

MOLECULAR CRYSTALS AND POLYMERS**Design, Synthesis and Crystal Growth of Second-Order Nonlinear Optical Materials**

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Our interest in molecular crystals for opto-electronic applications, such as ultrafast (GHz) electro-optic applications, or optical parametric generation, stems from the fact that the potential upper limits of macroscopic nonlinearities and long-term orientational stability of molecular crystals are significantly superior to those of polymers and Langmuir-Blodgett thin films. However, 90% of achiral organic molecules crystallize centrosymmetrically and not in a polar structure required for second-order nonlinear optics. As a result, only few highly hyperpolarizable chromophores have been developed into useful and efficient crystalline materials. Moreover, the crystallinity and crystal properties of the rod-like, highly extended π -conjugation systems are usually poor and problematic which is detrimental for practical applications.

With respect to the above problems, two new crystal engineering approaches were investigated in order to align, tune and optimize the acentric orientation of highly extended, dipolar chromophores in the crystalline state as well as to improve the crystal properties for nonlinear optics.

The use of the non-rod-shaped framework-hydrazone skeleton—as a π -conjugation core is a very useful tool to acentrically align and optimize chromophoric orientation in the solid state for nonlinear optical effects. Of 35 new molecules being synthesized, 12 are strongly second harmonic generation active. In addition, the cooperative effect of multiple electron-donors was firstly explored to enhance the molecular nonlinearity and improve the chemical stability of the hydrazone derivatives. 3,4-Dihydroxybenzaldehyde-4-nitro-phenylhydrazone, **3,4-DHNPH** was developed to be useful for electro-optic application because of the highly optimized chromophoric orientation, the favourable crystal growth properties and the high temporal stability.

The supramolecular synthetic approach based on the short hydrogen bond induced self-assembly of molecular aggregates shows a high tendency to induce an acentric packing and a higher degree of design feasibility in tuning and optimizing the chromophoric orientation within the crystalline lattice. In addition, co-crystals obtained by this approach often show greatly improved crystal and physical properties relative to its starting components. With further elaboration of this approach, a longer homologue of the merocyanine dye was designed and successfully synthesized.

Crystals of the most promising materials are mostly grown from solution. As an example, crystals of 4-N,N--dimethyl-amino-4'-N'-methyl stilbazolium tosylate (DAST) have been consistently grown with a size up to 10x10x4 mm³.

Sponsor: Swiss National Science Foundation

Second-Order Nonlinearities of Conjugated Organic Molecules

I. Liakatas, M. S. Wong and Ch. Bosshard

Organic materials are very interesting for ultra-fast (GHz range) electro-optic applications as their nonlinear optical response depends mainly on the polarizability of the electrons in contrast to inorganic materials where lattice vibrations play a dominant role. Our group is continuously working on the development of conjugated organic molecules with high second-order nonlinearities for crystals or incorporation into polymers.

We investigate the second-order nonlinearities of our molecules using electric field induced second harmonic generation (EFISH) and hyper-Rayleigh scattering (HRS). EFISH provides information about the projection of the molecular hyperpolarizability tensor (β) along the dipole moment of the molecule whereas HRS can distinguish the different components of the β tensor, something very useful for the characterization of our non-rod-shaped hydrazone molecules. In addition it allows the investigation of charged molecules since no external electric field has to be applied.

The large ground-state dipole moment of chromophores can offer an advantage of enhancing a high degree of orientational order in electric field poled polymeric thin film; therefore, a new series of zwitterionic chromophores based on the stilbazolium cationic chromophores were designed and synthesized. Dielectric measurements showed that they do exhibit very large permanent dipole moment (up to $\mu = 13 \times 10^{-29}$ Cm). Our EFISH measurements showed that our zwitterionic chromophores possess products of dipole moment times molecular hyperpolarizability ($\mu \cdot \beta$) two times higher than that of DANS, one of the best chromophores for poled polymer applications.

In organic crystals, molecules need to exhibit high nonlinearity as well as to crystallize in optimized acentric structures. Therefore, multi-donors substituted 4-nitrophenylhydrazones, which show a high preference for non-centrosymmetric packing, have been designed, synthesized, and investigated for their first-order hyperpolarizability β . Since these molecules are non-rod-shaped, HRS was used. We built up an HRS experiment at 1.5 μm which allowed us an off-resonant determination of the second-order molecular hyperpolarizabilities and comparison of different substituted hydrazone molecules. It was found that the cooperative effect of multiple moderate electron-donors exhibits a donating strength comparable to that of one strong electron-donor in enhancing the molecular nonlinearity and the chemical stability.

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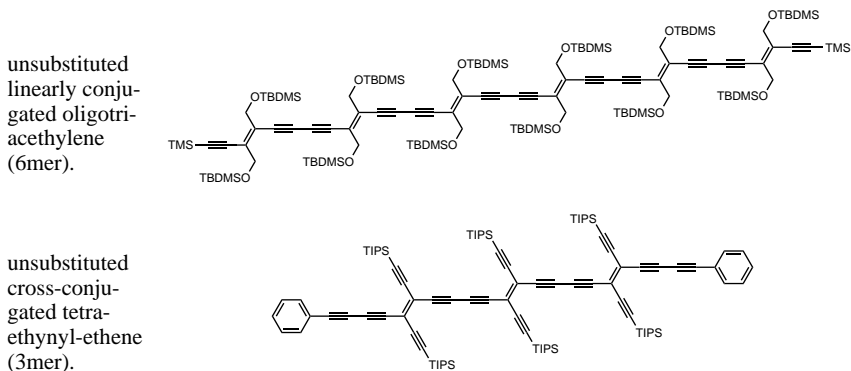
Third-Order Nonlinearities of Conjugated Organic Molecules

U.Gubler and Ch. Bosshard in collaboration with R. Martin, R. Tykwinski and F. Diederich, Laboratory of Organic Chemistry, ETH Zurich

For electronic and photonic applications, organic molecules with extended conjugation of the π -orbitals are of particular interest. Synthesis of conjugated molecules with well defined length is a laborious task and the dependence of physical properties from conjugation length is therefore not well known.

A sequence of unsubstituted, stepwise longer oligotriacetylenes (1-6mer, figure) was synthesised by the group of F. Diederich. The third-harmonic generation (THG) measurements in solution showed a power law dependence of the second-order hyperpolarizability γ . A comparison with two elongated polymer samples points to a saturation of the power law in the range of about 10 monomer units and an only linearly increase for longer molecules.

To check the influence of an additional cross-conjugation, perpendicular to the main backbone, unsubstituted oligotetraethynylethenes (1-3mer, figure) were produced and measured. The additional cross-conjugation raised the second-order hyperpolarizability γ by about one order of magnitude.



The substitution of the oligomer endgroups by electron donating ($-\text{N}(\text{CH}_3)_2$) or accepting groups ($-\text{NO}_2$) further increased the second-order hyperpolarizabilities γ . Only shorter oligomers could be modified (up to 2mers), due to problems with chemical stability. The asymmetric substitutions (an electron donor at one end, an electron acceptor at the other end) yielded the highest second-order hyperpolarizabilities (for asymmetric monomer: $\gamma = 8.5 \cdot 10^{-48} \text{ m}^5/\text{V}^2$).

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Electro-Optic Properties of Molecular Crystals

R. Spreiter and Ch. Bosshard

There is a great interest in materials for high bit rate ($> \text{Gb/s}$) photonic applications. This includes all-optical switching and electro-optic modulation or switching. At the interface between electronics and photonics, the electro-optic effect allows to control a light beam by an electrical signal. The electro-optic coefficient r of a material describes the change of the refractive index induced by applying an electric voltage to the material. For high speed, broad band applications it is essential to have access to materials with a large electro-optic coefficient r with little dependence on the frequency of the applied voltage. For fulfilling these requirements, organic molecular crystals are very promising.

In a crystal, the electro-optic effect has an electronic contribution and one from acoustic- and one from optical crystal lattice vibrations (phonons). These three different contributions show very different frequency dependence and response times. Usually the electro-optic effect is measured by applying a sinusoidal voltage to the crystal placed in one arm of a Michelson interferometer. To get the information about the different contributions, one has to measure the dependence of the overall effect on the frequency of the applied voltage. We now used a novel method, which allows to separate the different contributions to the electro-optic effect in one single measurement. Instead of a sinusoidal voltage, we applied a fast rise time step voltage to the crystal and measured the electro-optic response in the time domain. Due to the different response characteristics of the different contributions, we were able to separate the acoustic contribution from the others. Measurements were performed on the organic salt 4-*N,N*-dimethylamino-4'-*N'*-methyl stilbazolium tosylate (DAST), which shows one of the largest electro-optic effects ever measured.

For DAST we measured an acoustic contribution to the electro-optic effect of only 2 percents. The response time of the main electro-optic effect was less than 600 ps, limited only by the experimental set-up. This results show that DAST is a very favourable material for broad band electro-optics. The electro-optic coefficient is shown to be almost constant up to at least 1 GHz, probably much higher up to the resonance frequency of the optical phonons, which usually lies in the THz regime.

Sponsor: Swiss National Science Foundation

Nonlinear Optical Properties of Molecular Crystals

M. Bösch, F. Pan, S. Follonier, M. S. Wong and Ch. Bosshard

In the scope of this project, promising organic nonlinear optical crystals are investigated with special interest on highly extended π -conjugated systems (e.g. donor-acceptor di-substituted stilbene and hydrazone derivatives). A simple model shows that the requirements for the chromophore orientation in the crystal lattice depends on the application: for electro-optics the chromophores should be oriented parallel to each other, whereas for optical frequency-conversion the active molecules should be oriented with an angle of about 55° with respect to the polar crystal axis for the most interesting point groups.

The nonlinear optical coefficients as well as the refractive indices, which are important to (i) determine the relevant figures of merits of nonlinear optical and electro-optic applications and to (ii) determine possible phase-matched parametric interactions, are routinely investigated in Maker Fringe and Michelson interferometric experiments.

In the past year most of our nonlinear optical experiments on organic crystals concentrated on two materials developed in our laboratory. The first one is the newly developed hydrazone derivative 5-(methylthio)-thiophenecarboxaldehyde-4-nitrophenylhydrazone **MTTNP**H, optimized for parametric processes such as e.g. frequency-doubling. In the development of **MTTNP**H we relied on the use of the non-rod-shaped framework – hydrazone skeleton – as a π -conjugation core which is a very useful tool to acentrically align and optimize chromophoric orientation in the solid state for nonlinear optical effects. We have determined the linear optical (absorption, refractive indices) and nonlinear optical (nonlinear optical) properties of **MTTNP**H, with the largest effective phase-matchable nonlinear optical coefficient ($d_{32} > 150$ pm/V at $\lambda = 1318$ nm) in the near infrared ever reported to the best of our knowledge.

The second one is the co-crystal 4-{2-[1-(2-hydroxyethyl)-4-pyridylidene]-ethylidene}-cyclo-hexa-2,5-dien-1-one · methyl 2,4-dihydroxybenzoate, **Mero-MDB**, optimized for electro-optics due to the perfect parallel alignment of all chromophores. Interestingly, there exist two phases of **Mero-MDB** with the same lattice parameters but different linear and nonlinear optical properties.

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Fluorescence Phenomena in Organic Single Crystals

U. Meier and Ch. Bosshard

During the last years there has been a big effort in developing new organic materials with nonlinear optical properties for frequency conversion, electro optics and photorefractive applications. Theoretical descriptions of linear and nonlinear optical properties of these materials are based on chemical structure and energy configuration of the electronic states of the molecules with respect to the surrounding (solution or crystal). Since spectroscopic absorption and luminescence measurements provide the possibility of directly determining the transition processes between the different electronic states in organic molecules, the aim of this project is to investigate the intra- or intermolecular physical processes leading to luminescence phenomena of these organic materials.

Among our newly synthesized organic crystals for nonlinear and electro optic applications some co-crystal derivatives based on merocyanine dye and some stilbazolium salts 4-*N,N*--dimethylamino-4'-*N'*-methyl stilbazolium tosylate (DAST) show a strong fluorescence emission in the visible when illuminated in the near infrared. Several different excitation processes can generate the luminescent states in our organic materials; two photon absorption (TPA) or one photon absorption of the frequency doubled excitation pulse; direct TPA using an imaginary intermediate state or due to a short living real intermediate state; charge transfer states of the molecule (intramolecular) or excitonic states in the crystal (intermolecular, e^- & holes). To distinguish these different excitation processes in our nonlinear optical organic molecules and crystals, the dependence of the luminescence upon temperature, excitation intensity, polarization, and excitation wavelength are measured.

In contrast to DAST molecules in solution (one luminescence band observed at 620 nm) we observe two highly anisotropic luminescence bands in our DAST crystals (at 635 and 700 nm) when excited with laser light at 1064 and 532 nm. Remarkable differences in both luminescence position (some nm) and intensity (up to one order of magnitude) have been observed for different crystals and were attribute to their crystalline quality.

Sponsor: Swiss National Science Foundation

Photorefractive Effects in Organic Crystals and Polymers

S. Follonier, Ch. Bosshard and F. Pan, work on polymers in collaboration with M. Döbler and U. W. Suter, Institute of Polymers, ETH Zurich

Since the photorefractive effect (change of refractive indices induced by light) was first observed in inorganic crystals, much effort has been devoted to the understanding of the physical mechanism leading to this effect as well as to several applications (optical memories, phase-conjugation, phase-locking of diode arrays). The potential of organic materials as photorefractive media lies in the high sensitivity observed at near infrared wavelengths where low cost, high performance semiconductor laser diodes are available, and for polymers, in the ease of processing and low cost.

The aim of this project is twofold: Better understanding of the photorefractive effect in organic crystals, especially the charge generation and the transport mechanisms and the application of the acquired knowledge to the improvement of polymeric materials by choosing the optimised mixing of the several molecules responsible for charge generation (sensitiser e.g. C₆₀, TNF), transport (DEH agent), trapping and/or electro-optic effects. The temperature and wavelength dependence of the dark- and photoconductivities were determined to gain information on the charge generation and transport in organic crystals and polymers. Two-beam coupling as a function of the temperature, the wavelength and the polarization of the writing beams as well as four-wave mixing experiments lead to a better understanding of the photorefractive effect.

The project succeeded in the development of two new organic photorefractive crystals, namely DAST (4-*N,N*--dimethylamino-4'-*N'*-methyl stilbazolium tosylate) and DANPH (4-dimethylaminobenzaldehyde-4-nitrophenyl- hydrazone) which show photorefractive net gains at near infrared wavelengths up to $\lambda = 1064$ nm for writing times of the order of less than one second. This presents a significant improvement in writing times as well as the in sensitivity compared to the previous photorefractive organic crystals

In polyamides based on DDANS the contribution of the orientational and photorefractive effect could be separated by measuring the coupling of signal and pump beams as a function of temperature from room temperature up to the glass transition temperature. The photorefractive response could be enhanced by doping the polymers with photoconductors based on DEH, inducing higher photoconductivity and with TNF inducing higher sensitivity in the mid infrared regions.

Reference: S. Follonier, Ch. Bosshard, F. Pan, and P. Günter, "Photorefractive effects observed in 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium toluene-p-sulfonate", *Opt. Lett.***21** (20), 1655-1657 (1996)

Sponsor: Swiss National Science Foundation

Cascading of Second-Order Nonlinearities

Ch. Bosshard and U. Gubler

Cascading is a process where lower-order effects are combined to contribute to a higher-order nonlinear process. Recently the potential of cascading for all-optical switching was realized and large nonlinear phase shifts due to cascading (second-harmonic generation (SHG) and difference-frequency mixing (DFM)) were observed in several materials. Cascading also occurs in third-harmonic generation. In this process a fundamental wave at frequency ω produces a wave at frequency 3ω ($\omega + \omega + \omega = 3\omega$). In noncentrosymmetric materials also sum-frequency mixing ($\omega_1 + \omega_2 = \omega_3$) and second-harmonic generation ($\omega + \omega = 2\omega$) are allowed. The two latter processes can be used to also obtain a wave at frequency 3ω as well: We first generate an intermediate field at frequency 2ω through second-harmonic generation. This field can interact with the fundamental wave through sum-frequency mixing ($2\omega + \omega = 3\omega$) to generate a field at frequency 3ω itself.

When applied to third-harmonic generation, cascading can be used for the absolute determination of the third-order nonlinearity $\chi^{(3)}$ since it often is a self-calibrating process. This means the following: From a theoretical fit of an experimental third-harmonic generation curve of a crystal that shows cascaded processes one can directly obtain the ratio $\chi^{(3)}/(\chi^{(2)})^2$. Therefore, if the values of $\chi^{(2)}$ are known, the value of $\chi^{(3)}$ can be determined. A subsequent comparison with the standard material fused silica then yields $\chi^{(3)}$ of fused silica.

We have extended already existing work for the following reasons: (i) The reference value of $\chi^{(2)}$ of quartz (previously used) has considerably changed over the last 15 years (from 0.5 p m/V down to 0.3 pm/V at $\lambda = 1064$ nm). (ii) The ratio of $\chi^{(3)}/(\chi^{(2)})^2$ is not very well determined for crystalline quartz since $\chi^{(2)}$ of quartz is rather small. In the meantime high-quality crystals of KNbO₃ are available. KNbO₃ has much larger nonlinear optical susceptibilities $\chi^{(2)}$ with respect to its $\chi^{(3)}$ values and therefore allows a more precise determination of the ratio $\chi^{(3)}/(\chi^{(2)})^2$. (iii) It is of considerable interest to know the dispersion of $\chi^{(3)}$, on the one hand to get a reliable standard for the dispersion of $\chi^{(3)}$, on the other hand to get a better theoretical understanding of the dispersion behaviour in inorganic (and organic) materials.

Our experimental results so far lead to a new reliable standard for fused silica to be used in third-harmonic generation experiments at $\lambda = 1907$ nm ($\chi^{(3)} = 1.61 \times 10^{-22}$ m²/V²). The dispersion relations for $\chi^{(3)}$ are currently investigated.

Reference: Ch. Bosshard, "Cascading of Second-Order Nonlinearities in Polar Materials", *Adv Mat.* **8** (5), 385-397 (1996)

Electro-Optic Polymer Waveguide Modulators

I. Liakatas, M. Bösch, and Ch. Bosshard

Organic polymers have become an important class of nonlinear optical materials for electro-optic modulation. They have been the subject of intense research since they combine the nonlinear optical properties of conjugated π -electron systems with the feasibility of molecular engineering, i.e. creating new materials with appropriate optical, structural, and mechanical properties.

During the recent years the relaxation of the nonlinear optical activity in poled side-chain polymers has been investigated in our group and provided a deeper understanding of the relaxation of the oriented chromophores. In the beginning of this new project we focus on the development and characterization of new chromophores with improved nonlinear optical properties for use in side-chain polymers. Thin polymeric films are centrosymmetric and have to be poled to show second-order nonlinear optical effects. The polar orientation is achieved by electric field poling above the glass transition temperature. Therefore the critical parameter to achieve large electro-optic coefficients is the product of the static dipole moment and the molecular first-order hyperpolarizability, $\mu \cdot \beta$. We developed stilbazolium based zwitterionic chromophores, chromophores holding two ions, which possess very high values of the product $\mu \cdot \beta$. The dipole moment of these molecules was measured using concentration-dependent dielectric measurements and the hyperpolarizability was determined by electric field induced second-harmonic generation (EFISH). To investigate their poling behaviour these new chromophores were introduced into a guest-host polymer system. The spin casted polymer films were corona-poled and the nonlinear optical coefficients were measured with the Maker-fringe technique.

Nonlinear coefficients were found to be comparable to and the $\mu \cdot \beta$ product to be considerably higher than the one of the often used Disperse Red 1 due to the high ground state dipole moment of the new chromophores. The low solubility in the polymer matrix, however, sets a limit to the chromophore loading. Therefore, incorporation of the chromophores into a side-chain polymer system is needed and expected to lead to high performance materials for organic electro-optic devices.

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Molecular layer deposition of organic molecules and its characterization by scanning force microscopy

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Nonlinear optical thin films are one of the key elements in future optical devices for realizing high-speed, large-capacity information transmission and processing. Despite the extremely large nonlinear optical and electro-optical effects in some organic materials, the production of high quality organic thin films has been strongly hampered so far due to the large lattice mismatch and the weak interaction between polar organic materials and inorganic substrates.

We have grown organic nonlinear optical thin films using a newly developed organic molecular layer deposition (OMLD) technique, which utilizes sequential self-terminating growth of different organic functional molecules under ultra high vacuum (UHV) conditions to fabricate polymeric thin films with periodic structures perpendicular to the substrate. When the chromophores are preferentially oriented in growth direction, a strong macroscopic electro-optic effect is observed for light polarized parallel to the chromophores. This geometry e. g., is ideally suited for electro-optic waveguide modulators. Such oriented periodic structures already inherently possess the required symmetry and, therefore do not require poling.

We have deposited two pairs of monomers PAD (pyromellitic acid-dianhydride)/ DDE (4,4'-diamino-diphenylether), and TOC (terephthaloyl-dichloride)/ DDE on quartz substrates. Self-terminating growth of PAD on DDE and DDE on PAD has been observed at substrate temperatures of 40 and 70 °C, respectively. In addition, PAD was replaced by TOC as an electrophilic precursor in view of an easier polymerization reaction between PAD and DDE. Self-terminating growth of TOC on DDE and DDE on TOC has been realized at a substrate temperature of 21 °C for both materials.

The morphology of the organic thin films can be characterized by an ultra-high vacuum scanning force microscope (UHV SFM), designed, built and successfully tested in air. The detection is done by a piezoresistive strain sensor embedded in the cantilever. The deflection is measured directly from the change of the resistance of this sensor.

The tests of the SFM are carried out using calibration grids, and polycrystalline gold samples. Moreover, monatomic steps on graphite and WSe₂ have been observed in contact mode.

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