Strong Enhancement of Nonlinear Optical Properties Through Supramolecular Chirality

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A new approach to second-order nonlinear optical (NLO) materials is reported, in which chirality and supramolecular organization play key roles. Langmuir-Blodgett films of a chiral helicene are composed of supramolecular arrays of the molecules. The chiral supramolecular organization makes the second-order NLO susceptibility about 30 times larger for the nonracemic material than for the racemic material with the same chemical structure. The susceptibility of the nonracemic films is a respectable 50 picometers per volt, even though the helicene structure lacks features commonly associated with high nonlinearity. Susceptibility components that are allowed only by chirality dominate the second-order NLO response.

Second-order NLO effects are usually observed only from noncentrosymmetric materials (*1*). Commonly, such materials are constructed by incorporating donor-acceptor–substituted molecules that have a nonvanishing molecular hyperpolarizability (*2*) into noncentrosymmetric structures such as poled polymer films, Langmuir-Blodgett (LB) films, self-assembled films, or crystals (*3, 4*). The nonlinearity of such materials has been improved by optimizing the microscopic response of the molecules (*5*) or by improving their alignment or orientation in the macroscopic structure (*6*).

Another way to achieve noncentrosymmetry is to use chiral molecules. Such molecules are necessarily noncentrosymmetric, and their second-order NLO response is therefore nonzero (*7*). Even such highly symmetric macroscopic assemblies as isotropic solutions of a single enantiomer (a single mirror-image form) of a chiral molecule are noncentrosymmetric and can be used for second-order nonlinear optics, as shown by sum-frequency generation in sugar solutions (*8, 9*). The intrinsic value of the nonlinear susceptibility of such materials can be quite high (~0.4 pm/V). However, the process is not phase matchable, and its overall efficiency is therefore low. A more efficient approach has been to use chirality indirectly, to ensure molecular crystallization in a noncentrosymmetric group (*10*). Recently, nonlinear optics has also been used as a sensitive tool to study chiral surfaces (*11, 12*).

We show that high nonlinearity can be achieved by assembling the molecules of an enantiomerically pure helicene (*13*) into supramolecular arrays. The NLO response of their films is much higher than that of films of the corresponding racemic (50/50) mixture of the enantiomers, even though the constituent molecules in both films have the same chemical structure.

The molecules we studied were those of the tetrasubstituted helicenebisquinone shown in Fig. 1 (*13, 14*). In bulk samples, the nonracemic, but not the racemic, form of the material spontaneously organizes (*15*) into long fibers clearly visible under an optical microscope. These fibers comprise columnar stacks of helicene molecules (*15*). Similar columnar stacks self-assemble in appropriate solvents, such as *n*-dodecane, when the concentrations are greater than ~1 mM, and when they assemble, the circular dichroisms (CD) of the solutions increase significantly (*13*).

We prepared LB films (*16*) of the helicene by spreading a dilute chloroform solution (2×10^{-4} M) onto the pure water subphase of an LB trough. After the solvent had been evaporated at 20°C, the films were slowly compressed to a surface pressure of 20 mN/m. After stabilizing for 30 min, the films were deposited by horizontal dipping onto hydrophobic glass [for second-harmonic generation (SHG) measurements], fused quartz [for ultraviolet (UV)–visible absorption and atomic force microscopy (AFM) measurements], or silicon (for AFM measurements). The optical quality of the films was excellent. Although 60 is the largest number of layers deposited to date, there is no indication that the quality of films with more layers would be lower. Optical microscopy detected no fibers or other macroscopic features in the films. This means that in the LB films of even the nonracemic material, any supramolecular organization extends only to submicrometer lengths.

The samples were irradiated at a 45° angle of incidence with a fundamental beam from a Nd–yttrium-aluminum-garnet (Nd:YAG) laser (1064 nm, 50 Hz, 8 ns), and the SHG signals (532 nm) were detected in the transmitted direction. Half- and quarter waveplates were used to control the polarization of the irradiating beam, and the second-harmonic light was resolved into p- (in the plane of incidence) and s- (out of the plane of incidence) polarized components.

The SHG signals measured arise from the quadratic response of the material to the fundamental beam. This response is represented by the NLO polarization (*1*)

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

where *ijk* refer to the cartesian coordinates, $E_j(\omega)$ and $E_k(\omega)$ are components of the electric-field amplitude at the fundamental frequency ω, $P_i(2\omega)$ is a component of the nonlinear source polarization at the second-harmonic frequency 2ω, and χ_{ijk} is a component of the second-order susceptibility tensor. For sufficiently thin samples, the polarization leads to the amplitude of the second-harmonic field $E(2\omega)$ growing linearly with thickness (*1*). Consequently, the intensity of the second-harmonic field, which is proportional to the square of the amplitude, should increase quadratically with both the thickness of the film and the value of the susceptibility.

The films of the nonracemic helicene generated strong SHG signals whose intensity increased quadratically as a function of the number of deposited layers (Fig. 2A), which confirms the good structural and optical quality of the films. The strongest SHG signal from a one-layer nonracemic film was approximately 1000 times as intense as that from a similar racemic film, corresponding to a ~30-fold enhancement in the value of the susceptibility. This enhancement is extraordinary, because the individual molecules in both films have the same chemical structures.

For the nonracemic sample, the SHG signal was strongest when the incident beam was p-polarized and the SHG beam was s-polarized (p-in–s-out signal), whereas, for the racemic sample, the signal was strongest when both beams were p-polarized (p-in–p-out signal). For isotropic surfaces and thin films (*17*), the p-in–s-out signal is due to the components of the second-order susceptibili-

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ty tensor that are nonvanishing only in the presence of chirality (chiral components). The p-in–p-out signal, however, is allowed for all surfaces and thus is due to the achiral components of the susceptibility tensor. These results suggest that in the nonracemic samples, the dominant part of the susceptibility tensor is that associated with chirality. In the racemic samples, this part must cancel. An alternative explanation for the different behavior of the two types of samples is that the helicene packs differently in the racemic and nonracemic films.

To analyze these possibilities, we first investigated whether the dominant components of the second-order susceptibility tensor are allowed only by chirality. Although separating the chiral and achiral tensor components is straightforward for thin films that are isotropic, in-plane anisotropy significantly complicates such separation (*18*). Therefore, instead of relying on typical chiral effects (*19*), we determined the symmetry and nonvanishing tensor components of the samples, using several different measurements.

We first measured SHG signals while rotating the samples about their surface normal (*20*). Films of the racemic material were isotropic ($C_{\infty v}$ symmetry). On the other hand, the rotation pattern obtained for a five-layer nonracemic film and p-in–s-out signal (Fig. 2B) is anisotropic and suggests that the nonracemic film possesses C_2 symmetry. If such a film were achiral, that is, if it had C_{2v} symmetry, the signal shown in Fig. 2B would vanish at some rotational angle. Because it does not, there must be a finite chiral susceptibility component. Moreover, this component probably plays an important role, because the average signal is very large.

To separate the effects of chirality and anisotropy on the NLO response of the nonracemic films, we determined the components of the nonlinear susceptibility tensor of a five-layer film. We use a coordinate system with *z* along the surface normal and *x* and *y* in the plane of the substrate. The nonvanishing components of the susceptibility tensor of the C_2 group are χ_{zzz}, χ_{zxx}, χ_{zyy}, $\chi_{xxz} = \chi_{xzx}$, $\chi_{yyz} = \chi_{yzy}$, $\chi_{xyz} = \chi_{xzy}$, $\chi_{yxz} = \chi_{yzx}$, and $\chi_{zxy} = \chi_{zyx}$. For a hypothetical achiral sample with twofold symmetry (C_{2v}), a mirror plane containing the surface normal fixes the directions of the in-plane coordinates *x* and *y*. Furthermore, reflection in that plane implies that the components χ_{xyz}, χ_{yxz}, and χ_{zxy} are allowed only by chirality. However, our chiral C_2 sample has no mirror plane, and therefore the choice of *x* and *y* is arbitrary. In addition, rotation of the in-plane coordinates mixes the achiral and chiral tensor components. For example, when rotated, χ_{zxy} contributes to χ_{zxx}, χ_{zyy}, χ_{zxy}, and χ_{zyx}. Hence, none of the tensor components can uniquely be associated with chirality. To circumvent this arbitrariness, it is necessary to consider linear combinations of the tensor components that do not depend on the in-plane rotational angle. Such isotropic combinations are: χ_{zzz}, $\chi_{zxx} + \chi_{zyy}$, $\chi_{xxz} + \chi_{yyz}$, and $\chi_{xyz} - \chi_{yxz}$. The last of these combinations can be uniquely associated with chirality.

To determine the components of the susceptibility tensor, we used the polarization technique of (*21*) to measure the SHG signals from samples at several in-plane azimuthal rotational angles. We also verified that the isotropic combinations are independent of the assumed 0° orientation of the sample. The magnitudes determined for these combinations, referenced to a quartz wedge ($d_{11} = 0.3$ pm/V) (*22*), are shown in Table 1. The achiral combinations are seen to be at least 10 times smaller than the chiral one. The nonlinearity of the nonracemic samples is therefore dominated by the chiral tensor components. Thus, the chirality of the nonracemic sample contributes significantly to the different NLO responses of the racemic and nonracemic samples. That it is essentially the sole factor responsible for the difference was verified by observing that the absolute levels of the p-in–p-out signals, averaged over the in-plane rotational angle, were, within 20% error, equal for the racemic and nonracemic samples. Hence, the achiral parts of the nonlinearity are essentially the same for the racemic and nonracemic samples. Why the chiral susceptibility components are large is, however, not explained by these results.

The UV-visible absorption spectra of LB films of the racemic and nonracemic samples are identical and similar to those of nonracemic solutions in which the molecules are aggregated, not isolated (*13*). This suggests that the molecules of the racemic and nonracemic materials are organized into similar aggregates on a small scale. AFM images (Fig. 3) support this suggestion, for they show that the aggregated molecules in both films are further assembled into fibrous structures. However, the organization is greater in the films of the nonracemic material (Fig. 3, A and C). The structures in these are ~5 nm wide [about the width (4.1 nm) of the columns into which the molecules assemble in bulk (*14*)], several tens of nanometers long, and arranged in bundles. However, the scale of the organization in the LB films is sufficiently small that the structures cannot be seen optically, although the alignment of the bundles in the plane of the substrate probably accounts for the C_2 symmetry evidenced in Fig. 2B. In the racemic material (Fig. 3B), the fibrous structures are shorter and not as well

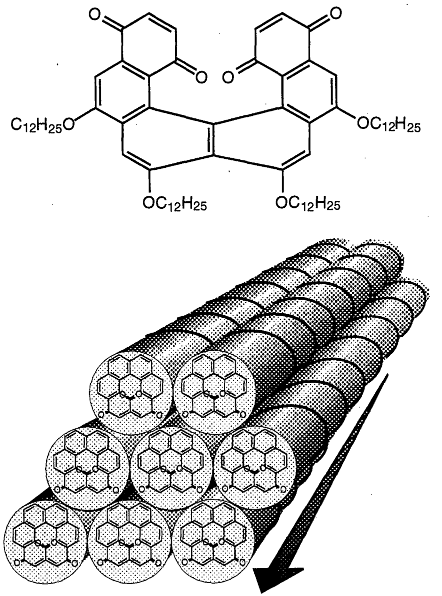

Fig. 1. (Top) Chemical structure of the helicene and (bottom) schematic representation of columns of stacked helicene molecules as observed in solid bulk samples (the side chains have been deleted for clarity, and the first helicenes are arbitrarily shown to be in the same rotational phase).

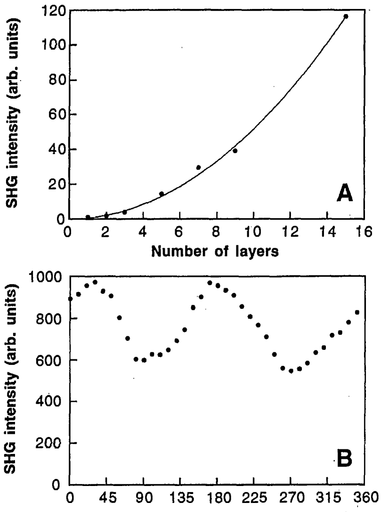

Fig. 2. Second-harmonic signals from the nonracemic LB films. (**A**) The signal as a function of the number of deposited layers. (**B**) The s-polarized second-harmonic signal for p-polarized fundamental beam as a function of the azimuthal (in-plane) rotation angle of a five-layer sample. The 0° azimuthal orientation is chosen arbitrarily.

Table 1. Absolute values of chiral and achiral isotropic combinations of susceptibility components of the nonracemic LB films.

Isotropic combination	Absolute value (pm/V)	Chirality
χ_{zzz}	6	Achiral
$\chi_{xxz} + \chi_{yyz}$	2	Achiral
$\chi_{zxx} + \chi_{zyy}$	4	Achiral
$\chi_{xyz} - \chi_{yxz}$	50	Chiral

organized in bundles. This suggests that the interactions between the enantiomers are not favorable for large-scale organization, which may relate to why the racemate does not form fibrous structures in bulk (*15*). The lesser degree of organization in the racemic material also conforms with the failure to see x-ray diffraction from these films, whereas it is seen from films of the nonracemic material. For the latter, x-ray diffraction shows the interlayer distances to be similar to the diameters of the helicene molecules and to the columns observed in bulk (*23*).

The above results suggest that the primary explanation for the high second-order NLO response of the helicenes is the aggregation into columnar stacks with large chiral (*xyz*-type) nonlinear tensor components. Spontaneous chiral segregation (*24*) probably occurs in the racemic films, with each enantiomer aggregating with itself and maintaining the large chiral components. In the racemic samples however, these dominant components of the two enantiomers are equal in magnitude but opposite in sign, which lowers the overall NLO response. Further organization of the aggregates into bundles appears to be less important for the NLO properties, although it accounts for the different rotational symmetry of the racemic and nonracemic films.

The 50 pm/V value of the dominant part of the nonlinearity ($\chi_{xyz} - \chi_{yxz}$; Table 1) is sufficiently high that the material could be useful (*25*). The linear absorption spectrum, however, suggests that the NLO response may be resonantly enhanced. Nevertheless, it is within one order of magnitude of the highest values reported (*26*). We find the result remarkable because (i) the nonlinearity is dominated by the chiral tensor components, which suggests that the traditional requirements for nonlinear molecules to be oriented out of the plane (*1*) are not important for structures based on the helicene derivative, and (ii) although the chemical structure does not fulfill classical requirements for high molecular nonlinearity (*2*), the NLO susceptibility is nevertheless relatively high, which suggests that further improvements might be achievable through synthesis.

The films of the nonracemic helicene have other virtues. A five-layer film showed impressive thermal stability. When stored for 250 hours in air at 150°C, it lost no SHG efficiency, and even short excursions above 200°C had no detrimental effect on the NLO response. Moreover, to prepare thick films, the vertical dipping procedure could be used, which is desirable because it is less time-consuming than horizontal dipping. Although the type of deposition achieved when the helicene was dipped vertically depended on the humidity, the temperature, and the way the substrate was prepared, we were able to make Y-type LB films (those deposited during both up and down strokes) whose optical qualities and nonlinear efficiencies equaled those of films formed by horizontal dipping.

The helicene films also suggest a new way to achieve phase matching. Phase matching is an important consideration in frequency conversion, in which the phase relation between the driving nonlinear polarization and the generated field can usually be maintained only over the distance of coherence length (*27*). However, phase matching over arbitrary distances can be achieved by using multilayer structures in which the sign of the nonlinearity is reversed after every coherence length (quasi–phase matching) (*28*). The sign of the chiral part of the nonlinearity can be reversed simply by changing the enantiomer of the molecule with no need for additional domain reversal. The use of the two enantiomers in a quasi–phase-matched structure also has the additional benefit that no net polarization rotation due to linear optical activity will occur. As a preliminary test of the mutual compatibility of the two enantiomers of the helicene, we prepared four layers of one enantiomer by vertical dipping and covered them with four layers of the other. For such thin films, the nonlinearities of the two enantiomers should cancel. The SHG signal from the sample vanished, which suggests that it might be possible to use helicenes to prepare quasi–phase-matched structures.

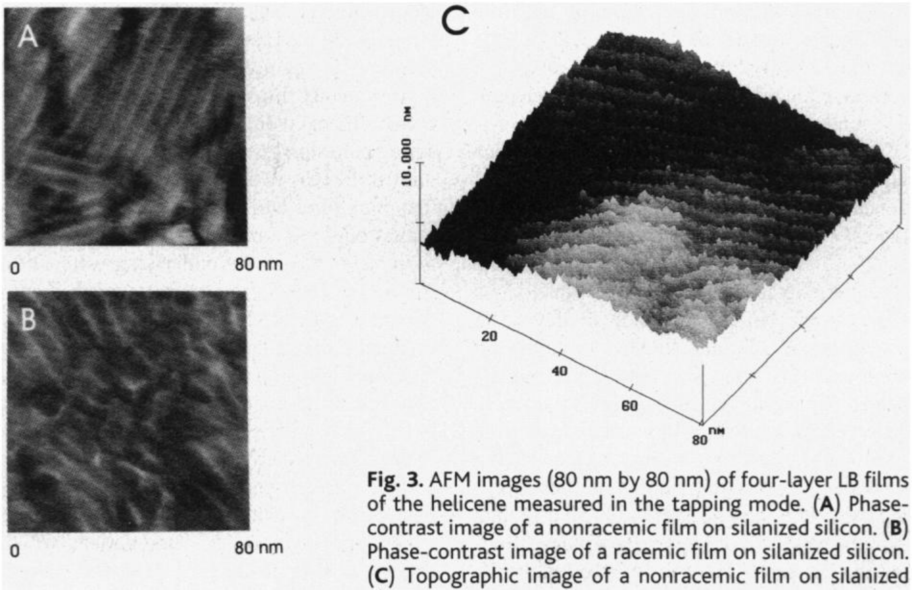

Fig. 3. AFM images (80 nm by 80 nm) of four-layer LB films of the helicene measured in the tapping mode. (**A**) Phase-contrast image of a nonracemic film on silanized silicon. (**B**) Phase-contrast image of a racemic film on silanized silicon. (**C**) Topographic image of a nonracemic film on silanized glass.

References and Notes

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