

Molecular and Macroscopic Second Order Nonlinear Optical Properties of Calix[4]arenes

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INTRODUCTION

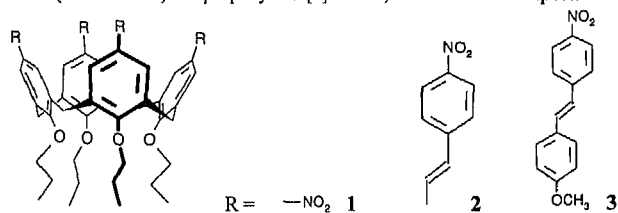
Organic molecules with π electron systems and unsymmetric charge distribution are promising for use in nonlinear optics (NLO), for example for frequency doubling of laser light and electro-optic switching.¹ In the molecules investigated so far the NLO-phore, that is the structural unit responsible for the nonlinear optical properties, consists of one single π -conjugated system with one or more electron-donating and -accepting substituents (so called D- π -A molecules). Extension of the conjugated system increases the nonlinear hyperpolarizability β , but unfortunately this is accompanied by a shift of the charge-transfer absorption band (CT band) to longer wavelength, thereby restricting the applicability in frequency doubling.²

Calix[4]arenes are cyclophanes that consist of four phenol moieties connected by methylene bridges.³ Selective functionalization of these phenols allows the combination of four D- π -A units within a single calix[4]arene molecule. The four D- π -A units can adopt different orientations with respect to each other, resulting in four different extreme conformations which do not interconvert when functionalized at the phenolic oxygen with substituents larger than ethyl. By proper choice of the reaction conditions the so called cone conformation, in which the four D- π -A units are oriented in the same direction, is obtained selectively. This cone conformation possesses the highest degree of unsymmetrical charge distribution which is required for second order NLO activity. In this work the molecular and macroscopic nonlinear optical properties of different calix[4]arenes will be discussed.

RESULTS AND DISCUSSION

Previous studies have shown that calix[4]arene **1**, with four *n*-propoxy substituents as the electron donor groups and four nitro substituents as the electron acceptor groups exhibit relatively large nonlinear optical effects (chart 1).⁴ Increase of the conjugation length of

Chart 1. Structures of calix[4]arenes substituted with *O*-*n*-propyl electron-donor and different acceptor groups: tetranitrotetrapropoxycalix[4]arene **1** and tetrakis(nitrostilbene)tetrapropoxycalix[4]arene **2**, and reference compound 3.



the π -system to a nitrostilbene unit (**2**) even strongly increases the hyperpolarizability value β , as obtained by electric field second harmonic generation (EFISH). The nonlinear and linear optical data obtained for **1** and **2**, and for reference compound **3** are summarized in table 1. Tetranitro-tetrapropoxycalix[4]arene **1** has a $\beta(0)$ value of 20×10^{-30} esu, about 50 % of the value of the reference compound 4-methoxy-4'-nitrostilbene **3** (MONS), which has a more extended π system. Tetrakis(nitrostilbene)-tetrapropoxycalix[4]arene **2** consists of four D- π -A units that are almost identical to MONS (**3**), so a four times higher β value would be expected for calix[4]arene **2**. However a $\beta(0)$ value of 127×10^{-30} esu, three times the β value of MONS, was found, because the four D- π -A units are not completely parallel oriented in the vase-like cone

Table 1. Dipole moments μ , charge transfer band maximum λ_{max} , hyperpolarizability β and resonance corrected hyperpolarizability $\beta(0)$ of calix[4]arenes **1** and **2**, and the reference compound **3**.^a

	μ (D)	$\mu \cdot \beta \times 10^{48}$ (esu) ^{b,c}	$\beta \times 10^{30}$ (esu) ^c	$\beta(0) \times 10^{30}$ (esu)	λ_{max} (nm)
1	13.8	414	30	20	291
2	15.3	4284	280	127	370
3	4.5	450	100	43	377

^a all measurements in CHCl_3 . ^b EFISH. ^c at 1064 nm.

conformation of the calix[4]arene. A remarkable advance of the combination of more D- π -A units in one molecule is the absence of the usually observed and undesired red shift of the charge transfer band upon increase of the β value.²

In order to study the macroscopic NLO properties thin films were prepared by spin coating of chloroform solutions of calix[4]arene-polymethacrylate (PMMA) mixtures on glass substrates.⁵ Subsequently, the required non-centrosymmetric arrangement of the NLO-phores was obtained by corona-poling with a strong DC electric field. The measured d_{33} nonlinear coefficients of calix[4]arenes **1** and **2** as a function of the weight percentage in PMMA are shown in figure 1. Clearly there is a

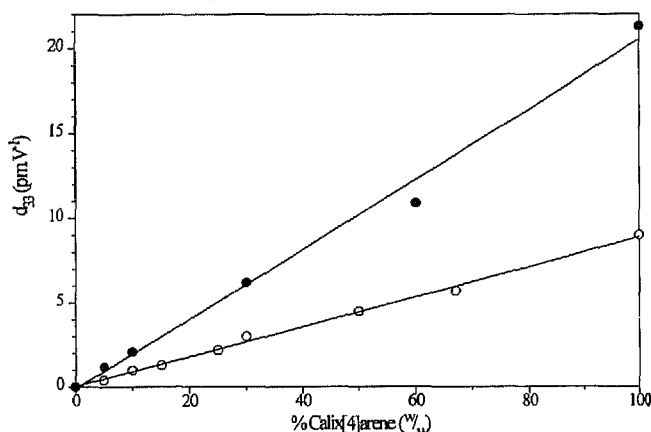


Figure 1. Frequency doubling coefficient d_{33} as function of the weight percentage of **1** (open symbols) and **2** (solid symbols), respectively.

linear relationship between loading and NLO activity, even at high chromophore loadings, whereas usually beyond chromophore loadings of 15 % (centrosymmetric) crystallization and thus loss of NLO activity occurs. Furthermore these calix[4]arene films have good optical

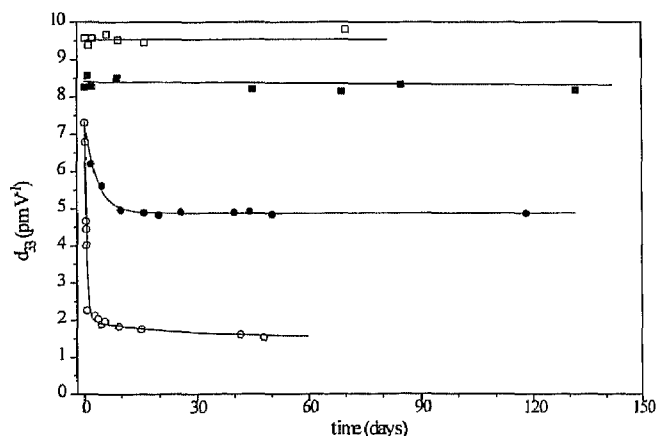


Figure 2. Decay of the frequency doubling coefficient d_{33} of films of neat **1** poled at 110 °C (circles) and 150 °C (squares) and stored at room temperature (solid symbols) and 80 °C (open symbols), respectively.

properties, i.e. they are transparent and exhibit a surprisingly high stability of the NLO activity in time, as is depicted in figure 2 for neat films of **1**, poled and stored under different circumstances. Poling at 110 °C results in films which exhibit a fast initial decay of 35 % within the first ten days after poling, when stored at room temperature, and of 85 % when stored at 100 °C. After this initial decay a long term stable value is reached. For films of **1** poled at 150 °C no decay is observed independent of storing temperature. This difference in NLO stability different poling temperatures is due to different phase compositions. In DSC measurements an irreversible thermal phase transition of compound **1** between 130 and 140 °C is observed (figure 3). The same transition is also detected for films poled at 110 °C, in contrast with films poled at 150 °C. The presence of this phase transition was confirmed by solid state NMR, X-ray spectroscopy and polarization microscopy. Probably a non-centrosymmetric but thermo-dynamically more stable packing is obtained upon heating.

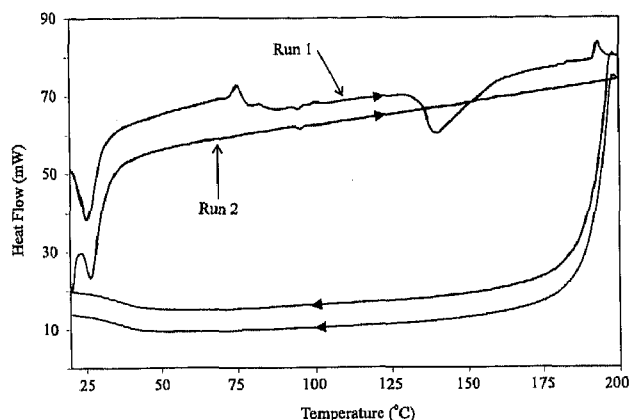


Figure 3. Differential scanning calorimetric runs of **1**.

In order to study the reason for the high stability of the aligned structure in films consisting of calix[4]arene based chromophores **1** in more detail, the structure of the *O*-alkyl donor groups was varied. NLO active films were prepared from tetranitrocalix[4]arene derivatives having longer and branched alkyl groups instead of the propyl substituents. In figure 4 the decay at 80 °C of these films directly after poling is shown.

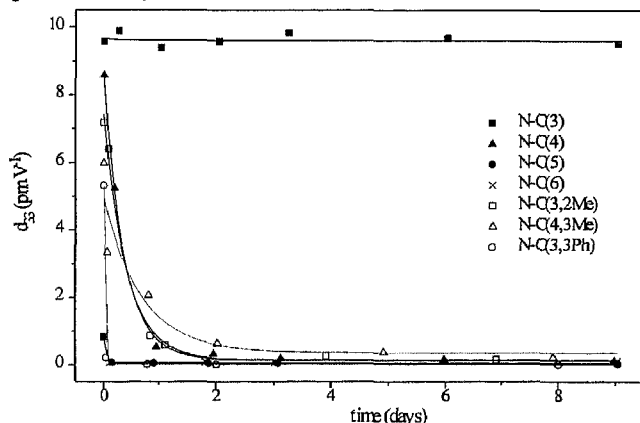


Figure 4. Decay of the frequency doubling coefficient d_{33} of films of tetranitrocalix[4]arene derivatives poled at 150 °C (or just below T_m if $T_m < 150$ °C) and stored at 80 °C. Sample codes: N = nitro acceptor, C = cone conformation, First number = length of alkyl chain, followed by branching position and substituent.

Only the derivative with the propyl substituent N-C(3) (compound **1**) remains stable. All the other films are NLO inactive after four days. No phase transition was observed in DSC measurements below 200 °C for the nitro-derivatives from which non-stable films were obtained.

Films of **2** exhibit high absolute d_{33} values: 25 to 40 pm/V, depending on the strength of the poling field. These films loose about 10 % of their initial NLO activity when stored over 70 days at room temperature and about 25 % when stored at 80 °C (figure 5). Apparently the nitrostilbene substituent is too large to obtain the same stable packing as is found in the aligned films of compound **1**. However, the absolute d_{33} values of films of **2** after 140 days are still more than two times higher than the values of films of **1**.

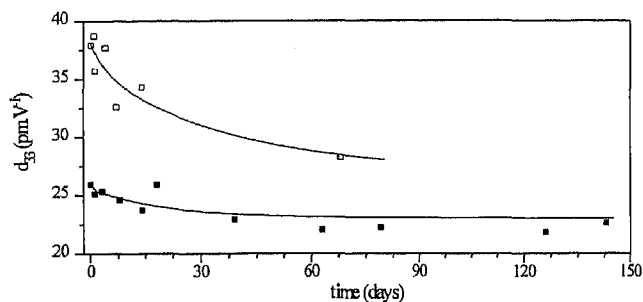


Figure 5. Decay of the frequency doubling coefficient d_{33} of films of neat **2** poled at 200 °C stored at room temperature (■) and 80 °C (□), respectively.

A different approach to obtain stable NLO films, namely covalent incorporation of the NLO active calix[4]arenes in a polymer chain, has also been explored. These results will be published elsewhere.⁶

CONCLUSION

The combination of four nonconjugated D- π -A dipoles in one molecule in calix[4]arenes results in molecules with interesting molecular NLO properties. These calix[4]arenes have high hyperpolarizability values, relatively low charge transfer band values and high dipole moments. We have shown that thin films can be made, consisting of mixtures of PMMA and calix[4]arenes, and even of calix[4]arenes only. The high dipole moments of these calix[4]arenes results in a high degree of orientation in the films upon E-field poling. These films are highly transparent and exhibit high and stable frequency doubling coefficients d_{33} . Films of **1** poled above the phase transition of 130 °C, as observed by DSC, X-ray spectroscopy and polarization microscopy, show no decay of NLO activity in time, whereas films of derivatives of **1**, which do not exhibit such a phase transition, loose their activity within four days. These observations indicate that the origin of this high stability of certain neat calix[4]arene films is a non-centrosymmetric and thermodynamically stable packing.

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