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Second-order nonlinear optical properties of chiral thin films

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This paper reviews work on the second-order nonlinear optical properties of chiral thin films and surfaces. In particular, we give an overview of the theoretical formalism and experimental procedures that have been used to describe second-harmonic generation from chiral surfaces or thin films. In addition, we discuss a series of experimental results which include second-harmonic generation studies from surfaces and thin films composed of chiral synthetic and biological molecules. When appropriate, we point out possible applications or suggest directions for further research.

Introduction

Chirality is equivalent to the lack of mirror planes in a system.[1] For example, chiral molecules possess no mirror planes and, as a consequence, occur in two enantiomers that are mirror images of each other. Chemists have long been interested in chiral molecules because of their importance in the fields of biochemistry, biology and pharmacology. All chiral molecules exhibit optical activity, *i.e.* a different interaction with left- and right-hand circularly polarized light. The circular-difference response changes sign between the two enantiomers of the chiral molecule. Examples of optical activity effects include optical rotation (rotation of the plane of polarization of incoming linearly polarized light), circular dichroism (different absorption of left- and right-hand circularly polarized light) and optical rotatory dispersion (wavelength dependent optical rotation).[2] These effects can be used to determine the absolute configuration of chiral molecules, their enantiomeric purity, and the secondary structure of proteins and DNA. The effects of optical rotation (OR), circular dichroism (CD) and optical rotatory dispersion (ORD) originate from the interference between electric dipole and weak magnetic dipole transition moments within a molecule.[3]

Chiral molecules can also exhibit non-linear optical activity, *i.e.* a different interaction with left- and right-hand circularly polarized light in a non-linear optical (NLO) process. For example, circular-difference effects have been theoretically predicted to occur in sum and difference frequency generation and optical phase conjugation from chiral fluid media.[4] However, the predicted non-linear optical activity effects are small and have never been observed experimentally. Recently, non-linear optical activity was demonstrated in second-harmonic generation (SHG) from chiral surfaces. For example, SHG spectra of chiral binaphthyl derivatives adsorbed at the air/water interface are dependent on the helicity of the incident circularly polarized fundamental light.[5] The observed circular-difference effects are large and can be explained within the electric dipole approximation of the field–matter interaction.[6] This new experimental technique was put forth as a sensitive tool to study surface chirality. Owing to the similarity with traditional circular dichroism, it is often referred to as SHG-CD. The usefulness of SHG-CD is based on the combination of second-harmonic generation and circular dichroism. SHG is inherently surface specific, and SHG-CD is therefore extremely sensitive to chirality of surfaces. Circular-difference effects in second-harmonic generation from Langmuir–Blodgett films[7,8] of chiral polymers have also been observed and, in some cases, magnetic dipole contributions to the non-linearity of the films had to be included to explain the observed experimental results.[9]

Another virtue of chirality in even-order non-linear optics is the inherent non-centrosymmetry of chiral materials, a necessary requirement for a material to be useful in even-order non-linear optics.[10,11] Therefore, even-order non-linear optical effects can be observed in highly symmetric media such as chiral isotropic liquids or solutions. For example, Rentzepis *et al.*[12] observed sum-frequency generation in isotropic solutions of enantiomerically pure arabinose and Shkurinov *et al.*[13] observed second-harmonic generation in an optically active liquid through a fourth-order non-linearity. In addition, it has recently been theoretically predicted that an electro-optic effect could exist in isotropic chiral media.[14]

In this paper we will limit ourselves to an overview of our work in the field of (surface) non-linear optical activity. In addition, we discuss work of other groups that have made important contributions to the field. When appropriate, we will point out possible applications and directions for further research.

General background

The non-linear response of a material at the second-harmonic frequency is described by the second-order non-linear polarization[10] eqn. (1),

$$P_i(2\omega) = \sum_{j,k} \chi_{ijk} E_j(\omega) E_k(\omega) \tag{1}$$

where χ is the electric dipole allowed second-order susceptibility, $E(\omega)$ the electric field amplitude of the incident light field and the indices ijk refer to Cartesian coordinates. A strict requirement for SHG to occur is the absence of centrosymmetry: in centrosymmetric media all susceptibility components vanish. However, at the surface of such a material, the centrosymmetry is necessarily broken and SHG can occur. Therefore, SHG has been used as a sensitive tool to investigate surfaces and interfaces.[15]

Usually it is sufficient to include only electric dipole interactions as described by eqn. (1) to describe the non-linear response of a material. However, it has been shown that, for certain chiral systems, magnetic dipole interactions have to be included to describe their non-linear response. This is done by including, up to first order, magnetic dipole interactions in the non-linear polarization and by defining a non-linear magnetization;[16,17] eqn. (2), where

$$\begin{aligned} P_i(2\omega) &= \sum_{j,k} \chi^{\mathrm{eee}}_{ijk} E_j(\omega) E_k(\omega) + \chi^{\mathrm{eem}}_{ijk} E_j(\omega) B_k(\omega) \\ M_i(2\omega) &= \sum_{j,k} \chi^{\mathrm{mee}}_{ijk} E_j(\omega) E_k(\omega) \end{aligned} \tag{2}$$

Table 1 Non-vanishing components of the tensors χ^{eee}, χ^{eem} and χ^{mee} for isotropic achiral and chiral surfaces. The surface is in the xy plane

Tensor	Achiral components	Chiral components
χ^{eee}	zzz, $zxx=zyy$, $xxz=xzx=yyz=yzy$	$xyz=xzy=-yxz=-yzx$
χ^{eem}	$xyz=-yxz$, $zxy=-zyx$, $xzy=-yzx$	zzz, $zxx=zyy$, $xxz=yyz$, $xzx=yzy$
χ^{mee}	$xyz=xzy=-yxz=-yzx$	zzz $zxx=zyy$, $xxz=xzx=yyz=yzy$

$B(\omega)$ is the magnetic induction field and the superscript in the susceptibility components associate the respective subscripts with electric dipole (e) and magnetic dipole (m) interactions. Both non-linear polarization and magnetization act as sources of second-harmonic generation.

In this paper we are primarily concerned with the non-linear optical properties of chiral thin films and surfaces. For the most common case of isotropic surfaces, the number of independent tensor components can be significantly reduced. For example, for an isotropic chiral surface (C_∞ symmetry) there are four independent components of χ^{eee}, seven independent components of χ^{eem}, and four independent components of χ^{mee}. For an isotropic achiral surface ($C_{\infty v}$ symmetry) there are only three independent components of χ^{eee}, three independent components of χ^{eem}, and one independent component of χ^{mee} (Table 1).[17] The components that are non-vanishing for chiral surfaces only are referred to as chiral components. Susceptibility components that are non-vanishing for any surface (chiral or achiral) are called achiral components.

We consider an experimental configuration where a laser beam at frequency ω is incident on a thin film or surface (Fig. 1). For such a sample, the dependence of the generated second-harmonic field on the source polarization and magnetization is linear. In addition, the magnetic induction field depends linearly on the electric field. Therefore, the intensity of second-harmonic light emanating from a surface or a thin film can always be expressed in the general form (3)

$$I(2\omega)=|fE_p(\omega)E_p(\omega)+gE_s(\omega)E_s(\omega)+hE_p(\omega)E_s(\omega)|^2 \qquad (3)$$

where $E_p(\omega)$ and $E_s(\omega)$ are, respectively, the p- and s-polarized components of the fundamental field incident on the surface. The parameters f, g, and h are linear combinations of the various second-order susceptibility components (electric dipole and magnetic dipole); they depend also on the linear refractive indices of the surface and are different for the reflected and transmitted second-harmonic waves. In addition, each parameter can be split into a p (f_p, h_p and g_p) and s component (f_s, h_s and g_s) corresponding to the p- and s-polarized components of the second-harmonic field. The detailed form of these parameters can be found in ref. 18. Important is that h_s, f_p and g_p are non-vanishing for any isotropic surface, while f_s, g_s and h_p become non-vanishing for an isotropic surface only when the surface is also chiral.

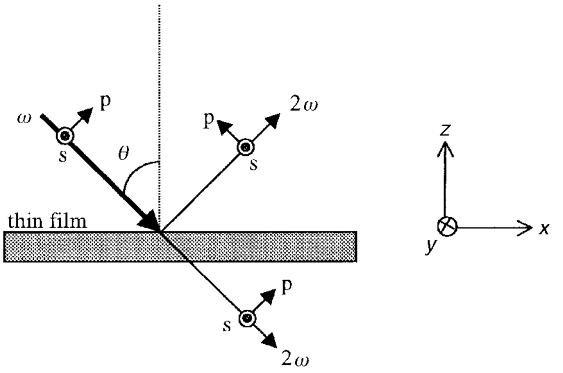


Fig. 1 Geometry of second-harmonic generation from a thin film or a surface. The fundamental beam at frequency ω is incident on the film at angle θ. The p- and s-polarized second-harmonic fields are generated in the reflected and transmitted directions.

Intensity-difference effects in SHG from chiral surfaces

If we consider circularly polarized excitation for which $E_p(\omega)=\pm iE_s(\omega)$ eqn. (3) reduces to (4).

$$I(2\omega)=|-f+g\pm ih|^2I^2(\omega) \qquad (4)$$

Hence, circular-difference effects will occur if $(-f+g)$ and h are simultaneously non-vanishing and if there is a phase difference between $(-f+g)$ and h. For surfaces that are isotropic in the plane of the surfaces, $(-f+g)$ and h are simultaneously non-vanishing only if the surface is also chiral. Hence SHG is a unique probe of chirality.[19] The circular-difference effects, associated with the chirality of the film or surface, can be defined as in eqn. (5).

$$\Delta I(2\omega)=I(2\omega)_{\text{left}}-I(2\omega)_{\text{right}}=4\,\text{Im}((f-g)h^*)I(\omega)^2 \qquad (5)$$

The observed circular-difference effects are equal in magnitude for the different enatiomers, but opposite in sign.

We must note however that achiral surfaces that are anisotropic in the surface plane can also exhibit circular-difference effects in SHG. For example, when the orientation of an achiral but anisotropic sample in the SHG set up makes the complete experimental geometry chiral, circular-difference effects can be observed.[20–22] In that case $(-f+g)$ and h are also non-vanishing and second-harmonic generation is no more a unique probe of surface chirality. Fortunately, it is quite straightforward to discriminate between anisotropic and chiral contributions to the circular-difference response: averaging the circular-difference effects over all azimuthal orientations of the sample eliminates the contribution of anisotropy to the observed circular-difference effects.[23]

It has been shown recently that appropriately chosen linear polarizations can also be used to probe surface chirality.[24,25] For example, the second-harmonic efficiency of a chiral thin film is different for excitation with light that is polarized +45 and −45° with respect to the p-polarized direction. This linear-difference effect has no analogue in linear optics. The linear-difference effect also depends on interference between the f, g and h coefficients: for +45 and −45° linearly polarized light, $E_p=\pm E_s$. Using equation (3), we obtain (6).

$$I(2\omega)=|f+g\pm h|^{2}I^2(\omega) \qquad (6)$$

Hence, linear-difference effects will occur if $(f+g)$ and h are simultaneously non-vanishing. However, no phase difference between $(f+g)$ and h is required. Instead these quantities must have appreciable in-phase parts. In this respect, linear-difference effects are complementary to circular-difference effects in SHG (where a phase difference between the expansion coefficients is required). The linear-difference effect can be quantified by[19] eqn. (7).

$$\Delta I(2\omega)_{-45}-I(2\omega)_{+45}=4\,\mathrm{Re}((f+g)h^{*})I(\omega)^{2} \qquad (7)$$

Experimental techniques

From an experimental point of view, non-linear optical activity can be studied in several ways. The most straightforward method is to measure the difference in second-harmonic efficiency of the sample for left- and right-hand circularly polarized light. When measured as a function of wavelength, the similarity between ordinary circular dichroism becomes clear.[5] Therefore, this technique has been called SHG-CD. Unfortunately, the amount of information that one can obtain is limited. For example, it is not possible to determine any tensor components or to discriminate between magnetic dipole or electric dipole interactions. Hence, the method can only be used to probe the presence of chirality and to discriminate between the enantiomers of a chiral molecule. In addition, SHG-CD is a resonance technique and is therefore limited to regions of the spectrum in which the molecules absorb light.

Unfortunately, not all molecules of interest can be probed in resonance condition, due to the limited wavelength tunability of most laser systems. Another method, based on optical rotatory effects in second-harmonic generation, does not require resonance conditions.[26] Owing to the similarity with optical rotatory dispersion, this technique is called SHG-ORD. Here, the polarization of the surface SHG radiation is rotated with respect to that of the input fundamental radiation in a direction indicative of the chirality of the surface molecules. For example, for a p-input polarization, the rotation angle is given by $\phi=\tan^{-1}(f_s/f_p)$. For an achiral sample, $f_s=0$ and no polarization rotation will occur.[27] For chiral samples, $f_s\neq 0$ and is opposite in sign for the two enantiomers. Therefore, the optical rotation will have the same magnitude but opposite sign for the two enantiomers. An example of such a measurement is shown in Fig. 2.

A third method is continuously to vary the state of polarization of the fundamental beam by means of a quarter-wave plate and to record the intensities of various second-harmonic signals. The initial fundamental beam can be p-polarized with respect to the sample. The wave plate is rotated through an angle of 360° and the s- and p-polarized components of the second-harmonic fields are recorded in reflection and/or transmission.[9] This technique is by far the most versatile. The polarization pattern obtained in this method can be used to determine (i) the magnitude and sign of the CD effects and (ii) the magnitude and phase of all expansion coefficients f, g, and h as well as those of the susceptibility components. In addition, the method is not limited to resonance: not only circular-difference effects are indicative of chirality, but also asymmetry in the polarization line shapes and the presence of the expansion coefficients f_s, g_s and h_p are indications of chirality. This is illustrated in Fig. 3: for a hypothetical chiral sample with all expansion coefficients real (Fig. 3B) no circular-difference effects are observed. However, the asymmetry in the polarization line shape with respect to the 0° rotation angle of the quarter-wave plate still reflects the chirality of the sample. When one of the expansion coefficients (Fig. 3C) becomes imaginary a circular-difference response will occur. For an achiral sample (Fig. 3A) no circular-difference effects and no asymmetry are observed. An experimental result is shown in Fig. 4.

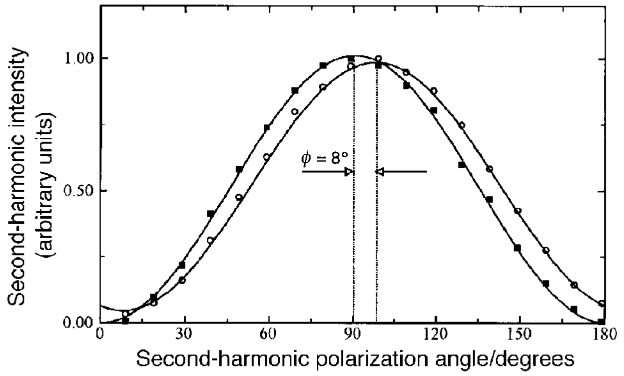


Fig. 2 Second-harmonic intensity *vs.* second-harmonic polarization angle for a racemic (squares) and a non-racemic (open circles) Langmuir–Blodgett film of compound **4**. The fundamental was p-polarized. The squares and open circles are the experimental data points and the solid lines represent a fit to a sine function. A polarization angle of 90° (0°) corresponds to p(s) polarization. The polarization of the second-harmonic light of the non-racemic film is rotated by an amount $\phi=8°$ with respect to the polarization of the second-harmonic light of the racemic film.

A fourth method is similar to the previous one, but instead of a quarter-wave plate a half-wave plate is used to probe for linear-difference effects. An initially p-polarized fundamental beam can be converted to +45 and −45° linearly polarized (with respect to the p-polarized direction) by the half-wave plate. The wave plate is rotated through an angle of 360° and the s- and p-polarized components of the second-harmonic fields are recorded in reflection and/or transmission.[24] However, it has been shown recently that it is not possible unambiguously to determine all the expansion coefficients.[19]

Experimental

Chiral thin films and surfaces of binaphthyl derivatives

The first experimental report of circular-difference effects in surface SHG came from Petralli-Mallow *et al.*[5] They studied

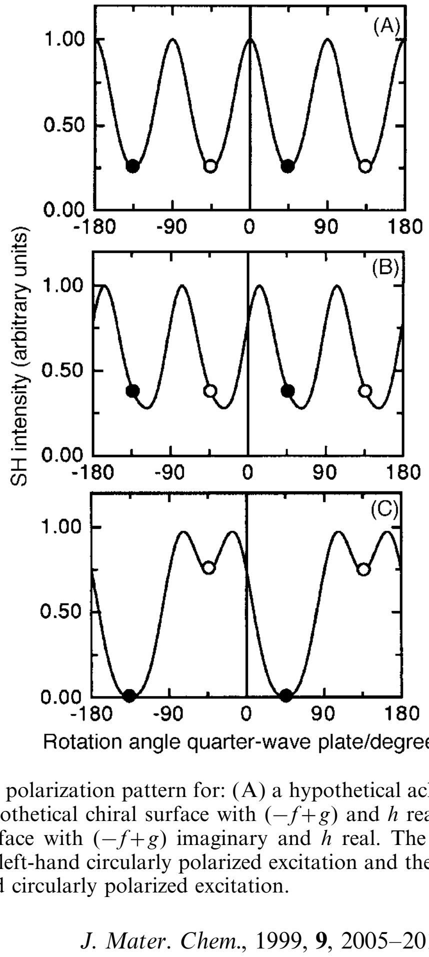


Fig. 3 SH polarization pattern for: (A) a hypothetical achiral surface, (B) a hypothetical chiral surface with $(-f+g)$ and h real, and (C) a chiral surface with $(-f+g)$ imaginary and h real. The open circles represent left-hand circularly polarized excitation and the filled circles right-hand circularly polarized excitation.

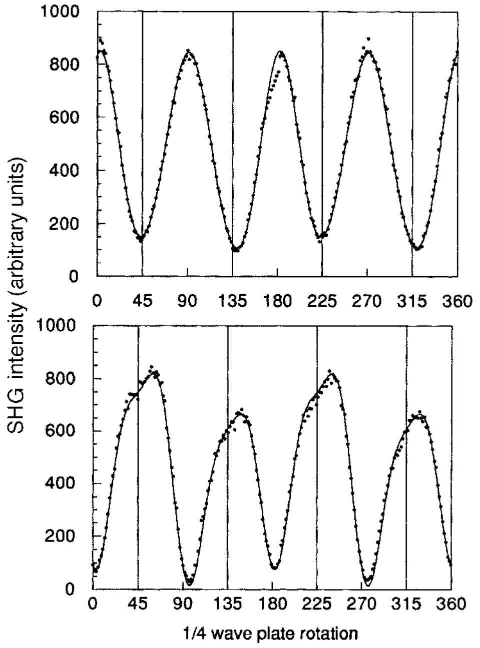
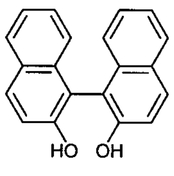


Fig. 4 Intensities of the p- (top) and s-polarized (bottom) second-harmonic fields in transmission *vs.* the rotation angle of the quarter wave-plate. The circular polarization (left-hand circular = 45 and 225°; right-hand circular = 135 and 315°) of the fundamental is indicated by the vertical lines in the figure. The black dots are experimental points and the solid lines represent a theoretical fit using eqn. (3).

second-harmonic generation from chiral 2,2′-dihydroxy-1,1′-binaphthyl molecules (structure **1**) adsorbed at an air/water interface. In their experiment they used the output from a tunable dye laser that was incident on a concentrated solution of the binaphthyl molecules at an angle of 60°. The second-harmonic light was detected in the reflected direction. When the fundamental laser beam was circularly polarized the SHG intensity emanating from the sample was highly dependent on the helicity of the incident light and strong circular-difference effects were observed. In addition, the circular-difference effects had the same magnitude but different sign for each enantiomer. The circular-difference effects in SHG were recorded as a function of wavelength in the region 290–315 nm where the binaphthyl molecules are absorbing and show weak traditional CD bands. The spectral shape of SHG-CD followed the ordinary CD bandshape and the observed circular-difference effects in SHG reached values as high as 100%. For comparison, the ordinary CD effect $\Delta\varepsilon/\varepsilon$ was approximately 0.1%. Since this technique combines second-harmonic generation (which is inherently surface sensitive) and circular dichroism it was put forth as a new and powerful tool to study surface chirality.

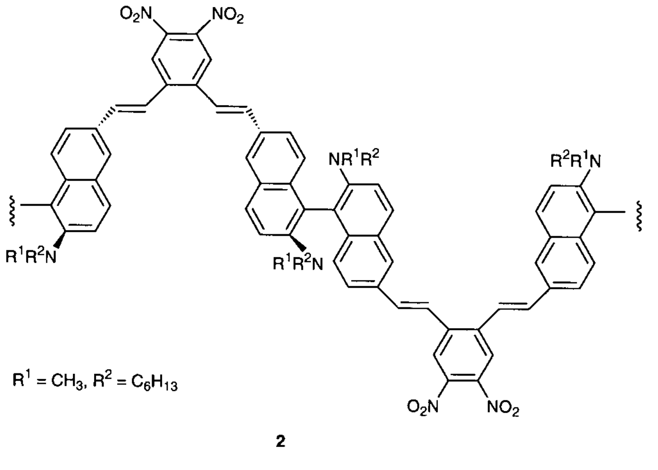


1

In subsequent papers, it was shown that the circular-difference effects in SHG were strong because they are electric dipole allowed and do not depend on interference between strong electric dipole contributions and weak magnetic dipole contributions (which is the case for ordinary CD and ORD).[6] In fact, no evidence was found of magnetic dipole contributions to the non-linearity of the surface. In particular, the effects arise from interference between chiral and achiral tensor components of the electric dipole allowed susceptibility tensor.[28]

The non-linear analogue of optical rotatory dispersion, *i.e.* SHG-ORD, was also proposed and used to study the same binaphthyl derivative at different interfaces.[26] Rotation angles of the order of 20° were measured for 2,2′-dihydroxy-1,1′-binaphthyl molecules adsorbed at different interfaces. The authors pointed out that SHG-ORD is independent of surface concentration, but that it can be used to probe a chiral excess concentration in mixtures of both enantiomers. Therefore, SHG-ORD could be useful as an analytical method, *e.g.* to determine if a surface preferentially absorbs one enantiomer over another or if a surface reaction produces an enantiomeric excess in an asymmetric synthetic step.

Recently, we studied Langmuir–Blodgett films of a chiral 1,1′-binaphthyl-based helical polymer (structure **2**).[29] The polymer used in this study was prepared from chiral 1,1′-binaphthyl-based monomeric units and optimized for non-linear optics by adding a π-conjugated bridge and electron donor and acceptor groups. The monomer units can be considered as an ensemble of rigid electric dipole units that form a propeller-like three-dimensional conformation due to the chirality of the binaphthyl units.[30–32] Therefore, the chirality of this system is derived from the main-chain configuration. High quality Langmuir–Blodgett (LB) films were prepared by horizontal dipping and the SHG properties were studied using a Nd:YAG laser. The polarization of the fundamental beam was continuously varied using a quarter-wave plate, while recording s- or p-polarized second-harmonic light in transmission. One of the compounds showed good non-linear optical efficiency and the chirality of the films manifested itself in a difference in second-harmonic efficiency when the films were irradiated with left- and right-hand circularly polarized light. The observed circular-difference effects were between 25 and 60%. No evidence of magnetic dipole contributions to the non-linearity of the films was found.



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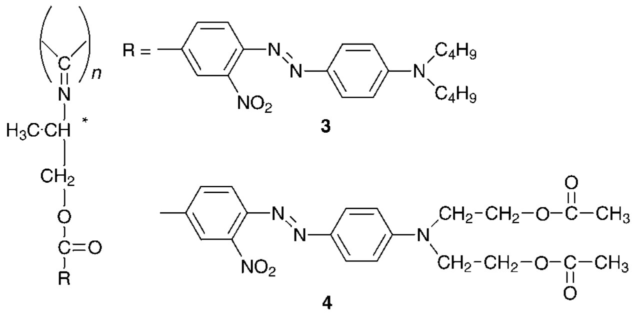
A detailed analysis of the SH polarization patterns allowed for the determination of all expansion coefficients *f*, *g*, and *h*, which were used to calculate all non-vanishing susceptibility components (symmetry is C_∞). The absolute magnitudes of the components were calibrated using a quartz wedge[33] and are given in Table 2. The chirality of the films is reflected by the presence of a small, but non-negligible (chiral) *xyz* component. The other achiral components are significantly higher and suggest favorable ordering of the chromophoric parts of the polymer in the LB films. Owing to the respectable magnitude of the susceptibility components, combined with good stability, these polymers could be considered as potential non-linear optical materials for future applications.

Table 2 Absolute values of the second-order susceptibility (χ^{eee}) components of the binaphthyl-based helical polymer **2** and classification of the components as chiral or achiral

Component of χ^{eee}	Absolute value/ pm V^{-1}	Chirality classification
xyz	2	Chiral
xxz	7	Achiral
zxx	5	Achiral
zzz	35	Achiral

Chiral thin films with high magnetic dipole susceptibilities

We have also investigated Langmuir–Blodgett films of chromophore-functionalized chiral poly(isocyanide)s. A Nd:YAG laser (1064 nm) was used to excite the LB films. A quarter-wave plate was continuously rotated in the fundamental beam and second-harmonic polarization patterns were detected in reflection and transmission. The samples used were a Langmuir–Blodgett film of the poly(isocyanide) shown in (structure **3**).[9] Important to note is the peculiar structure of the polymer: chirality and non-linearity are present on different levels of the molecular structure. Chirality is localized in the (helical) backbone and non-linearity in the achiral pendant chromophores.



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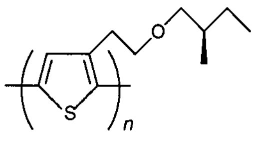
Strong circular difference effects and asymmetric polarization patterns, indicative of chirality, were obtained. In addition, the experimental results could not be explained without including magnetic dipole contributions to the non-linearity of the film. The largest such contribution was found to be of the order of 10% of the pure electric dipole contribution. Important to note is that non-linear optical activity can only be detected if chirality and non-linearity are simultaneously present in the material. Therefore, these properties must be coupled together in order for non-linear optical activity effects to be observed. We believe that this coupling occurs because of a simultaneous excitation of the NLO chromophores, leading to a helical charge displacement along the backbone of the polymer. Hence, non-linear optical activity can occur.

More recently, films of a similar poly(isocyanide) mixed with poly(*S*-1-acetoxymethylethyl isocyanide) (structure **4**) were analysed in detail.[34] The experimental technique described earlier was used to analyse an 18-layer Langmuir–Blodgett film. Analysis of the polarization pattern allowed the determination of the relative magnitudes of all electric dipole and magnetic dipole susceptibility components (Table 3). The main conclusions are that the magnitude of the largest magnetic dipole component is 20% of that of the largest electric dipole component, and that the largest magnetic dipole components are associated with chirality. The absolute magnitude of the electric dipole component *zzz* of Langmuir–Blodgett films of a similar polymer system was determined to be of the order of 9 pm V^{-1}.[35] Therefore, the highest magnetic dipole component would be of the order of 2 pm V^{-1}, and indicates that magnetic dipole contributions can be useful for non-linear optical applications. Optimizing the magnetic contributions would therefore increase the overall non-linearity of a material. It is still unclear why magnetic dipole interactions make such an important contribution to the non-linearity of thin films of this particular material. One possible explanation is that the electric dipole non-linearity of the films is partly suppressed by a near-random distribution of the non-linear chromophores in the polymer film. However, more research is needed to prove this hypothesis.

Table 3 Relative magnitude of the components of χ^{eee}, χ^{eem} and χ^{mee} for compound **4**

Tensor	Components	Chirality	Relative magnitude
χ^{eee}	zzz	Achiral	1.00
	$zxx = zyy$	Achiral	0.62
	$xxz = xzx = yyz = yzy$	Achiral	0.60
	$xyz = xzy = -yxz = -yzx$	Chiral	0.08
χ^{eem}	zzz	Chiral	0.23
	$zxx = zyy$	Chiral	0.12
	$xxz = yyz$	Chiral	0.01
	$xzx = yzy$	Chiral	0.05
	$xyz = -yxz$	Achiral	0.06
	$zxy = -zyx$	Achiral	0.13
	$xzy = -yzx$	Achiral	0.06
χ^{mee}	zzz	Chiral	0.15
	$zxx = zyy$	Chiral	0.00
	$xxz = xzx = yyz = yzy$	Chiral	0.00
	$xyz = xzy = -yxz = -yzx$	Achiral	0.03



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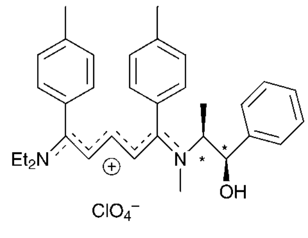
Evidence of high magnetic dipole contributions to the non-linearity has been found in other materials. For example, Langmuir–Blodgett films of a chiral poly(thiophene) (structure **5**) have magnetic dipole contributions of the same order of magnitude as the electric dipole non-linearities.[36] The sample studied was a ten layer Langmuir–Blodgett film of the regioregular chiral polythiophene poly[3-[2-((*S*)-2-methylbutoxy)-ethyl]thiophene].[37,38] In good solvents, like chloroform, the polymer is in a random coil conformation and does not exhibit optical activity in its π–π* transition. However, in the solid state, in poor solvents, or in appropriate combinations of solvents, the polymer is associated in small domains and the chiral side groups induce an enormous optical activity in the π–π* transition of the polythiophene. This association with a chiral conformation is accompanied by strong solvatochromism and the organized polymer is purple-red in colour ($\lambda_{max} = 512$ nm), while the random coil is orange-yellow ($\lambda_{max} = 445$ nm). To prepare the LB films a chloroform solution (in which the polymer is in its random coil) was spread on a water surface. Upon evaporation of the solvent the polythiophene folds into the chiral conformation (because the polymer is in the solid state) and changes from yellow to purple. The layers were deposited at 10 mN m^{-1} on hydrophobic glass slides using the horizontal dipping technique.

The films were measured by continuously varying the polarization state of the fundamental (1064 nm) laser beam by means of a quarter wave plate. An analysis of the s-polarized second-harmonic signal provided clear proof of the presence of strong magnetic dipole contributions (same order of magnitude as the electric dipole contributions) in the non-linearity of the films. Unfortunately, due to the instability of the sample, we were not able to determine relative magnitudes of the components of χ^{eee}, χ^{eem}, and χ^{mee}.

Schanne-Klein *et al.*[39] studied thin spin-coated films of the chiral dye shown in structure **6** and were able to separate electric and magnetic dipole contributions to the non-linearity of the films. The results are shown in Table 4. As in the case of the poly(isocyanide) films, the chiral magnetic dipole contributions are of the same magnitude as the chiral electric dipole contributions. The experiment shows that magnetic dipole contributions can be important even in non-resonant conditions (the molecule does not absorb at the second-harmonic wavelength).



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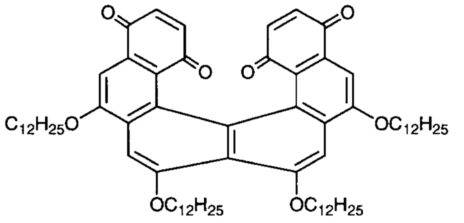
Chiral thin films of helicene derivatives

In a recent report the SHG properties of Langmuir–Blodgett films of a tetrasubstituted helicene bisquinone (structure **7**) were studied.[40] In bulk samples the enantiomerically pure form of the material spontaneously organizes into long fibers that are clearly visible under an optical microscope, while the racemic form does not aggregate. Also, in certain solvents, the pure enantiomer aggregates into columnar stacks, and this is associated with a large increase in the circular dichroism of the solutions.[41]



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Langmuir–Blodgett films of the racemic and non-racemic (or enantiomerically pure) helicene bisquinone were prepared by spreading dilute chloroform solutions (in which the molecule is not aggregated) on the water subphase of a Langmuir trough. Subsequently, the layer was compressed and transferred to hydrophobic glass slides by horizontal dipping. UV-vis absorption spectra, ordinary CD spectra and AFM (atomic force microscopy) clearly showed that the helicene bisquinone is present in its aggregated form in both racemic (*i.e.* composed of a racemic mixture of helicene bisquinone molecules) and non-racemic films (*i.e.* composed of enantiomerically pure helicene bisquinone).[40,42] A clear difference between the non-racemic and racemic films was observed in their SHG properties: the non-linear optical efficiency of the non-racemic films was a factor of 30 higher than that of racemic films. In addition, the dominant second-harmonic signal from the non-racemic films was only allowed by chirality.

Table 4 Relative magnitude of the components (or combination of components) of χ^{eee}, χ^{eem} and χ^{mee} for the chiral dye **6**

Tensor component	Chirality	Relative magnitude
χ^{eee}_{zzz}	Achiral	1.000
χ^{eee}_{zxx}	Achiral	0.080
χ^{eee}_{xxz}	Achiral	0.310
χ^{eee}_{xyz}	Chiral	0.012–0.018
$2\chi^{eem}_{xxz}+\chi^{mee}_{zxx}$	Chiral	0.03

LB films of the non-racemic films were further analysed and found to be anisotropic in the plane of the film (C_2 symmetry), which complicates the analysis of the data considerably. However, certain combinations of susceptibility components can be shown to be invariant under rotation around the surface normal and are given in Table 5. All the rotational invariants were determined by analysing SHG polarization patterns. No evidence was found of the presence of magnetic dipole contributions. The rotational invariant *xyz*-*yxz* is associated with chirality and was found completely to dominate the non-linear optical response of the non-racemic films. Note that in films made from traditional NLO materials the response is usually dominated by the *zzz* component. The magnitude of the chiral component *xyz*-*yxz* is within one order of magnitude of the highest values ever observed in LB films. Combined with the good thermal stability of the films (stable up to 200 °C) and the possibility of achieving phase-matched structures, this material can be considered as a promising candidate for device applications. The reason for the high non-linearity of the supramolecular structure was attributed to the formation of supramolecular aggregates with high non-linearity. In films made of the enantiomerically pure material, these non-linearities add up, while in racemic films they cancel.

Helicene structures have also been incorporated into metal phthalocyanines.[43] The molecules shown in structure **8** are constructed by fusing nickel and copper phthalocyanine cores to four non-racemic helicenes. These compounds tend to aggregate strongly in thin films and in appropriate solvents. Langmuir–Blodgett films of these materials (prepared by horizontal dipping) were studied by SHG. The symmetry of the films was C_∞ and an analysis of the second-harmonic polarization patterns allowed the determination of all susceptibility components (Tables 6 and 7). Just as in the case of the helicene bisquinone, the dominant component is *xyz*, which is only allowed by the chirality of the film.

Table 5 Absolute values of chiral and achiral rotational invariants of the susceptibility of the non-racemic LB films of the helicene-bisquinone **7**

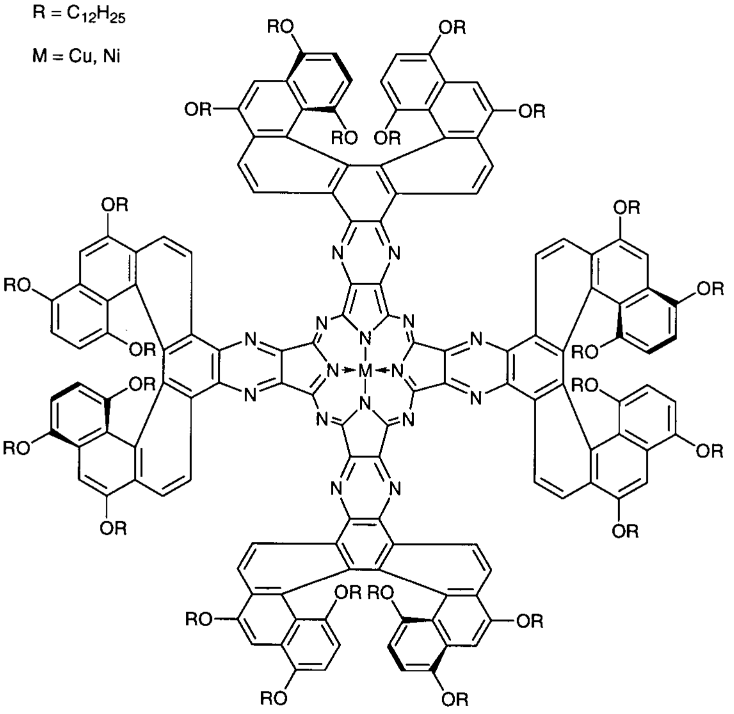
Rotational invariant	Absolute value	Chirality
zzz	6	Achiral
xxz+*yyz*	2	Achiral
zxx+*zyy*	4	Achiral
xyz−*yxz*	50	Chiral

Table 6 Absolute magnitudes of the components of the second-order susceptibility tensor of LB films of the helical copper phthalocyanine **8**

Susceptibility component	Absolute value/pm V^{-1}	Chirality
xyz	24	Chiral
xxz	3	Achiral
zxx	4	Achiral
zzz	6	Achiral

Table 7 Absolute magnitudes of the components of the second-order susceptibility tensor of LB films of the helical nickel phthalocyanine **8**

Susceptibility component	Absolute value/pm V^{-1}	Chirality
xyz	19	Chiral
xxz	4	Achiral
zxx	3	Achiral
zzz	15	Achiral



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Biological systems

Crawford *et al.*[44] explored the possibility of SHG-CD and SHG-ORD to study biological samples. They studied the dipeptide (*tert*-butyloxycarbonyl)tryptophanyltryptophan adsorbed at an air/water and a heptane/water interface. A Nd:YAG pumped dye laser that operated in the wavelength region 550–580 nm was used to record SHG-CD and SHG-ORD spectra. The SHG spectra from the LL and DD enantiomer showed equal but opposite dependences on the handedness of the fundamental laser beam and the DL diastereoisomer gave rise to different SHG spectra.

We demonstrated the strength of non-linear optical activity as a probe of chiral biological samples by studying circular difference effects in second-harmonic generation from bacteriorhodopsin.[45] Bacteriorhodopsin is the light-energy transducing protein present in the purple membrane of halophilic bacteria. In the membrane the protein is arranged into clusters of three that show stronger optical activity than individual protein molecules. Traditional CD spectra of suspensions of purple membrane in water typically show a relative circular-difference effect $\Delta\varepsilon/\varepsilon = 0.1\%$.

The samples we investigated consisted of bacteriorhodopsin molecules that were embedded in Langmuir–Blodgett films of soya phosphatidylcholine. In such a film the bacteriorhopsin molecules can exhibit local ordering in a lattice similar to the one that occurs in purple membrane. The samples were irradiated with a Nd:YAG laser and SHG polarization pattern were recorded in transmission. The chirality of the samples was reflected by a strong asymmetry in the polarization line shape.

Conclusions and future prospects

Second-harmonic generation from surfaces and thin films provides a new tool to study surface chirality. In this paper we have given an overview of (i) the theoretical formalism that has been used to describe SHG from chiral surfaces, (ii) the experimental procedures that are used to study polarization rotation and intensity-difference effects in SHG from chiral surfaces, and (iii) a series of representative experimental results.

From the examples discussed in this paper we think it clear that non-linear optical activity can evolve into an extremely useful method to study surface chirality, since traditional methods such as CD and ORD are not surface sensitive. In addition, the study of chiral NLO materials might lead to new insights to design completely new materials for applications in the field of non-linear optics and photonics. However, the technique still has to mature, from an experimental and theoretical point of view, before it can be routinely used as a measurement method. Issues that need to be resolved are: (i) what is the relation between the magnitude of the magnetic susceptibility components and molecular (or surface) structure, and (ii) is there a relation between the magnitude of the chiral susceptibility components and the magnitude of traditional CD or ORD effects. An answer to these questions might not only give a better insight in non-linear optical activity effects, but could also provide a better understanding of non-linear optical phenomena in general.

From an experimental point of view, the usefulness of the technique should be clearly demonstrated in research fields such as biochemistry, catalysis or pharmacology. For example, the study of configurational changes in proteins adsorbed at surfaces, adsorption of racemic mixtures of molecules on chiral surfaces, adsorption of achiral molecules on chiral surfaces, the study of enantiomeric excess obtained in asymmetric surface reactions and the determination of the enantiomeric excess in pharmaceutical products should help in establishing non-linear optical activity as a powerful tool of research.

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