Novel calixarenes in thin films for efficient second harmonic generation

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Calix[4]arenes are a novel type of molecules for nonlinear optics. In a single molecule four π-conjugated systems are combined. Corona poled guest-host polymer systems [calix[4]arenes-poly(methyl-methacrylate)] with transparency into the UV and loading up to 100% show a high degree of orientation. The maximum resonant d_{33} nonlinear coefficient measured at a fundamental wavelength of 590 nm is 51 pm/V. The d_{33} values of the thin films relax after poling to 65% of their maximum value. Results indicate self-organization of the molecules upon poling.

Interest in organic molecules for use in nonlinear optics (NLO) is still growing because of their potential use in optical communication, optical switching, frequency conversion, etc. As to this purpose incorporation of organic materials into thin films is necessary. Polymer systems are well suited for thin-film applications. Some basic types of NLO polymer systems are to be distinguished:[1] (i) Guest-host polymer systems, (ii) Functionalized polymers[2,3] and (iii) Polymer networks.[4] The first type is the most easy to prepare but shows some major disadvantages, as poor temporal stability of the molecular orientation after alignment and poor solubility (< 10 wt %) of the NLO chromophore in the polymer matrix. Functionalized polymers in which the chromophore is covalently attached to or incorporated in the polymer backbone allow a much larger chromophore concentration. Polymer networks allow only very little molecular mobility and therefore the polar ordering is stable.

In this letter first results of second harmonic generation (SHG) in corona poled thin films of newly synthesized calix[4]arenes in poly(methyl-methacrylate) (PMMA) are presented.

In a single calix[4]arene molecule (Fig. 1) four π-conjugated donor-acceptor systems are combined after functionalization of the phenolic rings.[5] The combination of four conjugated units increases the hyperpolarizability (β) of the molecule and is accompanied by a hypsochromic shift of the charge transfer band in the absorption spectrum. The wavelengths of maximum absorption (λ_{max}) and the onset of absorption (λ_{cutoff}) are comparable with molecules which have one single π-conjugated system. For the nitrocalix[4]arene derivative, which is investigated, $\beta_z = 1.4 \times 10^{-38}$ m⁴/V, $\lambda_{max} = 291$ nm and $\lambda_{cutoff} = 365$ nm.[1]

Thin films were prepared by spin coating of nitrocalix[4]arene-PMMA mixtures in chloroform on pyrex glass and ITO coated glasses. Typical film thickness was ~ 0.25 μm. After annealing for 10 min at 90 °C the films were aligned in a corona discharge[6,7] (10 kV) during 15 min at 110 °C. SHG efficiency was measured using a nanosecond Nd:YAG laser in combination with a dye laser as a source of fundamental radiation. A Soleil–Babinet compensator was used to adjust the polarization of the fundamental beam. The sample was rotated in the laser beam with its rotation axis perpendicular to the incident polarization direction. Separation of fundamental and harmonic radiation was achieved by use of a suitable filter set. Absolute d values were determined using a 1 mm z-cut α-quartz crystal ($d_{11} = 0.51$ pm/V at $\lambda = 1064$ nm) as a reference.

The strong electric dc field which is applied perpendicular to the surface induces an alignment of the NLO chromophores according to a Boltzmann distribution thus imposing a $C_{\infty V}$ symmetry onto the films. For such a symmetry only the d_{31} and the d_{33} nonlinear coefficients are nonzero.[8] If the thickness l_f of the film is small compared to the SHG coherence length it is readily shown that for detection at the Brewster angle ϑ_B the effective nonlinear coefficient d_f of the film can be expressed as,

$$d_f = \frac{1}{\pi} \left(\frac{I_f}{I_q} \right)^{1/2} \left(\frac{n_f}{n_q} \right)^{3/2} \frac{l_{c,q}}{n_f l_f} (n_f^2 - \sin^2 \vartheta_B)^{1/2} d_q \qquad (1)$$

where I_f and I_q are the harmonic signal intensities of the sample and the quartz reference, respectively. The coherence length in quartz is $l_{c,q}$ and d_q is the nonlinear coefficient of the quartz reference.
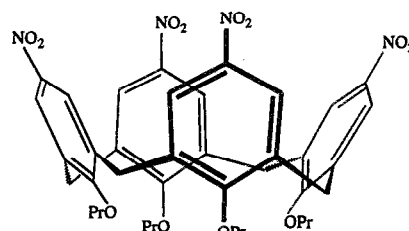
In the case of small dispersion and absorption, taking

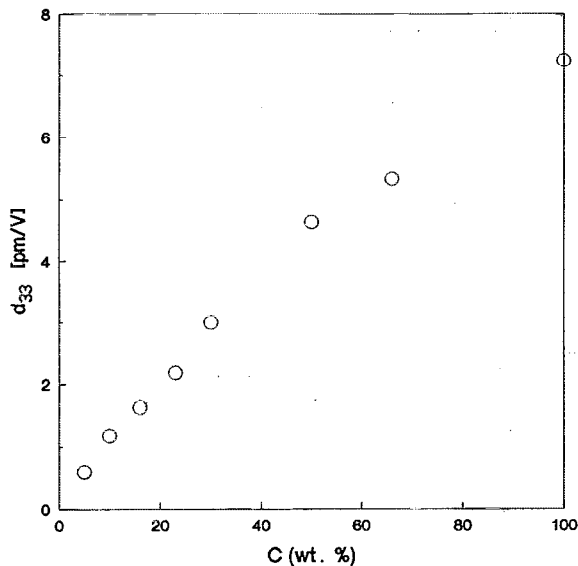FIG. 1. Tetranitro-tetra-(n-propoxy)calix[4]arene (cone conformation).

FIG. 2. The d_{33} nonlinear coefficient shortly after poling versus the nitrocalix[4]arene concentration in PMMA ($\lambda = 1064$ nm).

FIG. 3. The d_{33} nonlinear coefficient versus the energy $\hbar\omega$ of the fundamental radiation.

$d_{31} = d_{33}/3$, which is the case for a $C_{\infty V}$ symmetry,[8] d_{33} is given by,[7]

$$d_{33} = \frac{n_f}{\sin(\vartheta_B)} d_f. \qquad (2)$$

For low chromophore concentrations the poled polymer guest host system can be described by the rigid oriented gas model (ROGM).[9] The second order nonlinear coefficient d_{33} is then given by,

$$d_{33} = \tfrac{1}{2} N \beta_z f^{2\omega} (f^\omega)^2 \langle \cos^3 \theta \rangle \qquad (3)$$

where N is the chromophore density, $f^{2\omega}$ and f^ω are Lorentz–Lorenz type local field factors and θ is the angle between the molecular dipole axis and the electric field vector.

All of the prepared nitrocalix[4]arenes-PMMA films showed NLO activity after poling whereas unpoled thin films and crystals of calix[4]arenes do not show such an activity. Thin films are highly transparent and are suited for waveguide fabrication. The measured values of d_{33} as a function of the nitrocalix[4]arene weight percentage in PMMA are shown in Fig. 2. Measurements of the perpendicularly polarized second harmonic light showed that $d_{31} = d_{33}/3$ is a good approximation.

Increase of the corona discharge voltage or use of ITO coated glasses showed no changes in the measured d_{33} values of the nitrocalix[4]arene. Comparing d_{33} and β_z it was deduced that $\langle \cos^3 \theta \rangle \cong 0.68$. It is therefore supposed that maximum alignment at this poling temperature is reached. In approximately 10 days d_{33} decreases to 65% of its initial value measured just after poling. No significant further decrease was measured over a period of 8 months at room temperature.
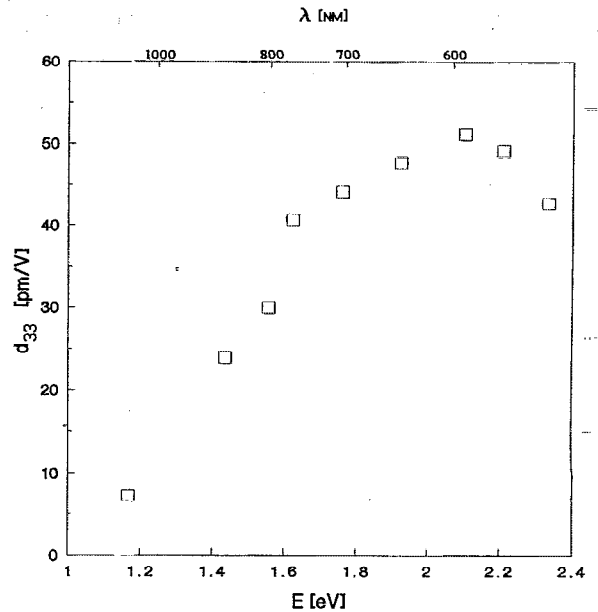
The nonlinear d_{33} coefficients were measured as a function of the fundamental frequency. Proper consideration was taken of the dispersion of the various parameters. Results are shown in Fig. 3. Maximum d_{33} values up to 51 pm/V at resonance are found for second harmonic frequencies in the vicinity of the absorption maxima. The resonance enhancement of the d_{33} nonlinear coefficient is about a factor 10.

No limits as to the solubility of the chromophore in the polymer matrix were observed. Layers up to 100% chromophore concentration were fabricated. The polar orientation of the corona poled films is stable after an initial decrease. The stability of the nonlinear coefficient at 65% of its maximum value indicates a new type of thin-film organization. The alignment of the chromophores is extremely large, indicated by the value $\langle \cos^3 \theta \rangle \cong 0.68$. As can be seen in Fig. 1 the relation between the nonlinear coefficient d_{33} versus the nitrocalix[4]arene concentration in PMMA is linear except for large concentrations at which the ROGM model is not valid any more. Note that poling was done at a temperature $T = 110\,°C$ being the glass transition temperature of PMMA. For low chromophore concentrations this temperature is favorable for poling, however, for higher concentrations it is rather an arbitrary value.

The advantageous combination of high d_{33} values and the transparency into the UV for the nitrocalix[4]arene makes these thin films especially suited for frequency doubling of the diode laser radiation (typically: 820→410 nm; $d_{33} = 27$ pm/V).

Calix[4]arene-PMMA thin films are easy to prepare and do not exhibit the disadvantages common to guest-host systems. These properties in combination with the high

values of the d_{33} nonlinear coefficient make the calix[4]arene-PMMA thin films very promising for NLO purposes.

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