

DSM Science & Technology Awards 2003

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Nonlinear optical properties of chiral polymers and supramolecular structures.

At low intensity of light the optical properties of materials are independent of the intensity. This is the realm of linear optics in which phenomena such as absorption, fluorescence, optical rotation... are put to use in a wide domain of research fields, ranging from astronomy to biology.

By the development of intense, coherent light sources, i.e. lasers, a new research domain was born: non-linear optics. Non-linear optical (NLO) processes are defined as processes where the induced optical polarization does not vary linearly with the electric field. Phenomena such as second-harmonic generation (SHG), third-harmonic generation (THG), the electro-optic effect (EO-effect), optical amplification, etc. ... are the basis of new developments and applications, reviving the whole field of optics. Second-order nonlinear optical processes – easily accessible - suffer however from a disadvantage: these processes are forbidden in centrosymmetric media (1). On the molecular level, this problem is easily overcome by synthesizing a molecule (NLOphore) according to a D- π -A template (donor- π conjugated bridge- acceptor)(2). The main problem is to translate these microscopic properties into a macroscopic system. Introducing NLOphores in a polymer matrix and orienting them in a polar order, e.g. by an intense electric field, is a standard technique to obtain NLO-active polymer films and waveguides. However, such a poled system is not thermodynamically stable since the NLOphores may relax to an isotropic distribution (3). Other solutions to avoid a macroscopic, centrosymmetric distribution of the molecules is by using the Langmuir-Blodgett technique, liquid crystals, self-assembly, Nevertheless, each of these techniques suffer from disadvantages.

Our goal was to create macroscopic media with second-order NLO properties, composed of self-organizing molecules. An important advantage of such self-organized media is their thermodynamic stability.

Our idea was to use chiral molecules as building blocks and relying upon some of their critical properties, i.e. their affinity for supramolecular organization (as seen in DNA, proteins, biomembranes...) and their inherent noncentrosymmetry. Further, the molecular noncentrosymmetry is preserved on the macroscopic level.

Finally, because of the unique linear optical properties (optical rotation, circular dichroism), included with the inherent noncentrosymmetry, chirality may be linked to very interesting nonlinear optical phenomena.

In our work we investigated three classes of chiral materials: chiral helicenes bisquinones, chiral polythiophenes and chiral polybisenaphthalenes.

The chiral helicenes were especially chosen for their strong ability to form supramolecular aggregates (4). For example, the nonracemic form of the chiral helicene bisquinone, shown in Fig. 1, self-aggregates into corkscrew-shaped assemblies, both in concentrated alkane solutions and in neat condition. In thin films these corkscrew-shaped assemblies further organize into thin lamellae.

We prepared thin films of the helicene shown in Fig. 1 by spincoating, and investigated their NLO properties (5).

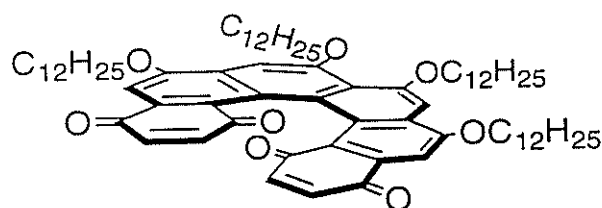


Figure 1: Chemical structure of the helicene bisquinone.

The spincoated films showed very strong SH-activity although no external force was used to introduce the necessary order. Instead, spontaneous supramolecular organization is the key to explain the strong NLO response of these films. Furthermore, the magnitude of the NLO response was such that the material could be useful for applications. Moreover, these films are thermodynamically stable over a large range of temperatures: the SH-signal was measured up to the melting points of the films ($\sim 220^{\circ}\text{C}$). The heating has no significant effect on their SH-response up to their melting point. Above their melting point, the SH-signal drops to zero. However, by cooling the films down, the SH-signal returns to the original value. This is a clear indication that the samples are thermodynamically stable.

An even more important result was obtained with a similar helicene bisquinone (Fig. 2) (6), (7). When a certain amount of dodecane is added, the helicene behaves as a nematic liquid crystal. The columns of helicenes that are formed in the liquid crystalline phase have dipole moments parallel to their long axes. Hence, the orientation of the columns can be influenced by an externally applied electric field: the columns become oriented exactly parallel to the field.

The NLO response of the liquid crystalline sample was very interesting. First of all, the SH-response of the sample was very strong. This was already quite surprising since most liquid crystalline NLO materials are known to have a very weak SH-activity. Second, the SH-response depends on only one nonlinear optical susceptibility component which only exists in chiral media. The chirality is therefore at the origin of the nonlinear optical properties of

these samples. When an electric field was applied over the sample, the molecules orient and the overall SH-response increases with a factor 3.5 (Fig. 3). This increase can be understood from the polar order induced in the sample by the electric field. Indeed, three more components of the nonlinear optical susceptibility (often referred to as polar components) contribute to the overall susceptibility and these extra polar components explain the increase in SH-response observed when applying the electric field. When switching off the electric field, the initial value of the SH-response was restored.

The most remarkable results were found when reversing the polarity of the electric field: the magnitude of all susceptibility components remains the same but the sign of the polar components is reversed. This inversion can be understood from the fact that the direction of the dipole reverses upon reversing the polarity of the applied field.

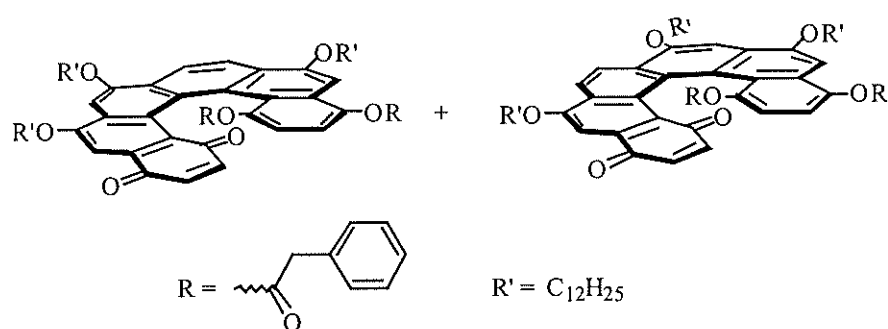


Figure 2: Mixture of helicene bisquinones.

The presence of chirality can also be measured in nonlinear optics: the SHG-efficiency will be different for left and right circularly polarized light. This effect is called SHG circular dichroism (SHG-CD) (8). The main difference with linear optics is that SHG-CD originates from an interference between several equally strong electric-dipole susceptibility components. In linear optics, on the other hand, optical activity effects such as optical rotation originate from an interference between electric and very weak magnetic components. As a result SHG-CD is much more sensitive to chirality than traditional optical rotation and circular dichroism. The necessity of interference between several susceptibility components to observe SHG-CD, was elegantly demonstrated in our liquid crystalline sample: in the absence of an orienting field, only one susceptibility component is present and no SHG-CD effects can be observed. When turning the electric field on, a SHG-CD effect is detected. Several components can now interact with each other, resulting in a CD-effect. However, reversing the polarity of the electric field, reverses the sign of the polar, achiral components and the CD-effects changes sign. This is a most remarkable result knowing that in linear optics the sign of the CD-effect can only be reversed by using the other enantiomer. Here we switch the CD by an external parameter, i.e. an electric field.

This change in sign of the achiral components induced by the reversal of an electric field, and reversing the CD-effect, could be used for applications such as optical switches, phase-shifters, and quasi-phase matching.

From these results, it is clear that supramolecular organization of chiral molecules can be used as a tool to engineer specific materials with important NLO-properties.

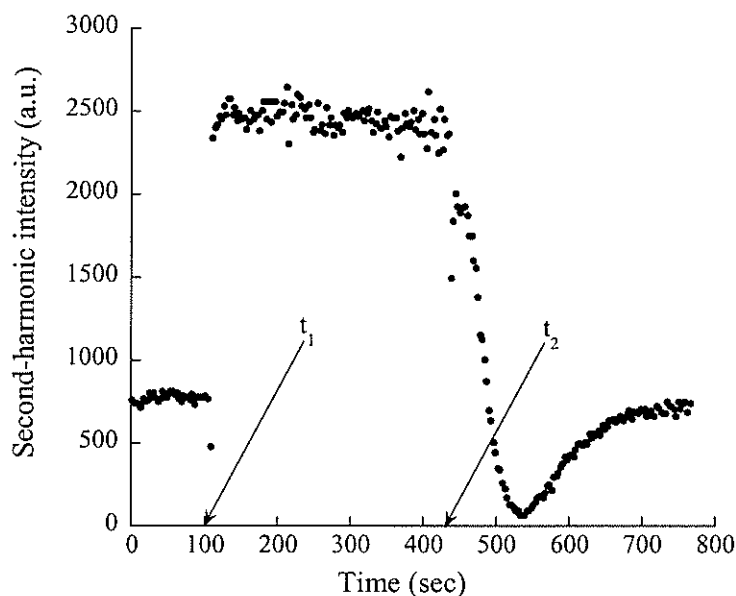


Figure 3: SH-response as a function of time. At time t_1 , the electric field was turned on. At time t_2 , the electric field was switched off.

Another material we investigated was a chiral polythiophene (Fig. 4). It is well known that these polymers form well-ordered aggregates in poor solvents and solid films. More specifically we investigated the NLO properties of spincoated films of the chiral poly-(3-alkylthiophene) shown in Fig. 4 (9-11). UV-Vis spectra indicated that these polythiophene films exhibit an absorption band with $\lambda_{\max}=535$ nm and a number of shoulders, characteristic for vibronic fine structure. This absorption band in the solid state is assigned to an aggregated, almost coplanar state of the polymer. The band corresponds to the $\pi-\pi^*$ transition. The optical activity of the $\pi-\pi^*$ transition is revealed by the appearance of a bisignate Cotton effect present in the CD-spectra. Also, in the CD-spectra, the vibronic fine-structure can be observed. The optical activity of the $\pi-\pi^*$ transition is not observed in good solvents (chloroform) or at high temperatures, but only in poor solvents (decanol or a mixture of chloroform and methanol) or in solid films. Apparently, the presence of strong optical activity is associated with an aggregated state. A helical packing of the predominantly planar chains is qualitatively consistent with the observed CD-spectra.

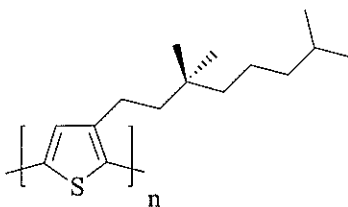


Figure 4: Chemical structure of a chiral poly-(3-alkylthiophene).

Based on our experience with the helicene bisquinone derivatives, we expected a similar SH-response resulting from a spontaneous supramolecular organization. In fact, linear dichroism spectra showed a certain amount of order along the surface normal of the films. This was confirmed by AFM images in which a layered structure was clearly visible. The SH-response, on the other hand, was very complex. For example, we observed a very strong SHG-CD effect that changed sign when the sample was rotated over 180° around an axis in the plane of the film. The effect is similar to the reversal of the CD-effect in the liquid crystalline helicene bisquinone sample upon changing the field polarity, however, in this case no electric field was used to induce polarity. This observation can only be explained by the presence of polar order in the polythiophene films. To the best of our knowledge, spontaneous macroscopic polar order has never been observed in polymeric samples.

We also found that besides electric-dipole contributions, there were also strong magnetic-dipole contributions to the nonlinear response. This was verified by a detailed analysis of the polarization properties of the SH-signals. This also confirmed previous results obtained for Langmuir-Blodgett films of a similar polythiophene where magnetic contributions had to be included in the SH-response to explain the experimental observations.

In conclusion, we could explain the SH-response of the polythiophene films only by assuming that a polar order is present in the films. Also, the second-order response is not only caused by electric-dipole interactions but also by strong magnetic-dipole interactions.

The last material investigated was a chiral polybisanthracene polymer (Fig. 5). Here we followed the same approach as in our previous studies. Thin films were prepared of the material by spincoating and the SH-response was investigated. However, no SH-response was detected in these films. Only after electric field poling, the films showed a clear SH-activity. We had to conclude that this material did not give the expected supramolecular organization that would result in symmetry properties that are favorable for SHG. Hence, this system seemed to fail where it was designed for. However, we observed another remarkable and useful result in these systems.

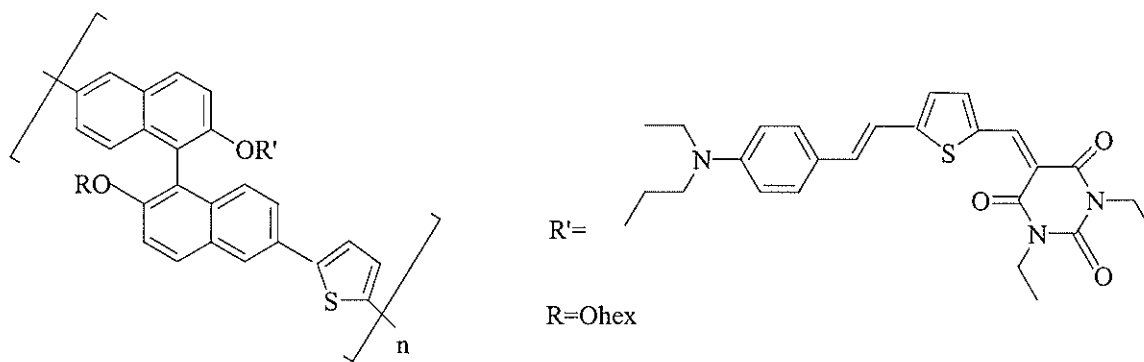


Figure 5: Polybisenaphthalene.

The polymer consists of a backbone with an NLO-active chromophore covalently attached. The weight percentage of the chromophore to the polymer was varied up to $\pm 50\%$ and the SHG efficiency increased linearly with the weight percentage. In classical polymeric NLO systems however, the SHG-efficiency reaches a maximum around 17 wt % NLOphore, followed by a strong decrease, which can be explained by detrimental dipole-dipole interactions opposing the necessary polar order (12). This aggregation effect is undesirable for applications, and has always been one of the major problems in second-order nonlinear optics.

Our hypothesis is that these unfavorable dipole-dipole interactions are absent in our system because the mobility of the NLOphores is strongly restricted : the chromophores are covalently attached to a very rigid backbone which prevents aggregation of the chromophores. In order to test our hypothesis, an NLOphore was dissolved in a PMMA (polymethylmethacrylate) matrix. Films were spincoated and poled. In this system the SHG-response was maximum at 17 wt %, and strongly decreased at higher loading levels. One could argue however, that simply attaching the chromophore covalently to any polymer backbone would already lead to a system in which the dipole-dipole interactions are strongly suppressed. Therefore, a similar chromophore was covalently attached to a flexible polymer backbone but also for this system, a decrease of the SH-response was observed at loading levels higher than 20 wt%. Hence, we can conclude that a rigid polymer backbone is absolutely necessary.

To conclude, we were able to create complex chiral systems with extraordinary symmetry properties. Due to a high degree of self-organization, the systems were able to give a SH-response. Important to notice is that chirality is often the key to the nonlinear optical response in these systems. Chirality and supramolecular organization opens a direction in nonlinear optics to develop thermodynamically stable systems needed for NLO applications and NLO devices.

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