in short face to face contacts, since the molecules are packed in a head-to-center manner with stacking alternatively the *tert*-butyl groups. A similar head-to-center type stack is actually observed in the X-ray crystallographic analysis of the neutral molecule 1, in which the molecule is fully planar except for the *tert*-butyl groups and the distance between the molecular planes is around 3.51 Å.

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Chiral Effects in the Second-Order Optical Nonlinearity of a Poly(isocyanide) Monolayer**

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Even-order nonlinear optical processes are forbidden, in the electric-dipole approximation, in material systems that possess a center of symmetry.[1] The present challenge in materials development for second-order nonlinear optics is therefore to find noncentrosymmetric molecules that have a large molecular hyperpolarizability and that can be organized in a noncentrosymmetric macroscopic arrangement to give rise to a nonvanishing second-order susceptibility. On the other hand, symmetry properties of magnetic-dipole and electric-quadrupole transitions are different from those of electric-dipole transitions. For example, even-order processes involving a single magnetic-dipole or electric-quadrupole transition in place of one of the electric-dipole transitions can be allowed in cases in which pure electric-dipole nonlinearities are forbidden.[2–4]

Chiral molecules are particularly interesting for future applications in nonlinear optics for two different reasons. First, their molecular structure is necessarily noncentrosymmetric and, consequently, certain even-order nonlinearities become electric-dipole allowed in highly symmetric macroscopic samples.[5] Second, magnetic-dipole transitions of chiral molecules can be very strong with strengths up to ~20 % of those of electric-dipole transitions.[6] For example, second-harmonic generation involving magnetic-dipole transitions from a racemic and centrosymmetric crystal of chiral molecules has been observed.[7]

In this Communication we provide evidence of strong chiral effects in the second-order nonlinearity of poly(isocyanide)s. We do this by observing second-harmonic generation from a monolayer of these chiral polymers. As an

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experimental technique, we use second-order optical activity,[8-12] i.e., different response of the second-harmonic generation process to left- and right-hand circularly-polarized light. The chirality gives rise to a new component of the electric-dipole-allowed second-order susceptibility tensor of the polymeric surface layer. Furthermore, magnetic-dipole transitions are also shown to contribute to the surface nonlinearity. The interference between the electric and magnetic contributions allows us to assess their relative magnitudes. Note that prior to this work, magnetic-dipole (and electric-quadrupole) nonlinearities of only the bulk media surrounding the surface layer have been considered as a complicating factor in surface nonlinear optics.[13,14] Hence our results also provide the first evidence of magnetic contributions to the nonlinearity of a surface itself.

In our experiments we used the S enantiomer of a functionalized poly(isocyanide) (Fig. 1) as the chiral nonlinear
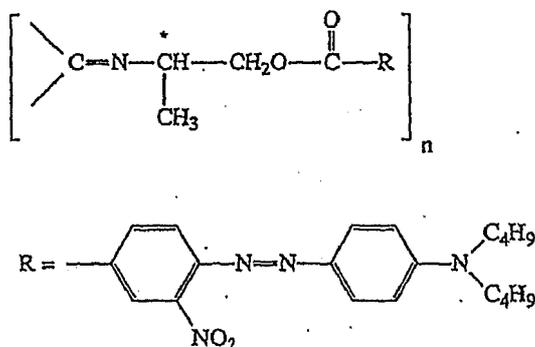

Fig. 1. The chiral poly(isocyanide) used in the experiments.

optical medium. The key property of poly(isocyanide)s is the rigid and extended helical chain conformation of the backbone. The helical structure is also stable in solutions, in floating Langmuir layers, and in deposited Langmuir–Blodgett films.[15] The polymer was spread from a chloroform solution on the water surface of a Langmuir through. After evaporation of the solvent and after several minutes of stabilization at constant surface pressure (5 dyne/cm), the layer was deposited onto hydrophilic glass slides by the Langmuir–Blodgett technique. A deposition ratio of unity was always observed indicating a very good quality of the deposited monolayer. The samples used were coated only on one side of the glass substrate.

Our experimental setup is schematically shown in Figure 2. The fundamental beam of a Q-switched and injection-seeded Nd:YAG laser (1064 nm, 10 ns) is weakly focused to pump the poly(isocyanide) monolayer at a peak intensity of ~100 MW/cm². The sample is oriented at a ~45° angle of incidence with respect to the fundamental beam. The initial linear polarization of the beam is p-polarized with respect to the sample and can be converted to left- and right-hand circular by a quarter-wave plate. The waveplate is rotated
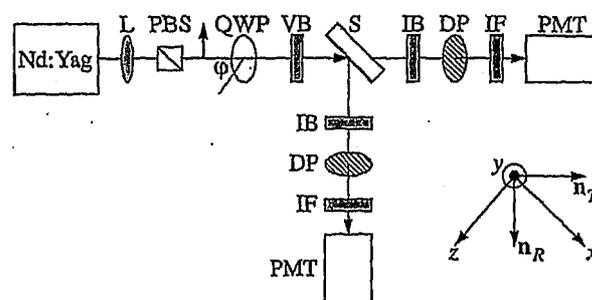

Fig. 2. Schematic representation of the experiment. The fundamental beam of a Nd:YAG laser (1064 nm) is p polarized with respect to the sample (S) using a polarizing beam splitter (PBS). The polarization is varied by a quarter-wave (QWP) plate from linear to right and left-hand circular. The beam is focussed by a lens (L) onto the sample. The flashlamps of the laser are isolated from the experiment by a visible-blocking filter (VB). The reflected and transmitted second-harmonic beams are passed through an infrared blocking filter (IB) and a 532 nm interference filter (IF) before detection by photomultipliers (PMT). Dichroic sheet polarizers (DP) are used to analyze the distribution of second-harmonic radiation in s and p polarizations.

through an angle of 360° and the intensities of the s- and p-polarized components of the second-harmonic fields at 532 nm are recorded in reflection and transmission. Sufficient polarization purity of the experiment is verified by making sure that no circular-difference effects are observed in the second-harmonic field generated from a control sample of a Langmuir–Blodgett film of an achiral molecule.[16]

No second-harmonic signal was detected from a clean substrate indicating that the nonlinear response arises from the molecular layer. For the case of the chiral poly(isocyanide) monolayer and for all four recorded signals, the efficiency of second-harmonic generation is found to depend on the helicity of the fundamental beam. The results for the s-polarized reflected and transmitted fields are shown in Figure 3 with respective plots generated using a simple theoretical model. Note that the circular-difference responses of the transmitted (Fig. 3a) and reflected (Fig. 3b) s-polarized second-harmonic fields are unequal. This result can not be explained within the well-established theories[17,18] of electric-dipole-allowed surface second-harmonic generation, which predict that the two s-polarized signals should behave similarly.

The experimental results are explained by including the contributions of magnetic-dipole transitions to the second-order nonlinearity. A detailed theoretical analysis is presented elsewhere.[10] However, the essential features of the model are as follows. To the first order in the magnetic interaction, the nonlinear polarization of the chiral surface is taken to be as shown in Equation 1, where summation over repeated indices is implied and where E and B are the electric field and the magnetic induction field, respectively. Furthermore, the superscript e (m) implies that the respective subscript refers to a Cartesian component of an electric (magnetic) transition moment. Hence, χ^{eee} is the usual electric-dipole-allowed second-order susceptibility tensor and χ^{eem} accounts for the magnetic contributions to the electric polarization. Similarly, the nonlinear magnetization of the surface is given by
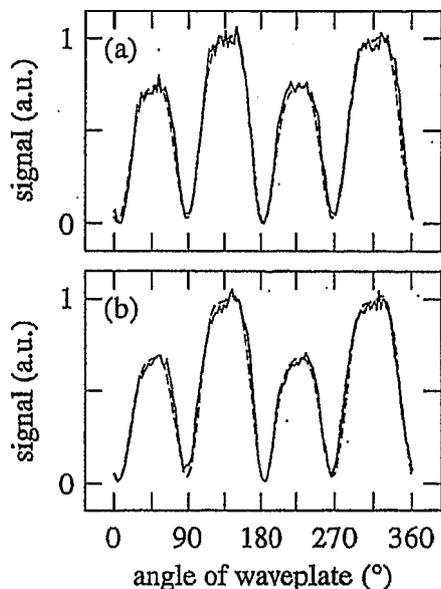
Fig. 3. Experimental (solid lines) and theoretical (dashed lines) results for the intensities of the transmitted s (a) and p (b) polarized second-harmonic fields as functions of the rotation angle of the quarter-wave plate. The rotation angles of 45° (225°) and 135° (315°) correspond to the left- and right-hand circular polarizations, respectively.

Equation 2. For real molecular wavefunctions, the electric-dipole transition moments are real quantities while the magnetic-dipole transition moments are imaginary.[6] Hence, for off-resonant excitation, the tensor components χ_{ijk}^{eee} are real and the tensor components χ_{ijk}^{eem} and χ_{ijk}^{mee} are imaginary.

The molecular layer consists of a collection of electric and magnetic dipoles that radiate at the second-harmonic frequency. For dimensions larger than molecules but smaller than the wavelength, the effective oscillating dipole moments are directly proportional to the nonlinear polarization and magnetization given by Equations 1 and 2. In the far field, the electric component of the second-harmonic field that is radiated by the oscillating electric and magnetic dipoles is proportional to Equation 3[19] where n is the direction of observation and is different for the reflected and transmitted fields.

$$P_I(2\omega) = \chi_{ijk}^{eee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{eem} E_j(\omega) B_k(\omega) \quad (1)$$

$$M_I(2\omega) = \chi_{ijk}^{mee} E_j(\omega) E_k(\omega) \quad (2)$$

$$E(2\omega) \sim [n \times P(2\omega)] \times n - n \times M(2\omega) \quad (3)$$

In our experimental situation, the poly(isocyanide) monolayer is taken to be in the x–y plane, and the wavevector of the fundamental beam is taken to be in the x–z plane with an angle of incidence of θ with respect to the monolayer. The incident field can always be expanded in the basis of the s- and p- polarized unit vectors as shown in Equation 4.[12]

Furthermore, the magnetic field is given by Equation 5, where **k** is the wave vector of the incident field. Consequently, the nonlinear driving terms of Equations 1 and 2 can only depend on the three products shown in Equation 6, where φ represents possible modulation of the polarization state of the input field. In the present experimental situation, φ is the rotation angle of the quarter-wave plate and the angles +45° and −45° correspond to the left- and right-hand circularly-polarized incident fields, respectively. Furthermore, Equation 3 defines a linear mapping of the nonlinear sources to the second-harmonic field whose components are then necessarily of the general form shown in Equation 7. The expansion coefficients f, g, and h for the s polarized field components are shown in Equations 8.[10]

$$E(\omega) = E_s \hat{e}_s + E_p \hat{e}_p \quad (4)$$

$$B(\omega) = [k \times E(\omega)]/k \quad (5)$$

$$F(\varphi) = E_p^2, \quad G(\varphi) = E_s^2, \quad H(\varphi) = E_s E_p \quad (6)$$

$$E(2\omega) = fF(\varphi) + gG(\varphi) + hH(\varphi) \quad (7)$$

$$f_{Ts}^{Rs} = \sin\theta \, [-2\chi_{xyz}^{eee}\cos\theta - \chi_{xxx}^{eem} + \chi_{zzz}^{mee}\sin^2\theta + \chi_{zxx}^{mee}\cos^2\theta \mp 2\chi_{xxz}^{mee}\cos^2\theta]$$

$$g_{Ts}^{Rs} = \sin\theta \, [\chi_{xxz}^{eem} + \chi_{zxx}^{mee}] \quad (8)$$

$$h_{Ts}^{Rs} = \sin\theta \, [2\chi_{xxz}^{eee} - (\chi_{xzy}^{eem} + \chi_{xyz}^{eem}) \cos\theta \mp 2\chi_{xyz}^{mee}\cos\theta]$$

In Equations 8, the superscripts (subscripts) on the left-hand side of the equations correspond to the upper (lower) signs on the right-hand side. Note that compared to the nonvanishing components of the χ^{eee} tensor of achiral isotropic surfaces (zzz, zxx, xxz), Equation 8 depends on the additional component xyz of this tensor as well as on various components of the χ^{mee} and χ^{eem} tensors.

. The fits of Figure 3 have been obtained for the following relative values of the expansion coefficients: $f_{Rs} = 0.2 + i0.48$, $g_{Rs} = i0.1$, $h_{Rs} = 5.1$; $f_{Ts} = 0.2 + i0.59$, $g_{Ts} = i0.1$, $h_{Ts} = 5.1$. Note that the difference in the coefficients f_{Rs} and f_{Ts} can only be explained by the presence of the magnetic tensor component χ_{xxz}^{mee}. Furthermore, the nonvanishing values of the coefficients g_{Rs} and g_{Ts} also support the presence of magnetic-dipole contributions. A complete analysis of the experimental results suggests that the largest magnetic tensor components are of the order of 10% of the pure electric-dipole components.[10] Furthermore, the chiral (xyz) component of the χ^{eee} tensor is of the order of 3% of the largest (zzz) component of this tensor. It should also be noted that the observed circular-difference effects arise from a phase difference between the expansion coefficient h and the other two components (f and g). To the first approximation,[10] this phase difference arises from the 90° phase difference between the electric and magnetic contributions to the nonlinearity.

Our experimental results show that strong chiral effects are associated with the second-order nonlinear optical response of poly(isocyanide)s. Our measurement technique

based on nonlinear optical activity is dependent on the simultaneous presence of chirality and nonlinearity in the material investigated. It is particularly intriguing to note that, for the case of poly(isocyanide)s, these two properties occur on different levels of the molecular structure with non-linearity localized in the achiral chromophores and with chirality in the backbone.

On the other hand, these two properties must be coupled together for the nonlinear chiral effects to occur. We believe that this coupling is due to simultaneous nonlinear excitations of the chromophore side groups by the fundamental field, which gives rise to an overall helical charge displacement in the poly(isocyanide). This helical charge displacement is of course necessary for the nonlinear optical activity to occur. Note that the explanation of linear optical activity in macromolecules relies on a similar mechanism.[20]

The fact that the chiral and nonlinear properties can occur on different levels of molecular structure and still be coupled together suggests that these two properties of novel materials can be optimized rather independently. This results provides additional degrees of freedom for the synthesis of new chiral materials with a high nonlinearity. Our results show also that the overall nonlinear optical properties of chiral molecules can be significantly enhanced by optimizing the magnetic contributions to the nonlinearity. This could be very important in the field of electro-optics where the development of materials with a very high nonlinear optical response is of paramount importance. As far as our experimental technique is concerned, we expect it also to be applicable to the study of structural and symmetry properties of biological macromolecules such as nucleic acids and polypeptides.

In conclusion, we have observed strong chiral effects in the second-order nonlinearity of poly(isocyanide)s. We have demonstrated the presence of such effects in second-harmonic generation from a monolayer of these chiral polymers. The chirality gives rise to a new electric-dipole-allowed component of the second-order susceptibility tensor and to significant magnetic-dipole contributions to the nonlinearity. The magnetic-dipole nonlinearity is estimated to be of the order of 10% of the electric-dipole nonlinearity. The occurrence of chirality and nonlinearity on different levels of the poly(isocyanide) structure suggests that the chiral and nonlinear properties of new materials can be optimized independently without losing the coupling between these properties.

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New Angular Molecular Donor Containing Two Tetrathiafulvalene (TTF) Units Fused to Selenophene: Synthesis, X-Ray Structure, Cyclic Voltammetry and Conducting Charge Transfer Complex with TCNQ**

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The past two decades have witnessed the development of organic molecular conductors and superconductors, in which the analogues and derivatives of tetrathiafulvalene (TTF) have played a major role.[1] At the same time, the remarkable advances in electrical conducting polymers have been highlighted by the extensive research on polythiophene (PT) owing to its environmental stability in both its doped and undoped states.[2]

The stability of PT is attributable in part, at least, to the aromaticity of its composed thiophene units. Some useful information can be gleaned from the limited number of donor systems which incorporate both thiophene and tetra-chalcogenafulvalene units. In recent reports, thiophene[3] and oligomeric thiophene[4] have been used in composing π-extended TTF systems, resulting in a significant decrease in oxidation potentials compared to those of the constituent building blocks.

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