fact, the devices could not be operated in air owing to significant degradation as a function of oxygen and/or water partial pressure. Whereas *storage* in air hardly changed the $I-V$ characteristic (e.g., 40% reduction of conductivity after 3 weeks for EC4T) and luminance or output power, *operation* in air led to a rapid degradation. For example, the output power decayed by a factor of five within 10 s for EC6T and within 20 s for EC7T; EC4T and EC5T could not even be measured. Thus, we operated the LEDs in an inert N_2 atmosphere, which provided relatively stable conditions such that EC7T and EC6T showed little degradation (e.g., 25%) after 15 min of operation at 2 mA. The reason for the rapid degradation in air (and also the slight degradation in a nitrogen atmosphere) is most likely oxidation of the Al electrode, which increases the barrier height and hence reduces the injection probability of electrons. The question remains why different oligothiophenes cause different degradation behavior. At present we can think of two possible answers: a) a different degree of dissociation or follow-up reactions of the oligothiophenes, perhaps at the inner electrode surface, in oxidizing atmosphere and in the presence of a current and/or electric field, and b) different diffusion velocities of O_2 and/or H_2O through the thin molecular film. The thermal molecular motion induced by the current may be responsible for rapid diffusion in operation while the different film morphologies (see above) may have caused the differences amongst the oligomers. More work is needed to give a clearer answer and to solve the problem of poor LED stability.

Finally, we should briefly comment on the output power, which was measured by a calibrated laser power meter and is also displayed in Figure 2 for EC6T (dash-dotted curve, right hand scale). The light emission starts at voltages as low as 2.5 V (for a 160 nm thick EC6T film) and reaches a maximum around 8 V, as can be derived from the inset, which shows the power conversion (not quantum) efficiency curve. This curve varies relatively little (factor of two) as a function of voltage but has only a modest maximum of $4 \times 10^{-5}\%$. (The value for EC7T is even smaller by a factor of four; the value for EC5T is markedly higher but could not be measured with sufficient accuracy.) These values have not been corrected for geometric effects, for internal reflection and absorption, and for internal energy conversion processes. If estimated corrections are taken into account the values become considerably higher (by about a factor of 100) and the quantum efficiency may be 10^{-2} – $10^{-3}\%$. This is still very low and far from being satisfactory, in particular in view of applications. We have some evidence that the low efficiency has various causes, such as film morphology, electrode material with too high a work function, interface bonding and reactions, and the physical properties of the molecules. We believe that it can be improved by orders of magnitude if materials and preparation conditions are optimized. Such work is in progress.

In conclusion, we have demonstrated the first operation of light-emitting devices based on (end-capped) oligothiophenes

(EC n T, $n = 4$ to 7) and the dependence of their transport properties and spectral distributions on the chain length of the oligomers. Our LEDs were prepared by vacuum sublimation and could be operated at relatively low voltages (starting at about 2.5 V) and moderate current densities (e.g., 7 mA/cm²). Furthermore, we have noted the influence of film morphology and oxidizing atmosphere, and we have briefly discussed the possible reasons for the instability and low efficiency of our LEDs.

Received: September 23, 1993

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Highly Ordered Films of Neat Calix[4]arenes for Second Order Nonlinear Optics

By Erik Kelderman, Gerard J. T. Heesink, Lode Derhaeg, Thierry Verbiest, Piet T. A. Klaase, Willem Verboom, Johan F. J. Engbersen, Niek F. van Hulst, Koen Clays, Andre Persoons, and David N. Reinhoudt*

π -Conjugated organic molecules with both electron-donating (D) and electron-accepting (A) substituents are

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[**] This investigation was supported by the Netherlands Foundation of Chemical Research (SON) and the Foundation for Fundamental Material Research (FOM) with financial aid from the Netherlands Organization for Scientific Research (NWO). P. T. A. K. was funded by the Dutch Ministry of Economic Affairs under the Innovation Oriented Program on Polymers (IOP-PCBP).

promising for use in nonlinear optics, for example, frequency doubling of laser light and electro-optical switching.^[1-4] In the molecules investigated so far, the nonlinear optical (NLO) phore consists of one single π -conjugated system with one or more donors and/or acceptors (D- π -A molecules). Extension of the conjugated system increases the nonlinear hyperpolarizability β but also shifts the charge-transfer absorption band (CT band) to longer wavelengths, thereby restricting the applicability for frequency doubling.^[1-4] In order to obtain a material with a high nonlinear susceptibility $\chi^{(2)}$ the density of NLO active molecules must be as high as possible, and these molecules must be oriented non-centrosymmetrically in one direction.

Recently,^[5] we have described a novel class of NLO-phores, namely calix[4]arenes, which combine up to four D- π -A moieties in one molecule. Calix[4]arenes are cyclophanes that consist of four phenol moieties connected by methylene bridges.^[6] The number and the positions of the D- π -A units with respect to each other can be varied because calix[4]arenes can be made rigid in four different extreme conformations^[5-7] with different relative orientations of the individual NLO-phores. When all four phenolic oxygens are alkylated by groups larger than ethyl the different conformations become configurations, which are no longer interconvertible even at elevated temperatures.^[7b]

The configuration in which the four D- π -A units are oriented most in one direction is called the cone configuration and is shown in Scheme 1. The calculated vectorial contribution of the four NLO units in the calix[4]arene in this cone configuration to the β value is about 3.5 times as large as that of one single D- π -A unit. However, it was found that when all four aromatic rings of a calix[4]arene in the cone configuration are functionalized with donor and acceptor substituents that the β value is about three times as large as the value of a single D- π -A substituted reference compound. The slightly lower value than expected from the vectorial contribution can be explained^[8] by interference of the cofacial π -systems in calix[4]arenes. Recently, Di Bella et al.^[8] also reported in a theoretical study that the hyperpolarizability (nonlinear susceptibility) and absorption properties of non-covalently linked NLO-phores are strongly dependent on the number, distance, and orientation of the molecules. They calculated that when the interplanar cofacial distance is between 4 and 10 Å the π -systems of the molecules will interact, resulting in lower $\chi^{(2)}$ values than would be expected by vectorial addition of the individual β values. The distances between the four π -systems in calix[4]arenes are about 4 to 8 Å and the mutual influence on $\beta(\chi^{(2)})$ could clearly be demonstrated.^[5]

A positive effect of the close interaction of the π -systems is that upon increasing the number of NLO units, from one to four in the calix[4]arene in the "aligned" cone configuration, a blue shift (hypsochromic shift) of the charge-transfer band maximum (λ_{CT}) is observed. This hypsochromic shift is expected for the cofacial interactions in the calix[4]arene in the cone configuration in which the interplanar distances are

about 4.5 Å and can be qualitatively rationalized in terms of the through-space excitonic coupling model.^[8, 9] According to this model, for cofacial parallel molecules the excited state is no longer degenerate, giving rise to a blue shift of the wavelength absorption maximum.

In these calix[4]arenes we have succeeded in introducing a large number of D- π -A units per volume unit which are (already) oriented in one direction at the cost of only a very small decrease of the β value. The next challenge is to orient these calix[4]arene molecules in a thin film with again a large density of NLO active molecules and with a large orientation factor. In a previous paper we have reported that a large density of tetranitro-tetrapropoxycalix[4]arene in poled thin films could be obtained with an appreciable degree of orientation.^[5] In this paper we describe the molecular and thin-film NLO properties of three tetra-D- π -A-substituted calix[4]arenes (**1–3**), shown in Scheme 1. The poling of these calix[4]arenes, which have high β values^[5] will hopefully result in thin films with high $\chi^{(2)}$ values. The orientation of the calix[4]arenes in these films will be described as well as the stability of the NLO response of these films at room temperature and at 100 °C.

Scheme 1.

The molecular β values of calix[4]arenes **1–3** and reference compounds **4–7** were measured by both the electric field induced second harmonic (EFISH) generation technique^[3, 10] and the recently developed hyper Rayleigh scattering (HRS) technique^[11] with a fundamental wavelength of 1064 nm generated by a Nd:YAG laser source. These $\beta(1064)$ values, the dipole moment, and the charge-transfer band maximum are summarized in Table 1.

The dipole moments of the tetranitro-tetrapropoxycalix[4]arene **1** and the tetrakis(nitrostilbene)-tetrapropoxycalix[4]arene **2** in the cone configuration are three times as large as that of 4-nitroanisole **4** and 4-methoxy-4'-nitrostilbene (MONS) **5**. The 5,17-dihydroxy-tetrakis(nitrophenylazo)-11,23-dipropoxy calix[4]arene **3** has been compared with both 4-hydroxy-3,5-dimethyl-4'-nitroazostilbene **6** and the methylated derivative 4-methoxy-3,5-dimethyl-4'-nitroazostilbene **7**, since the molecule can be considered as a combination of these two compounds. The dipole moment of calix[4]arene **3** is three times as large as that of the methylated

Table 1. Dipole moments μ , charge-transfer band maximum λ_{CT} , and hyperpolarizability β measured by EFISH and HRS for the calix[4]arenes 1–3 and the reference compounds 4–7 [a].

Compound	μ [D]	β (EFISH [b, c] [10^{-30} esu])	β (HRS) [b, d] [10^{-30} esu]	λ_{CT} [nm]
1	13.8	30	27	291
4	4.6	12	12	302
2	15.3	280	278	370
5	4.5	100	105	377
3	13.0	161	231	356
6	5.5	92	[e]	386
7	4.3	42	[e]	365

[a] All measurements were performed in CHCl_3 . [b] The EFISH and HRS experiments were performed with a fundamental wavelength of 1064 nm. [c] Error 20%. [d] Error 25%. [e] β values could not be determined because the absorption of the generated second harmonic light was too great.

reference compound 7. Both the β (EFISH) and β (HRS) values of the calix[4]arenes 1 and 2 are about three times as large as those of the reference compounds 4 and 5. In the EFISH experiment only the contributions of the β components in the direction of the dipole moment are measured, whereas in the HRS experiment the sum of all β components is determined. Therefore, the larger β (HRS) value for dihydroxy-tetrakis(nitrophenylazo)-dipropoxycalix[4]arene 3 compared with its β (EFISH) value indicates a contribution from a β component which does not coincide with the dipole axis. This can be attributed to the remaining flexibility of the two phenolic moieties in 3, which may rotate through the annulus of the calix[4]arene.

The λ_{CT} values of all the calix[4]arene derivatives are comparable with those of the reference compounds. However, for the reference compounds 6 and 7 the higher charge-transfer band wavelength maxima in combination with a probably low β (HRS) value resulted in too much absorption of the generated second harmonic light to allow a reliable determination of their β (HRS) values.

The $\beta(1064)$ value of the tetrakis(nitrostilbene) derivative 2 of 280×10^{-30} esu (142×10^{-30} esu at 1910 nm) is comparable with that of *N,N*-dimethylamino-4-nitrostilbene (DANS, 83×10^{-30} esu at 1910 nm).^[3] Moreover, the lower λ_{CT} value of 370 nm of 2 compared with the λ_{CT} value of 427 nm of DANS renders the calix[4]arene much more transparent for frequency doubling to shorter wavelengths.

In order to study the macroscopic NLO properties of the calix[4]arenes 1–3 we have prepared oriented thin films by spin-casting and subsequent poling by a strong DC electric field.^[4] Because of the higher dipole moments of the calix[4]arenes 1–3 compared with the reference compounds 4–7, we expected a more efficient poling of the calix[4]arenes in a strong DC electric field. We started our investigations with so-called doped polymer films of tetranitro-tetrapropoxycalix[4]arene 1 in poly(methylmethacrylate), PMMA. These doped films can be very easily made by spin-casting of a chloroform solution of calix[4]arene and polymer. This technique can be used to study molecules that are suitable for second order nonlinear optics, but it is almost never used to

prepare poled films that will be used in devices.^[4] The reason is that, normally, these films suffer from poor stability at room temperature and especially at elevated temperatures. A second drawback is the low solubility (often lower than 10 wt-%) of NLO active molecules in the polymer matrix. For example, the initial frequency doubling coefficient d_{33} of 0.4 pm V^{-1} , measured at a fundamental wavelength of 1064 nm, of a film of the maximally soluble 4.5 wt-% DANS in a PMMA matrix is inactive after one month at room temperature.^[12] Surprisingly, films with very high concentrations of tetranitro-tetrapropoxycalix[4]arene 1 in the cone configuration in PMMA could be prepared with good optical properties and high stability. The measured $d_{33}(1064)$ values as a function of the weight percentage of 1 in PMMA are shown in Figure 1.

Fig. 1. Frequency doubling coefficient d_{33} of films prepared by corona poling ($E_p \approx 200\text{--}300 \text{ V } \mu\text{m}^{-1}$) at 110°C , as a function of the weight percentage of cone tetranitro-tetrapropoxycalix[4]arene 1 (short dashes) in different polymeric matrices ($\bullet$, poly(methylmethacrylate); $\square$, poly(phenylmethacrylate); Δ , polystyrene; $\circ$, poly(4-methylstyrene), $\blacksquare$, neat 1) and cone tetrakis(nitrostilbene)-tetrapropoxycalix[4]arene 2 (long dashes) in a PMMA matrix (∇ , neat 2). Error 10%.

In order to investigate the possibility of molecular interactions of the doped films of the cone configuration of tetranitro-tetrapropoxycalix[4]arene 1 with the host polymer, we have prepared poled polymer films of 1 with different types of polymers. The side chains of the selected polymers may be complexed in the cavity of the calix[4]arenes, similar to what is found for the complexation of the methyl group of toluene in *tert*-butylcalix[4]arene.^[6] However, as is shown in Figure 1, the increase of the d_{33} values with the weight percentage of 1 is rather similar for the doped films of the different polymers. Moreover, the stability of the various doped films behaves the same (see below). Since these polymers have different side chains, complexation of the nitrocalix[4]arenes (under poling conditions) is therefore very unlikely.

Another possible form of organization in the poled films would be the formation of separate domains of highly polar calix[4]arenes and the polymers. Head-to-tail aggregation has recently been observed for liquid crystalline capped calix-

[4]arenes.^[13] The probability of formation of separate calix[4]arene domains in the doped polymer films is supported by the fact that the d_{33} values increase linearly with the weight percentage of **1**. The most striking result from these experiments is the possibility of poling neat films of **1** with high efficiency and a d_{33} value of about 7.2 pm V^{-1} .

In approximately 10 days at room temperature the d_{33} values of all the (doped) films decrease to 65% of their initial values measured directly after poling, this again indicates domain formation of the calix[4]arenes in the (polymeric) matrix. However, almost no further decrease of this signal is observed at room temperature, as is depicted for the film of neat **1** in Figure 2. Even after 2 years the measured d_{33} value of these films remains at 65% of the value measured directly after poling.

Fig. 2. Decay of the frequency doubling coefficient d_{33} of a film of neat tetranitro-tetrapropoxycalix[4]arene **1** at room temperature (●) and at 100 °C (○). These films were prepared by corona poling at 110 °C. Error 10%.

According to Lin et al.^[14] the decrease of the d_{33} signal in poled films can be expressed as the sum of two exponential functions, as given by Equation 1.

$$d_{33} = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \quad (1)$$

By fitting the decay curve with this equation, the fast decay indicated by the τ_1 value was calculated to be 3.5 days, whereas the long term stability, expressed by the τ_2 value, is of the order of 10^6 days (2700 years). The stability of the films was also investigated at elevated temperatures.^[15] In Figure 2 the decrease of the second harmonic generation (SHG) signal of the film with neat **1** at 100 °C is also shown. At the beginning of the experiment ($t = 0$ h) the $d_{33}(1064)$ value of the film had already decreased to 65% of the value measured directly after poling. Again, the decay of the d_{33} signal can be expressed by Equation 1. The calculated τ_1 value at 100 °C is 3.5 h and the τ_2 value is more than 200 days. It should be noted that the relatively stable value that is reached after keeping the film at 100 °C for 24 h is still 20% of the value measured directly after poling.

Poling of pure materials without polymer support has been reported earlier for materials such as 2-cyclooctylamino-5-nitropyridine (COANP) and (*S*)-2-*N*- α -(methylbenzylamino)-5-nitropyridine (MBANP).^[16] These materials, however, do not form a stable phase since they are obtained as a glass by freezing in the non-centrosymmetric orientation induced by the E_p field. The glass transition temperatures (T_g) of MBANP and COANP are only 0 °C and -10 °C, respectively; at T_g the E_p -field-induced orientation is lost, whereas the d_{33} value of poled neat nitrocalix[4]arene films **1** are stable even at 100 °C for a long period of time.

The important orientation factor in the case of $C_{\infty v}$ symmetry induced in poled films is $\langle \cos^3 \theta \rangle$ which can be calculated by Equation 2.^[17]

$$\langle \cos^3 \theta \rangle = \frac{\chi^{(2)}}{N F(\omega) \beta_z} \quad (2)$$

In Equation 2, N is the density of nonlinear optical molecules in the film and F is the local field factor.^[18] According to the Langevin function holding for molecules with a small dipole moment, up to about 5 D, a linear increase of the orientation factor as a function of the poling field is expected.^[4] For molecules with larger dipole moments, the initially linear increase levels off for higher poling fields when the maximum polar alignment is approached. The films for the frequency doubling experiments were prepared by corona poling.^[19] Unfortunately, the E_p field in corona poling is not exactly known. However, the nonlinear susceptibility $\chi^{(2)}$ is related not only to the coefficient of frequency doubling d_{33} ($d = 0.5 \chi^{(2)}(-2\omega)$) but also to the electro-optic coefficient r_{33} ($r = 2 \chi^{(2)}(-\omega)/n^4$).^[2] The latter coefficients have been determined from films made by contact poling (Fig. 3). For contact poling the effective poling field can be exactly determined. Since the origin of both phenomena in organic materials is polarization of the π -electrons, the two different $\chi^{(2)}$ values for the films obtained by corona and contact poling with the same effective poling field should be almost identical when measured far from resonance.^[2]

The r_{33} value of a material is obtained essentially by measuring the change of the refractive index Δn of a film between two electrode plates as a function of a DC electric field.^[20] Spin-coated films containing 75 wt-% of tetranitro-tetrapropoxycalix[4]arene **1** in PMMA matrices were poled at 105 °C and the r_{33} value was measured at 633 nm. When $r_{33}(633)$ is plotted as a function of the poling field (E_p), as shown in Figure 3, surprisingly a non-Langevin behavior is observed.

The r_{33} values increase quadratically upon increasing the poling field up to $60 \text{ V } \mu\text{m}^{-1}$ and then level off when the maximum alignment is approached at higher poling fields. For the films obtained by contact poling with $50 \text{ V } \mu\text{m}^{-1}$ the orientation factor calculated from Equation 2 is about 0.3.^[18] In this calculation the $\beta_z(-2\omega)$ of 30×10^{-30} esu measured at 532 nm has been used, assuming a negligible dispersion for $\beta_z(-\omega)$ at 633 nm. The large orientation fac-

tor of 0.3 achieved for **1** with a dipole moment of 13.8 D by an E_p field strength of $50 \text{ V } \mu\text{m}^{-1}$ would have been expected for molecules that have a dipole moment of about 40–60 D, according to the isotropic model.^[13, 17] This result indicates cooperative interactions in the formation of films of nitrocalix[4]arenes in a strong E_p field. The maximum orientation factor obtained for the films prepared by the higher corona poling field of about $200\text{--}300 \text{ V } \mu\text{m}^{-1}$ for the frequency doubling experiments is close to unity,^[21] which means that all the dipoles are aligned in the direction of the E_p field. That this value is higher than that found for contact poling is in accordance with the observed strong increase of the orientation factor as a function of the E_p field.

Van der Vorst and Picken^[17] have theoretically investigated the poling behavior of side-chain polymers in strong electric fields. They found that for these polymers the orientation factor increases much faster than would be expected on the basis of the Langevin function according to the isotropic model. This is attributed to an enhanced polar order of the (liquid crystalline) side chains upon poling. An example of a side-chain polymer (containing about 75 wt-% of DANS groups as the NLO active groups) showing this behavior was reported by Buckley.^[22] The curve calculated according to the theoretical model^[17] and the curve observed for the polymer published by Buckley^[22] strongly resemble our result presented in Figure 3.

Fig. 3. The electro-optic coefficient r_{33} of a film of 75 wt-% of tetranitro-tetrapropoxycalix[4]arene **1** in a PMMA matrix as a function of the poling field E_p , prepared by contact poling at 105°C . Error 10%.

Until now no other materials for thin film fabrication have been reported that have such a high polar orientation. In urea crystals a similar orientation^[2] is observed, but this material cannot easily be integrated in a waveguide due to limited processability.

So far we have shown that films of tetrapropoxy-tetranitrocalix[4]arene **1** in the *cone* configuration, with or without a polymeric matrix, can be oriented with very high orientation factors up to unity. In order to obtain materials with still higher nonlinear susceptibilities tetrapropoxy-tetrakis(ni-

trostilbene)calix[4]arene **2** was poled in a PMMA matrix under identical corona poling conditions as were applied for **1**. The frequency doubling coefficient d_{33} as a function of the weight percentage of **2** is given in Figure 1. A linear relation is found up to 60 wt-%. The $d_{33}(1064)$ values for tetrakis(nitrostilbene)calix[4]arene **2**, however, are only twice as large as the $d_{33}(1064)$ values for comparable films of tetranitrocalix[4]arene **1**, whereas the $\beta_z(1064)$ value of **2** is ten times larger than that of **1**. Apparently, the high orientation factors observed for **1** are not obtained for **2** under these conditions. For a neat film of **2** poled at 110°C , a surprisingly low d_{33} value of about 5 pm V^{-1} is found, corresponding to an orientation factor of only 0.1. However, this orientation factor could be drastically increased by performing the poling at higher temperatures. The d_{33} values for different poling temperatures of neat films of tetranitro-tetrapropoxycalix[4]arene **1**, tetrakis(nitrostilbene)-tetrapropoxycalix[4]arene **2**, and dihydroxy-tetrakis(nitrophenylazo)-dipropoxycalix[4]arene **3** are given in Figure 4.

Fig. 4. The frequency doubling coefficient d_{33} as a function of the poling temperature T_p of films of neat tetranitro-tetrapropoxycalix[4]arene **1** (●), tetrakis(nitrostilbene)-tetrapropoxycalix[4]arene **2** (○), and dihydroxy-tetrakis(nitrophenylazo)-dipropoxycalix[4]arene **3** (◊), prepared by corona poling. Error 10%.

As can be seen in Figure 4 the d_{33} values of both the nitrostilbenecalix[4]arene **2** and the nitrophenyl azocalix[4]arene **3** increase at higher poling temperatures, whereas the nitrocalix[4]arene **1** has already reached its maximum alignment around 160°C ($T_m(\mathbf{1}) > 310^\circ\text{C}$). The higher degrees of orientation at higher poling temperatures must be due to the larger mobility of the molecules in the solid films at these elevated temperatures. At temperatures of about 210°C the nitrophenylazocalix[4]arene **3** melts ($T_m = 212\text{--}214^\circ\text{C}$) and poling at higher temperatures will probably not increase the d_{33} value further, because the heat movement of the molecules in the melt will resist the poling orientation. The nitrostilbene **2** at this temperature is still 100°C below its decomposition temperature ($T_{\text{decomp}} = 310^\circ\text{C}$), allowing for possibly even higher orientation factors than the 0.6 deter-

mined for films prepared at 210 °C by corona poling. Most interestingly, the films can also be oriented by poling at room temperature, yielding already appreciable d_{33} values, especially for the nitrocalix[4]arene **1**.

The thermal stability of the d_{33} value of the films of nitrostilbene **2** at room temperature is comparable with that of the nitrocalix[4]arene **1**. Both show a decrease of about 35% of the initial d_{33} values in the first week and then remain stable at room temperature for more than a year. The nitrophenyl-azocalix[4]arene **3**, on the other hand, does not give films that are stable in time. After a small decrease during the first two days, the d_{33} values decrease sharply and become zero after one week. Possibly the intra-molecular flexibility of the phenolic moieties of the dihydroxy-tetrakis(nitrophenyl-azo)-dipropoxycalix[4]arene **3** (see above), can explain the fast degradation of the d_{33} value of this compound at room temperature.

In conclusion, high molecular β values are obtained for D- π -A substituted calix[4]arenes in the cone configuration, which combine a high density of NLO units with a high degree of orientation. Poling of neat films of these D- π -A substituted calix[4]arenes at elevated temperatures results in the maximum density of NLO active molecules having a very high or almost absolute polar alignment. The obtained macroscopic $\chi^{(2)}$ values of these films are, therefore, probably the highest values that can be obtained for these types of NLO units. At room temperature d_{33} values of the films of tetranitro-tetrapropoxycalix[4]arene **1** and tetrakis(nitrostilbene)-tetrapropoxycalix[4]arene **2** are stable, retaining 65% of the maximum value measured directly after poling. Moreover, films of neat tetranitro-tetrapropoxycalix[4]arene **1** are relatively stable even at 100 °C, retaining 20% of the maximum d_{33} value measured directly after poling.

Received: August 20, 1993

Final version: September 28, 1993

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Low Power Nonlinear Optical Response of C₆₀ and C₇₀ Fullerene Solutions**

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The study of the optical nonlinearity in fullerenes has received considerable attention because of their possible applications in nonlinear optical devices.^[1] Similar to organic conjugated polymers and inorganic semiconductors, fullerenes exhibit various types of third-order nonlinear effects, such as third-harmonic generation, two-photon absorption, optical limiting, self-focusing and self-defocusing.^[1] The lat-

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[**] Financial support for part of this work was provided by the European Office of the US Army and by EOLAS, the Irish Science and Technology Agency.