angle of incidence with a fundamental beam from a Nd:YAG laser (1064 nm, 50 Hz, 8 ns) and detecting the second-harmonic light in the transmitted direction. Half and quarter waveplates were used to control the polarization of the irradiating beam, and the second-harmonic light could be resolved into p- and s-polarized components. The second-harmonic signals measured arise from the quadratic response of the sample to the fundamental laser beam. This response is represented by the nonlinear polarization

$$P_i(2\omega) = \sum_{j,k} \chi_{ijk} E_j(\omega) E_k(\omega)$$

where ijk refer to the Cartesian coordinates, $E_j(2\omega)$ and $E_k(2\omega)$ are the components of the optical field at the fundamental frequency, χ_{ijk} is a component of the second-order nonlinear susceptibility tensor and $P_i(2\omega)$ is a component of the nonlinear source polarization at the second-harmonic frequency. For sufficiently thin samples and in the absence of any surface effects, the polarization leads to the amplitude of the second-harmonic field $E(2\omega)$ growing linearly with thickness. Consequently, the intensity of the second-harmonic light, which is proportional to the square of the amplitude, should grow quadratically with the thickness of the films.¹⁰

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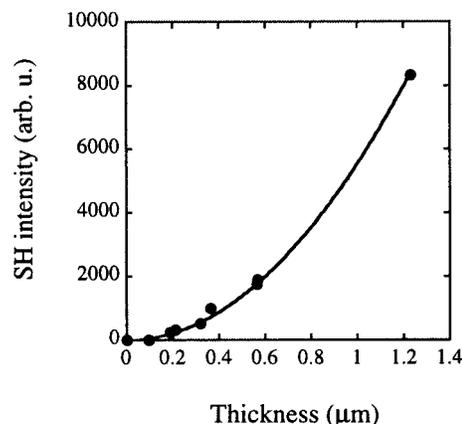


Figure 2. Second-harmonic intensity versus the thickness of the spin-coated films of **1**. The filled circles are the experimental data points; the solid line is a quadratic fit to the experimental data. Data points at 0.6 and 1.2 μm were from samples prepared by heating; the other data points were from spin-coated samples.

3. Experimental Results

Surprisingly, nonracemic films of **1** and **2** showed a fairly strong second-harmonic response, indicating that the films are noncentrosymmetric and have at least a D_∞ symmetry. Furthermore, the second-harmonic signal increases quadratically with thickness for both films. For example, as illustrated in Figure 2, the second-harmonic signal (for a p-polarized fundamental beam) for films of compound **1** grows quadratically for thicknesses ranging from 0.1 to 1.2 μm .

To analyze the second-order susceptibility, the symmetry of the films was first analyzed by measuring the intensities of the second-harmonic light. The sample was irradiated with polarized fundamental light at 45°, and the second-harmonic light emanating from the sample was detected while the sample was rotated around its surface normal. For compound **1**, no variation in the second-harmonic intensity was observed as the sample was rotated, indicating that the samples were isotropic in the plane of the film (Figure 3). Hence, the symmetry of the sample is either C_∞ or D_∞ . To discriminate between these symmetries, we analyzed the dependence of the polarization of the second-harmonic light on the polarization of the fundamental beam. For an s-polarized fundamental, the p- and s-polarized second-harmonic signals were always zero. For a p-polarized fundamental, only the s-polarized second-harmonic was nonvanishing. The only symmetry compatible with this observation is D_∞ , which is chiral. For this symmetry there is only one nonvanishing susceptibility component, χ_{xyz} (the z -coordinate was taken perpendicular to the film plane, and x and y were taken in the plane of the film). By calibrating the p–s signal against a quartz reference, we found χ_{xyz} to be 2 pm/V. Note also that this component is uniquely associated with chirality and should vanish in achiral (or racemic) samples. This was clearly illustrated by the fact that samples made from the racemic material showed no second-harmonic response. Hence, handedness (or the material's chirality) is responsible for the second-order nonlinearity observed in the nonracemic samples.

A similar analysis was carried out for samples of compound **2**. In this case the symmetry was D_2 (Figure 3), in which there are three independent nonvanishing susceptibility components, $\chi_{xyz} = \chi_{xzy}$, $\chi_{yzx} = \chi_{zyx}$, and χ_{zxy}

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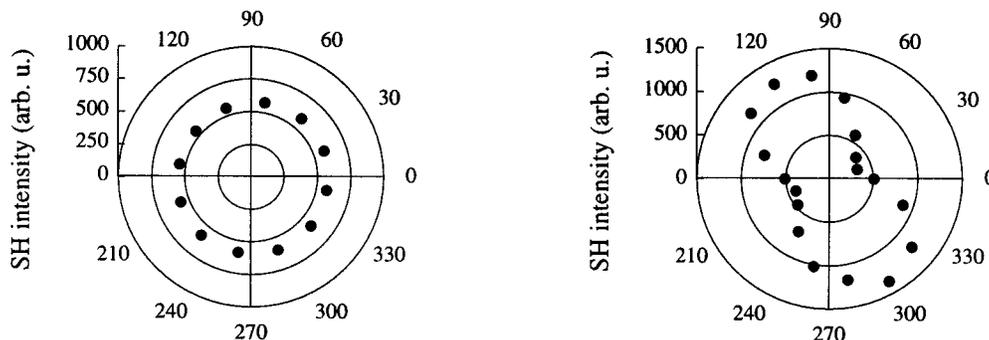


Figure 3. Second-harmonic intensity versus the azimuthal rotation angle of a thin film of **1** with in-plane isotropy (left figure) and a film of **2** with 2-fold symmetry in the film plane (right figure).

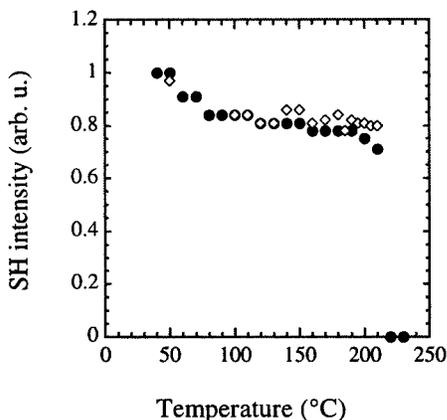


Figure 4. Second-harmonic intensity versus temperature for compound **1**. The filled circles represent the heating cycle; the open diamonds represent the cooling cycle.

$= \chi_{zyx}$. However, for this symmetry, the value of the susceptibility components depends on the choice of the in-plane coordinates x and y . Therefore, it is convenient to consider linear combinations of susceptibility components that do not depend on the in-plane rotation angle.¹¹ Such a combination is for example $\chi_{xyz} - \chi_{yxz}$, which was calibrated to have a value of 9 pm/V.

Since the helicene derivatives spontaneously assemble into films with strong SHG properties, one would expect the nonlinearity to be stable over a wide temperature range. In fact, heating films of **1** and **2** up to temperatures over 200 °C has no significant effect on their SH efficiency. Above the melting point (211 °C for **1** and 235 °C for **2**), the material becomes an isotropic liquid with no SHG

properties and the signal drops to zero (Figure 4). However, after the samples are cooled to below the melting points, the SH signals spontaneously return to their original values, indicating that the samples are thermodynamically stable.

It is remarkable that SHG is observed at all from these samples. Spin-coating usually results in completely isotropic samples that do not allow SHG. In the case of the helicene molecules, we propose that they organize into liquid crystalline-like layers that stack together, giving rise to the D_2 and D_∞ symmetry observed. Furthermore, the susceptibility values of 2 and 9 pm/V are also extraordinary, since such highly symmetric thin films with considerable second-order nonlinearity are, as far as we know, unknown. Furthermore, the 9 pm/V for films of compound **2** is close to values that are useful for nonlinear optical applications.¹² For this reason and because they are so thermally stable, the compounds studied here, or related ones, might be useful in nonlinear optical and photonic applications.

Acknowledgment. This work was supported by research grants from the Fund for Scientific Research—Flanders (FWO-V, No. G.0338.98 and 9.0407.98), from the Belgian government (No. IUAP P4/11), and from the University of Leuven (No. GOA/2000/03). T.V. is a Postdoctoral Fellow of the Fund for Scientific Research—Flanders. The work of C.N., K.E.S.P., and T.J.K. was supported by the U.S. National Science Foundation by means of a grant (CHE 9802316) and a graduate fellowship to K.E.S.P.

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