High Hyperpolarizabilities of Donor-π-Acceptor-Functionalized Calix[4]arene Derivatives by Pre-organization of Chromophores

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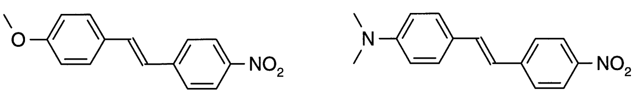
A systematic investigation of the *concept of pre-organization* of nonlinear optical (NLO) active chromophoric groups in calix[4]arene derivatives and the influence on the absolute second-order nonlinear optical coefficients is reported. Several calix[4]arenes were synthesized by modification of the electron-withdrawing groups at the upper rim of the aromatic and extension of the conjugated π system of the pre-organized chromophoric groups. Electrical field induced second harmonic generation (EFISH) experiments showed high μβ(0) values up to $1165 \cdot 10^{-48}$ esu. Compared with the corresponding reference compounds, enhancements of the μβ(0) values varying up to 2.5 times per chromophore were observed which proves the benefit of pre-organization of NLO-active units in a multi-chromophoric system. Another important advantage is that the increase in NLO activity observed for these systems is not accompanied with a shift of the absorption band to longer wavelengths exceeding 20 nm. This makes these calix[4]arene derivatives promising building blocks for the development of stable, NLO-active materials that are suitable for frequency doubling.

Introduction

Structures that are highly polarizable in a non-symmetric fashion are promising for use in second-order nonlinear optical (NLO) applications, such as electro-optic modulators, frequency doubling and holographic memories.[1] An important class of compounds that exhibits non-symmetric polarizability are organic molecules that contain electron-donating and -accepting groups connected via a conjugated π system.[2] The efficacy of the non-symmetric polarization is expressed as the second-order polarizability or hyperpolarizability term β. Typical examples of π-conjugated organic donor-acceptor chromophores are 4-methoxy-4′-nitrostilbene (MONS, **1**) and 4-dimethylamino-4′-nitrostilbene (DANS, **2**) as depicted in Figure 1, which have μβ(0) values of $190 \cdot 10^{-48}$ and $450 \cdot 10^{-48}$ esu, respectively.[3]

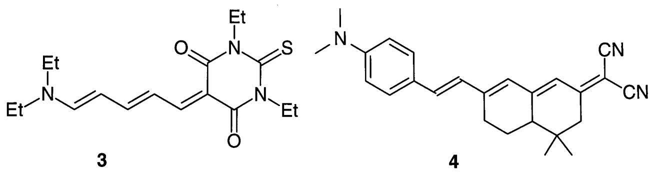
Figure 1. Structures of 4-methoxy-4′-nitrostilbene (MONS, **1**) and 4-dimethylamino-4′-nitrostilbene (DANS, **2**)



1 **2**

Generally, the hyperpolarizability of a molecule increases with increasing donor and acceptor strength and with increasing length of the conjugated π system. For most organic donor-π-acceptor systems the two-level model for β is an adequate approximation of the full perturbation theory because the charge-transfer exited state dominates the perturbation sum.[4] With this two-level model Marder et al.[5] have shown that certain combinations of electron-donating and -accepting groups with π-conjugated systems can give large nonlinear optical responses, as is the case for the barbituric acid derivative **3**. Unfortunately, highly polarizable, polyenic systems have the disadvantage of having an intense absorption band at high wavelength and mostly a poor chemical stability. A way to improve the low thermal and/or chemical stability is the fixation of a part of the polyenic π system within a cyclic structure, as in compound **4** (Figure 2) studied by Yoon et al.[6] Furthermore, π bonds of heterocycles of low aromaticity, like thiophene, have been incorporated as part of the π-conjugated NLO system.[7]

Figure 2. Non-bridged (**3**) and bridged (**4**) polyenic chromophores[6]



3 **4**

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A different concept in the design of molecules with high nonlinear optical activities is the pre-organization of several chromophores in one single macromolecule.[8] This concept takes advantage of the fact that the nonlinear coefficient of a molecule is proportional to $\mu\beta$, the product of the molecular dipole moment μ and the second-order hyperpolarizability β. For a rigid multi-chromophoric system the dipole moment (μ_{multi}) may be approximated by the vector summation of the dipole moments (μ_{mono}) of the individual chromophores when these are the principal contributors to the multi-chromophoric system (Equation 1).

$$\mu_{\text{multi}} = N \langle \cos\theta \rangle \mu_{\text{mono}} \qquad (1)$$

In this Equation N is the number of chromophoric groups per multi-chromophoric molecule and θ the average angle of the chromophoric groups with the dipole axis of the multi-chromophoric molecule. Similarly, the hyperpolarizability of the rigid multi-chromophoric system in the direction of the dipole axis (β_{multi}) can be written as a summation of the contributions of all NLO activities (β_{mono}) of the single chromophoric units, involving the orientation factor $\langle \cos^3\theta \rangle$ for the averaged degree of alignment of these chromophores along the dipole axis (Equation 2).[1][2]

$$\beta_{\text{multi}} = N \langle \cos^3\theta \rangle \beta_{\text{mono}} \qquad (2)$$

Using Equations 1 and 2, the product $(\mu\beta)_{\text{multi}}$ of a multi-chromophoric system is given by Equation 3.[9]

$$(\mu\beta)_{\text{multi}} = N^2 \langle \cos^4\theta \rangle (\mu\beta)_{\text{mono}} \qquad (3)$$

From Equation 3 the enhancement of nonlinear optical coefficient $(\mu\beta)_{\text{multi}}$ of a multi-chromophoric system relative to the sum of all individual *chromophoric units* can be deduced. Obviously, the nonlinear optical coefficient of a multi(N)-chromophoric system $(\mu\beta)_{\text{multi}}$ is larger than that of N individual chromophores $N(\mu\beta)_{\text{mono}}$, if $N\cdot\langle\cos^4\theta\rangle$ is larger than unity. For a multi-chromophoric system consisting of four chromophoric units this means that the averaged angle of alignment of these chromophores along the dipole axis must be lower than 45° [$N\cdot\cos^4(45°) > 1$]. An important further advantage of the concept of pre-organization of NLO-active chromophores in one molecular system is that increased $\mu\beta$ values are usually obtained without an undesired shift of the absorption band of the molecule to longer wavelengths. The $\mu\beta$ value of tetranitrotetrapropoxycalix[4]arene (**9a**, Scheme 1) shows an enhancement per chromophoric unit of 1.7, compared to the single chromophoric reference compound **11a**. This illustrates the advantage of pre-organization of chromophores in the calix[4]arene structure.[10] It should be noted that steric and electronic effects between the chromophoric units are not taken into account in Equation 3. For example, the electron-donating effect of the propoxy groups in the calix[4]arene can be lower than that of the propoxy group in the reference compound, due to steric hindrance which forces the propoxy groups out of perfect conjugation.[11] In addition, electronic mixing of the π-conjugated systems of the chromophoric groups can result in up to 15% decrease in NLO activity.[12]

Recently, a few other examples of pre-organized multi-chromophoric polymers were reported. Kauranen et al.[9] used the helical structure of poly(isocyanide) polymers to organize NLO-active chromophoric side chains in a non-centrosymmetric way. This results in a "Christmas tree"-like structure with a high dipole moment along the polymer backbone. The consequence of this organization is a 1.5-fold enhancement of the $\mu\beta(0)$ value per chromophore. Verbiest et al.[13] described a similar system based on organization of NLO-active chromophores around the polypeptide backbone of a probably helical poly(methylglutamate) structure, resulting in a high $\mu\beta(0)$ value of $10.000\cdot10^{-48}$ esu per chromophore. This value corresponds to a 35-fold enhancement per single chromophore. The difference in enhancement factor in the two polymer systems can be explained by a higher degree of alignment in the latter case. Both pre-organized multi-chromophoric systems show the above-mentioned advantage that the increased nonlinear optical activity is not accompanied with an unfavorable shift of absorption to longer wavelengths. However, the organization of these highly NLO-active macromolecules at the NLO *material level* was not reported.

The use of calix[4]arenes can offer good prospects to obtain molecules with a high degree of pre-organization and good NLO activity. Moreover, they are easily to align in materials by *E*-field poling due to their limited size.[14] Calix[4]arenes are vase-shaped cyclophanes consisting of four phenol moieties connected by methylene bridges.[15] By substitution of the phenolic oxygen groups with propyl substituents and functionalization of the upper rim with electron-accepting groups, we have previously reported the synthesis of a number of calix[4]arene derivatives with promising NLO activity.[16] In this paper we have extended this work and have systematically investigated the *concept of pre-organization* of NLO-active chromophores in calix[4]arene derivatives, and studied the influence of pre-organization on the absolute second-order nonlinear optical coefficients. Calix[4]arenes with different electron-accepting groups and with extended conjugated π systems have been synthesized, and their nonlinear activities have been analyzed. Moreover, the effect of hydrogen-bonding hydroxy groups as electron-donating groups in calix[4]arenes on the nonlinear optical activity was studied.

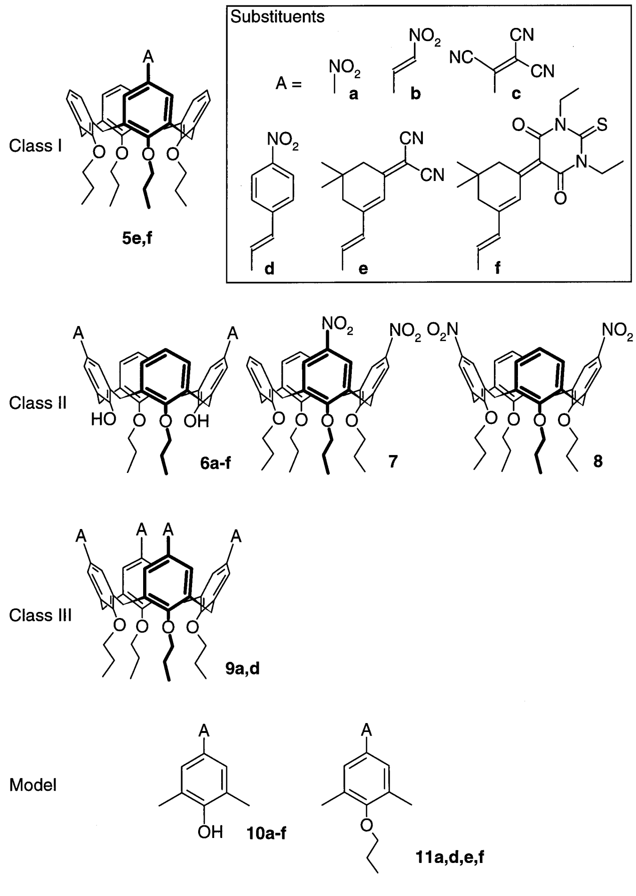
Design and Synthesis

In principle, the variation of the chromophoric units in calix[4]arenes can be achieved by variation of the electron-donating and electron-accepting groups at the four aromatic moieties. However, although calix[4]arenes with sulfur-[17] and nitrogen-[18]containing electron-donating groups have been reported, either synthetic[19] or steric reasons[20][21] prevent the systematic variation of these groups in calix[4]arene structures. Therefore, the effects of pre-organization of chromophores in calix[4]arenes and the influence on the hyperpolarizability of the calix[4]arene system has been studied by the systematic variation of the *electron-*

accepting group, the conjugated π system, and by comparison of the resulting hyperpolarizabilities with those of the mono-chromophoric reference compounds.

The structures of the chromophoric calix[4]arene derivatives that were investigated, and their corresponding reference compounds are depicted in Scheme 1. *Three classes* of upper-rim-substituted calix[4]arenes can be distinguished: Class I are the monosubstituted calix[4]arenes, Class II are the disubstituted, and Class III are the tetrasubstituted calix[4]arene derivatives. Six different acceptor groups (**a**−**f**) have been introduced to the upper rim of the calix[4]arenes, but not all possible combinations could be or were actually synthesized. Besides the nitro substituent (**a**), also substituents with longer conjugation length (**b**−**f**) and with stronger electron-withdrawing properties (**c**, **e**, and **f**) were selected. In the acceptor substituents **e** and **f** the chemical stability of the polyenic π system is enhanced by the presence of alkyl bridges, like in compound **4** (Figure 2).[6] Furthermore, the thiobarbituric acid group of acceptor substituent **f** has the advantage of an increased aromatic character in the charge-separated resonance structure. In this way the loss in aromaticity of the phenolic units of the calix[4]arene upon charge separation is compensated, which facilitates polarization of the D-π-A system and consequently may result in higher NLO activity.[22]

Scheme 1



Class I: The mono-functionalized derivatives **5e** and **5f** and the corresponding reference compounds **11e,f** (Scheme 1) were synthesized by a Knoevenagel condensation according to a strategy developed by Lemke[23] (Scheme 2). Condensation of monoformyltetrapropoxycalix[4]arene (**12**) and 3,5-dimethyl-4-*n*-propoxybenzaldehyde (**14**) with **15** and **16** gave the tetrapropoxycalix[4]arenes **5e,f** and the reference compounds **11e,f**, respectively.

Class II: The disubstituted calix[4]arene derivatives **6b**, **6e**, and **6f** (Scheme 1) and their reference compounds **10b**, **10e**, and **10f** were prepared analogously to the monosubstituted derivatives (Scheme 2), starting from 1,3-diformyl-2,4-dipropoxycalix[4]arene[24] (**18**) and the commercially available 3,5-dimethyl-4-hydroxybenzaldehyde (**13**).

5,17-Dinitro-25,27-dipropoxycalix[4]arene (**6a**) was synthesized by selective nitration of 25,27-dipropoxycalix[4]arene (**17**) using $NaNO_2$/HCl in dichloromethane in the presence of a catalytic amount of $La(NO_2)_3$ (Scheme 3).[25] Dinitrocalix[4]arenes **7** and **8** (Scheme 1) were synthesized according to a literature procedure.[16a][26] The reference compound **11a** (Scheme 1) was synthesized from the commercially available 2,6-dimethyl-4-nitrophenol (**10a**) by alkylation with *n*-propyl iodide in refluxing CH_3CN in the presence of K_2CO_3 as a base.

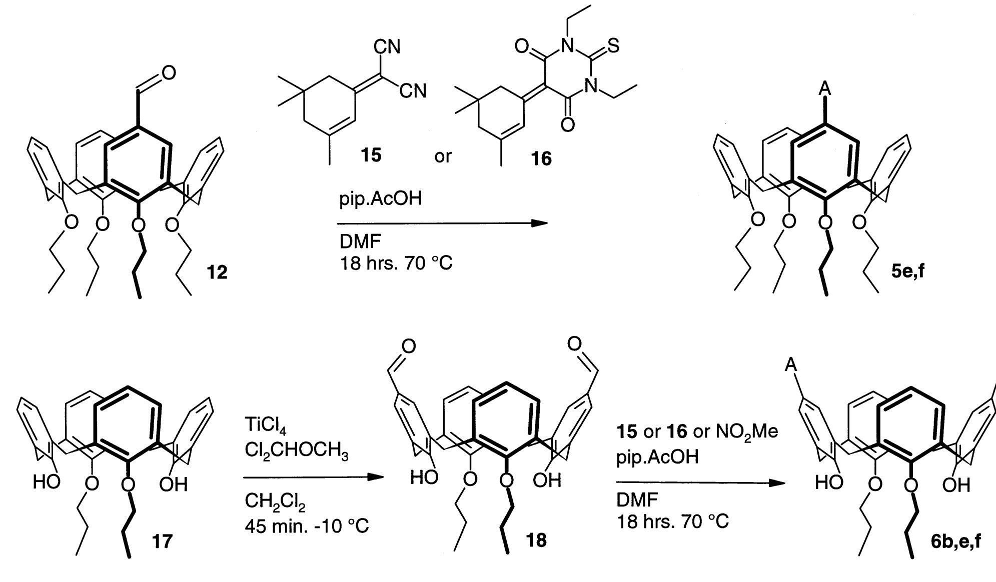
The 5,17-di(tricyanoethylene)-25,27-dipropoxycalix[4]arene (**6c**) was prepared by reaction of 25,27-dipropoxycalix-[4]arene[27] (**17**) and tetracyanoethylene in pyridine for 15 hours (Scheme 3). By using similar conditions, the corresponding reference 2,6-dimethyl-4-(1,1,2-tricyanoethenyl)-phenol (**10c**) was synthesized starting from 2,6-dimethylphenol.

Bis(*p*-nitrostilbene)calix[4]arene derivative **6d** and the corresponding reference compound **10d** (Scheme 1) were synthesized by condensation of diformylcalix[4]arene **18** and 3,5-dimethyl-4-hydroxybenzaldehyde, respectively, with *p*-nitrophenylacetic acid in DMF using piperidine as the base.

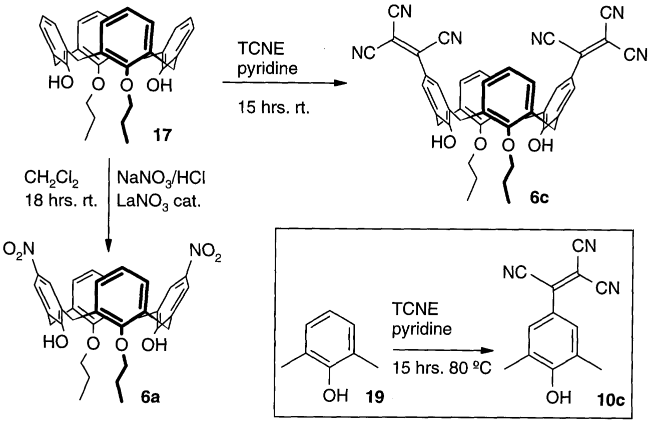
As the 1,3-dipropoxycalix[4]arene derivatives **6a-f** have still two unsubstituted phenol units, three conformations (cone, partial cone, 1,3-alternate, but not the 1,2-alternate conformation) are in principle possible by rotation of the hydroxy groups through the annulus.[28] However, only the cone conformation is observed in a single-crystal X-ray structure of 1,3-dinitro-2,4-dipropoxycalix[4]arene (**6a**) (Figure 3), similar to the X-ray structure of 1,3-diethoxycalix[4]arene reported by Bugge et al.[29] Apparently, strong hydrogen-bond interactions of the two hydroxy groups with the neighboring oxygen atoms of the alkoxy groups strongly favour the cone conformation in these compounds.

The presence of intramolecular hydrogen bonds in solution was proven by infrared spectroscopy. The 1,3-dipropoxycalix[4]arene derivatives **6a**−**f** exhibit a strong absorption in the range 3157−3290 cm^{-1}, which is typical for a strong OH hydrogen bond.[30] In contrast, the corresponding reference compounds **10a**−**f** show an absorption in the range of 3585−3604 cm^{-1}, which is typical for a free hydroxy group.[30] Further evidence for the presence of intramolecular hydrogen bonds in solution was obtained from ^{1}H-NMR spectra in which all compounds exhibit a sharp resonance for the OH protons as well as a distinct AB pat-

Scheme 2. Synthetic route to mono- (**5e**,**f**) or 1,3-di- (**6b**,**e**,**f**) -functionalized calix[4]arene chromophores by condensation reactions



Scheme 3. Synthesis of 1,3-dinitro- and 1,3-di(tricyanoethylene)-2,4-dipropoxycalix[4]arene, **6a** and **6c**, respectively, and of reference compound **10c**



tern for the protons of the methylene bridges in the calix[4]arene structure.

Class III: Tetranitrocalix[4]arene **9a** was obtained starting from tetra-*tert*-butylcalix[4]arene **20** by a modified *ipso*-nitration[31] procedure, using a mixture of 100% HNO_3 and trifluoroacetic acid (TFA) in dichloromethane (Scheme 4). The use of TFA results in shorter reaction times, less decomposition, shorter purification procedures and higher yields[32] than the procedures described earlier using glacial acetic acid[31a] or 65% HNO_3 and H_2SO_4[31b]. Tetra(nitrostilbene)calix[4]arene **9d** (Scheme 1) was synthesized according to a literature procedure.[33] However, functionalization of the calix[4]arenes with four conjugated groups **e** or **f** by the same condensation reaction starting from tetraformyltetrapropoxycalix[4]arene was not successful, probably due to steric hindrance between the polyene acceptor substituents.[33]

Scheme 4. Synthesis of tetranitrocalix[4]arene (**9a**) by *ipso*-nitration

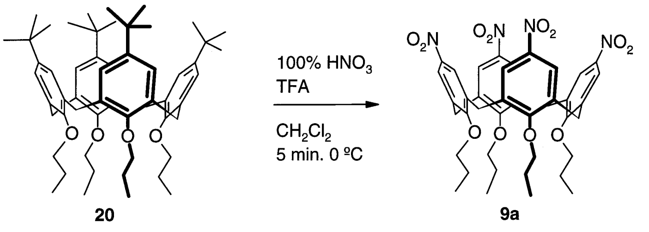
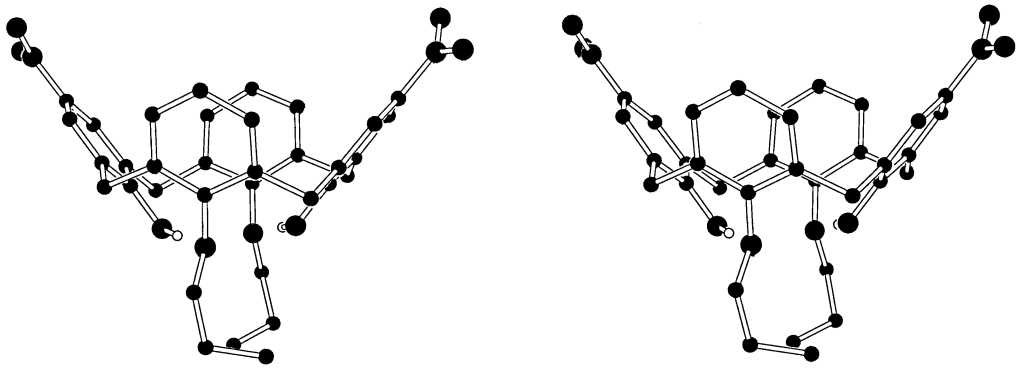


Figure 3. X-ray structure of 1,3-dinitro-2,4-dipropoxycalix[4]arene (**6a**; stereo view) showing the presence of intramolecular hydrogen bonds



Nonlinear Optical Properties

The hyperpolarizabilities of the calix[4]arene derivatives and their reference compounds were determined by electric field induced second harmonic generation (EFISH) with a fundamental wavelength of 1906 nm.[34] Table 1 gives the dispersion-corrected[35] μβ values obtained from these EFISH measurements, together with the absorption band maxima (λ_{max}). The results will be discussed for the three classes of the calix[4]arene derivatives and their reference compounds below.

Class I: The *mono*substituted tetrapropoxycalix[4]arenes **5e** and **5f**, having the well-polarizable π-acceptor groups **e** and **f**, show μβ(0) values of 299 and $330 \cdot 10^{-48}$ esu, respectively. This illustrates the favourable effect of extension of the conjugated electron-accepting group as these values are already significantly higher than that of the *tetra*nitro-substituted analog **9a** which has a μβ(0) value of $131 \cdot 10^{-48}$ esu. Furthermore, comparison with the μβ(0) of the reference compounds **11e** and **11f** shows that the incorporation of the chromophoric unit in the tetrapropoxycalix[4]arene as in **5e** and **5f**, results in a remarkable *twofold* increase of the μβ(0) value. Besides the higher dipole moment of the latter compounds, the close proximity of the three other propoxy groups in the calix[4]arene compounds may also contribute to an increased β by extra stabilization of the positive polarization of the propoxy group in the chromophoric unit. The red-shift of the absorbtion band of about 20 nm points indeed in the direction of an improved polarizability.

Class II: The elongation of the π-conjugated system in the disubstituted nitrocalix[4]arene derivatives **6a**, **6b**, and **6d** increases the μβ(0) values from 51 to 144 and $464 \cdot 10^{-48}$ esu, respectively. The tricyanoethylene derivative **6c** has approximately the same μβ value as the nitrovinyl derivative **6b** which has about the same conjugation length. Comparison of the μβ(0) values of nitrostilbene derivative **6d** ($464 \cdot 10^{-48}$ esu), dicyanovinyl derivative **6e** ($845 \cdot 10^{-48}$ esu), and diethylthiobarbituric acid derivative **6f** ($1165 \cdot 10^{-48}$ esu) having an approximately equally long conjugated π system shows that the incorporation of a less aromatic, polyenic π system in combination with stronger electron-accepting groups, is advantageous for the NLO activity.[36] Such structural modifications increase the polarizability which is also expressed in the red shift of the absorption bands from 400 (**6d**) to 516 nm (**6f**).

For the 1,3-difunctionalized calix[4]arenes studied (**6a−f**) the μβ(0) values are 1.6 to 3.7 times higher than those of their reference compounds **10a−f** (Table 1). This increment is higher than the factor of 1.4 that can be calculated from Equation 3, using θ = 39° for the angle between the chromophores and the dipole moment of the whole molecule, obtained from the X-ray structure of **6a** (Figure 3).[37] The predicted *enhancement per chromophoric unit* would be only 0.7, thus a decrease in activity, in these disubstituted systems. Experimentally, however, enhancements per chromophore of 0.8 up to 1.9 are observed (Table 1). So combining two molecules **10b** and **10c** in calix[4]arenes **6b** and **6c**, respectively, is unfavourable for the net second-order NLO activity. The enhancement per chromophore for the other disubstituted calix[4]arenes is higher than unity. In solution the averaged angle θ of the two chromophoric groups with the molecular dipole axis probably will be smaller due to the mobility of the aromatic units in the calix[4]arene. Moreover, in the calix[4]arenes **6a−f** the hydroxy groups are involved in intramolecular hydrogen-bond donation which results in an increasing electron-donating ability of these groups. This increase in polarizability is also reflected in a red-shift of the absorbtion band of 14 to 26 nm compared to the corresponding reference compounds, which is mainly caused by the intramolecular hydrogen bond. In addition, the proximity of the neighboring propoxy groups in the calix[4]arene may contribute to the stabilization of the partly positively charged polarization state of the phenolic donor groups, as was already mentioned for **5e** and **5f**. The latter effect may also account for the relatively high μβ(0) values found for the 1,2- and 1,3-substituted dinitrotetrapropoxycalix[4]arenes **7** and **8**. The almost equal μβ(0) values of these compounds indicate that the relative position of the D-π-A units in the calix[4]arene moiety is not of much influence for the NLO activity.

Table 1. Resonance-corrected μβ(0) values, ν_{OH} and λ_{max} of calix[4]arene derivatives **5e**, **f**, **6a−f**, **7**, **8**, **9a**,**d**, and the reference compounds **10a−f** and **11a**,**d−f**[a]

	compound		μβ(0) [10^{-48} esu][b]		enhancement per chromophore	λ_{max} [nm]	
	calix	(*model*)	*calix*	(*model*)		*calix*	(*model*)
class I	**5e**	(**11e**)	299	(153)	2.0	434	(414)
(1 chrom.)	**5f**	(**11f**)	330	(176)	1.9	498	(476)
class II	**6a**	(**10a**)	51	(15)	1.7	332	(318)
(2 chrom.)	**6b**	(**10b**)	144	(79)	0.9	380	(362)
	6c	(**10c**)	183	(114)	0.8	440	(420)
	6d	(**10d**)	464	(125)	1.9	400	(386)
	6e	(**10e**)	845	(301)	1.4	448	(432)
	6f	(**10f**)	1165	(375)	1.6	516	(494)
	7	(**11a**)	46	(19)	1.2	307	(296)
	8	(**11a**)	45	(19)	1.2	302	(296)
class III	**9a**	(**11a**)	131	(19)	1.7	291	(296)
(4 chrom.)	**9d**	(**11d**)	862	(85)	2.5	370	(372)

[a]All measurements in $CHCl_3$ at room temp. − [b]EFISH with a fundamental wavelength of 1906 nm; data are corrected for dispersion with the two-level model.[35]

Class III: Comparison of the tetranitrotetrapropoxycalix[4]arene **9a** with the tetrakis(*p*-nitrostilbene)tetrapropoxycalix[4]arene[38] **9d** shows that the μβ(0) value increases upon elongation of the π system from $131 \cdot 10^{-48}$ esu to $862 \cdot 10^{-48}$ esu. This increase (6.5 ×) is somewhat lower than that observed for the disubstituted calix[4]arene derivatives **6a** and **6d** (9.2 ×). According to Equation 3, when four chromophores are combined within one calix[4]arene, the average angle θ between the dipolar axis of the chromophores and the dipole axis of the whole molecule should be less than 45° in order to obtain a net NLO enhancement per chromophore. Both in solution and in the solid state tetraalkylated calix[4]arenes adopt a pinched-*cone* conformation in which the angle of one pair of opposite chromophores with the molecular dipole axis is close to 0°, and the angle of the other pair of chromophores with this dipole axis is 58°.[15] For the tetrasubstituted tetrapropoxycalix[4]arenes, magnifications by a factor 2.3 per chromophore can be calculated based on an average chromophore-dipole angle θ of 29°.[16][39] Experimentally, enhancements per chromophore of 1.6 and 2.5 are found for the tetranitro- (**9a**) and tetrakis(nitrostilbene)calix[4]arene **9d**, respectively, compared to the mono-chromophoric reference compounds **11a** and **11b**. Moreover, the combination of four chromophores in a tetrapropoxycalix[4]arene is accompanied by a small, favorable blue-shift of the charge-transfer band. This clearly shows the advantage of pre-organization of chromophores in a multi-chromophoric system.

Conclusions

Calix[4]arenes with high μβ(0) values up to $1165 \cdot 10^{-48}$ esu were obtained by modification of the electron-withdrawing group and extension of the conjugated π system of pre-organized chromophoric groups. The advantage of pre-organization of NLO-active moieties into a rigid multi-chromophoric calix[4]arene system was clearly shown for the calix[4]arene derivatives **6a**, **d–f**, and **9a**,**d**. Compared with the corresponding reference compounds, enhancements per chromophoric unit of the μβ(0) values varying up to 2.5 times per chromophore were observed. An important advantage of the use of multi-chromophoric calix[4]arenes is that the resulting increase in NLO-activity is not accompanied with a large shift (> 20 nm) of the absorption band to longer wavelengths. Tetrasubstituted calix[4]arenes even show a favorable blue-shift. This makes NLO-active calix[4]arenes promising building blocks for the development of stable, NLO-active materials. An example of such a stable NLO material based on tetranitrotetrapropoxycalix[4]arene **9a** which is suitable for frequency doubling has been reported by us recently.[16b][16c][16d]

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Experimental Section

X-ray Crystallography Study: Data were collected with an Enraf-Nonius CAD4 diffractometer, ω-2θ scan mode, without absorption correction. Every 200 reflections 3 standard reflections were monitored. The structure was solved by direct methods using SIR92[40] in the Enraf-Nonius software package[41] and were refined by full-matrix least-squares methods. Atomic scattering factors were taken from ref.[42]. The weighting scheme used was $w = 4\, F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2(I) + (pF_o^2)^2$ with $p = 0.04$. The single crystal of **6a** (colorless prism, 0.3 × 0.2 × 0.2 mm) was grown from CH_2Cl_2/MeOH. The asymmetric unit consists of one molecule. All atoms were treated anisotropically. Hydrogen atoms were also included and refined isotropically. One propoxy tail suffered from disorder: the end methyl group was split up (occupancy of 0.7 vs. 0.3) and no hydrogen atoms were attached to them. Further experimental details are given in Table 2 and are available at the Cambridge Crystallographic Data Centre.[43]

Table 2. Single-crystal X-ray diffraction data of **6a**

crystal data	monoclinic	$P2_1/n$
	$a = 12.217(6)$ Å	$V = 2956(1)$
	$b = 13.467(6)$ Å	$Z = 4$
	$c = 18.543(8)$ Å	$D_x = 1.35\ g \cdot cm^{-3}$
	$\beta = 104.42(3)°$	$\mu = 0.090\ cm^{-1}$
data collection	Mo-K_α ($\lambda = 0.71073$ Å)	θ/2θ scan; $\theta = 2.5-30°$
	$T = 130$ K	9170 measured reflections
	$h = -17, 16$	8578 independent reflections
	$k = 0, 18$	4562 observed refl. [$I > 3\ \sigma(I)$]
	$l = 0, 26$	$R_{int} = 4.1\%$
refinement	$R = 6.6\%$	522 parameters
	$R_w = 9.7\%$	$(\Delta/\sigma)_{max} = 0.70$
	$S = 2.84$	$\Delta\rho_{max} = 0.57$ e/Å^3

EFISH: These measurements were performed as described in ref.[34] with a fundamental wavelength of 1906 nm.[35] Typical concentration range: 0.1–2 mmol·l^{-1}.

General: Melting points: Reichert melting point apparatus. – ^{1}H NMR and ^{13}C NMR: Bruker AC 250; $CDCl_3$ as the solvent (unless stated otherwise), residual solvent protons or Me_4Si as internal standard. – MS FAB: Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. – UV/Vis: Hewlett Packard 8452A diode array spectrophotometer (Accuracy: +/– 2 nm). – Elemental analyses: Carlo-Erba Strumentazione 1106. – IR: Jasco A-100 infrared spectrophotometer.

Synthesis: Hexane (referring to petroleum ether with boiling range 60–80°C) and CH_2Cl_2 were freshly distilled from K_2CO_3. DMF was dried over molecular sieves (4 Å) for at least 3 d. Other reagents were reagent grade and were used without further purification. Flash column chromatography was performed with silica 60 (0.040–0.063 mm, 230–400 mesh) from E. Merck. All reactions were carried out in argon. All commercially available compounds were purchased from Aldrich or ACROS. The yields of the compounds that have been synthesized were not optimized. In the assignment of the NMR spectra "iph" denotes the isophorone ring. The presence of residual solvent in analytical samples was always proven by ^{1}H NMR.

5,11-Dinitro-25,26,27,28-tetrapropoxycalix[4]arene (**7**), 5,17-dinitro-25,26,27,28-tetrapropoxycalix[4]arene[16a][26] (**8**), 5,11,17,23-tetrakis[(*E*)-1-(4-nitrophenyl)ethenyl]-25,26,27,28-tetrapropoxycalix[4]arene[33] (**9d**), 5-formyl-25,26,27,28-tetra-propoxycalix[4]arene[33] (**12**), 25,27-dipropoxycalix[4]arene[27] (**17**), and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene[44] (**18**) were synthesized according to literature procedures.

General Procedure for the Knoevenagel Condensations of the Aldehydes **12**, **13**, **14**, *and* **18** *with* **15**[23], **16**[45] *and Nitromethane. − Formation of* **5e**,**f**; **6b**,**e−f**; **10b**,**e**,**f**, *and* **11e**,**f**: A solution of 1 equivalent of the aldehyde, 1.2 or 3 equivalents of **15**, **16** or nitromethane and 0.5 equivalent of piperidinium acetate in DMF (15 ml per gram aldehyde) was stirred at 80°C for 1−4 h. The reaction mixture was quenched by adding HOAc and CH_2Cl_2 was added. The organic layer was washed with water (3 ×), sat. NH_4Cl solution (2 ×), and brine (1 ×), and dried with $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified by column chromatography (Hex/CH_2Cl_2 1:1, unless stated otherwise).

Calix[4]arene **5e**: The residue was purified by column chromatography with EtOAc/Hex 5:95 as the eluent. Red crystals, yield 39%, mp 221−223°C (EtOH). − ^1H NMR: δ = 6.8−6.3 (m, 14 H, HC=, and ArH), 4.4−4.5, 3.1−3.2 (2 m, 8 H, $ArCH_2$), 3.8 (m, 8 H, OCH_2), 2.59, 2.39 (2 s, 4 H, CH_2 iph), 1.9 (m, 8 H, CH_2CH_3), 1.0 (m, 12 H, CH_2CH_3), 1.07 (s, 6 H, CH_3 iph). − ^{13}C NMR: δ = 169.37 [$C{=}C(CN)_2$], 158.90, 156.66, 156.53, 154.71 (ArCOPr, $R_2CCH{=}CH$), 138.21, 129.48, 126.78 (CH=), 136.06, 135.47, 135.20, 134.61 (ArCCH=, $ArCCH_2$), 128.53, 128.10, 127.97, 127.90, 122.43, 122.10, 121.72 (ArCH), 113.84, 113.12 (CN), 77.28, 76.87, 76.73, 76.69 [$C(CN)_2$, OCH_2], 43.05, 39.27 (CH_2 iph), 32.02 [$C(CH_3)_2$], 31.03 (CH_2Ar), 28.01 (CH_3 iph), 23.34, 23.28, 23.24 (CH_2CH_3), 10.38, 10.30 (CH_2CH_3). − FAB MS; *m/z*: 789.4 $[M+H]^+$ (calcd. 789.5). − UV/Vis ($CHCl_3$): λ_{max} = 434 nm; ε = $42\cdot10^3\ l\cdot mol^{-1}\cdot cm^{-1}$. − $C_{53}H_{60}N_2O_4\cdot0.33\ H_2O$: calcd. C 80.07, H 7.69, N 3.52; found C 79.92, H 7.64, N 3.54.

Calix[4]arene **5f**: The residue was purified by column chromatography with Hex/CH_2Cl_2 2:1 as the eluent. Purple powder, yield 22%, mp 112−120°C (Hex/CH_2Cl_2). − ^1H NMR: δ = 8.37 (s, 1 H, HC=C iph), 6.5−6.2 (m, 11 H, HC=, and ArH), 6.98 (s, 2 H, ArH), 4.6−4.4 (m, 8 H, CH_2N and $ArCH_2$), 3.1−3.2 (m, 4 H, $ArCH_2$), 3.9 (m, 8 H, OCH_2), 3.11, 2.43 (2 s, 4 H, CH_2 iph), 2.0−1.8 (m, 8 H, CH_2CH_3), 1.39−1.22 (m, 6 H, CH_3CH_2N), 1.1−0.9 (m, 18 H, CH_3 iph, and CH_2CH_3). − ^{13}C NMR: δ = 178.08, 171.04, 161.17, 160.91, 158.53, 155.79, 151.80, 112.10 (R_2C=, ArCO, C=O, C=S), 137.40, 129.24, 128.53, 128.31, 127.82, 125.51 (ArCH, CH=), 132.80, 128.82, 127.40 (ArCCH=, $ArCCH_2$), 78.52 (OCH_2), 44.79, 43.72, 43.61, 38.95 (CH_2N, CH_2 iph), 31.87 [$C(CH_3)_2$], 31.50 (CH_2Ar), 28.62 (CH_3 iph), 23.50 (CH_2CH_3), 12.61 (CH_3CH_2N), 10.92 (CH_2CH_3). − FAB MS; *m/z*: 922.4 $[M^+]$ (calcd. 922.5). − UV/Vis ($CHCl_3$): λ_{max} = 498 nm; ε = $58\cdot10^3\ l\cdot mol^{-1}\cdot cm^{-1}$. − $C_{58}H_{70}N_2O_6S\cdot0.33\ H_2O$: calcd. C 74.97, H 7.66, N 3.01; found C 75.29, H 8.09, N 2.92.

5,17-Dinitro-26,28-dipropoxycalix[4]arene (**6a**): A mixture of 26,28-dipropoxycalix[4]arene (**17**; 6.3 g, 12.4 mmol), $NaNO_3$ (8.4 g, 99.2 mmol) and 37% HCl (25 ml) was stirred in 50 ml of H_2O and 100 ml of CH_2Cl_2 at room temp. for 40 h in the presence of a catalytic amount of $LaNO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 40 ml). The combined organic layers were washed with sat. NH_4Cl (2 × 40 ml) and brine (1 × 40 ml), dried with $MgSO_4$, and after evaporation of the solvent, the crude product was crystallized from CH_2Cl_2/MeOH. After filtration, **6a** was obtained as a slightly yellow powder in 60% yield. Mp > 320°C (dec.) (CH_2Cl_2). − ^1H NMR: δ = 9.44 (s, 2 H, OH), 8.05 (s, 4 H, $ArHNO_2$), 7.00 (d, *J* = 7.5 Hz, 4 H, ArH), 6.85 (t, *J* = 7.3 Hz, 2 H, ArH), 4.30, 3.51 (ABdd, $^2J_{AB}$ = 13 Hz, 2 × 4 H, $ArCH_2$), 4.03 (t, *J* = 6.2 Hz, 4 H, OCH_2), 2.09 (m, 4 H, CH_2CH_3), 1.33 (t, *J* = 7.4 Hz, 6 H, CH_3). − ^{13}C NMR: δ = 159.7, 151.7 (ArCO), 139.8 ($ArCNO_2$), 131.9, 128.3 ($ArCCH_2$), 129.7 125.7, 124.6 (ArCH), 78.8 (OCH_2), 31.3 ($ArCH_2Ar$), 23.5 (CH_2CH_3), 10.9 (CH_3). − FAB MS; *m/z*: 0 599.4 $[M + H]^+$ (calcd. 599.3). − IR ($CHCl_3$): ν_{OH} = 3220 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 332 nm; ε = $22\cdot10^3\ l\cdot mol^{-1}\cdot cm^{-1}$. − $C_{34}H_{34}N_2O_8$: calcd. C 68.34, H 5.72, N 4.68; found C 68.22, H 5.84, N 4.62.

5,17-Bis-[(E)-1-(nitro)ethenyl]-26,28-dipropoxycalix[4]arene (**6b**): Orange crystals, yield 16%, mp 214−215°C (CH_2Cl_2). − ^1H NMR: δ = 9.07 (s, 2 H, OH), 7.86, 7.46 (dd, *J* = 13.6 Hz, 4 H, $ArCH{=}CHNO_2$), 7.24 (s, 4 H, ArH), 6.88 (d, *J* = 13.8 Hz, 4 H, ArH), 6.88 (t, *J* = 6.6 Hz, 2 H, ArH), 4.22, 3.36 (ABdd, $^2J_{AB}$ = 13 Hz, 8 H, $ArCH_2$), 3.94 (t, *J* = 6.2 Hz, 4 H, OCH_2), 2.01 (m, 4 H, CH_2CH_3), 1.26 (t, *J* = 7.4 Hz, 6 H, CH_3). − ^{13}C NMR: δ = 157.96, 151.76 (ArCO), 139.72, 134.11 (CH=), 132.39, 129.22 ($ArCCH_2$), 130.27, 129.38, 125.70 (ArCH), 121.07 (ArCCH=), 78.67 (OCH_2), 31.34 ($ArCH_2Ar$), 23.49 (CH_2CH_3), 10.92 (CH_3). − FAB MS; *m/z*: 651.2 $[M + H]^+$ (calcd. 651.3). − IR ($CHCl_3$): ν_{OH} = 3254 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 380 nm; ε = $33\cdot10^3\ l\cdot mol^{-1}\cdot cm^{-1}$. − $C_{38}H_{38}N_2O_8$: calcd. C 70.14, H 5.89, N 4.30; found C 70.26, H 6.03, N 4.15.

5,17-Bis(tricyanoethenyl)-26,28-dipropoxycalix[4]arene (**6c**): A solution of 25,27-dipropoxycalix[4]arene (**17**; 2.0 g, 3.94 mmol) and tetracyanoethylene (1.3 g, 9.84 mmol) in pyridine (40 ml) was stirred at room temp. for 24 h. Subsequently, the solvent was evaporated and the residue was taken up in CH_2Cl_2 (100 ml), washed with 1 N HCl (3 × 30 ml), brine (1 × 30 ml) and dried with $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified by column chromatography (CH_2Cl_2/hexane 7:3) to afford **6c** as orange crystals in 71% yield. Mp > 320°C (dec.) (CH_2Cl_2/hexane 2:8). − ^1H NMR: δ = 10.05 (s, 2 H, OH), 7.89 [s, 2 H, ArH(TCNE)], 7.02 (d, *J* = 7.3 Hz, 4 H, ArH), 6.98 (t, *J* = 6.6 Hz, 2 H, ArH), 4.29, 3.52 (ABdd, $^2J_{AB}$ = 13.3 Hz, 2 × 4 H, $ArCH_2$), 4.04 (t, *J* = 6.3 Hz, 4 H, OCH_2), 2.11 (m, 4 H, CH_2CH_3), 1.33 (t, *J* = 7.3 Hz, 6 H, CH_3). − ^{13}C NMR: δ = 161.74, 151.44 (ArCO), 140·10 [ArCC(CN)=], 131.51, 130.12 ($ArCCH_2$), 131.20, 129.91, 126.40 (ArCH), 120.42 [ArC(CN)=], 114.06, 112.60, 112.19 (CN), 85.63 [=$C(CN)_2$], 79.08 (OCH_2), 31.28 ($ArCH_2Ar$), 23.43 (CH_2CH_3), 10.89 (CH_3). − FAB MS; *m/z*: 710.4 $[M^-]$ (calcd. 710.3). − IR ($CHCl_3$): ν_{OH} = 3157 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 440 nm; ε = $53\cdot10^3\ l\cdot mol^{-1}\cdot cm^{-1}$. − $C_{38}H_{38}N_2O_8$: calcd. C 70.14, H 5.89, N 4.30; found C 70.26, H 6.03, N 4.15.

5,17-Bis-[(E)-1-(4-nitrophenyl)ethenyl]-26,28-dipropoxycalix[4]arene (**6d**): A solution of 5,17-diformyl-26,28-dipropoxycalix[4]arene (**18**; 0.81 g, 1.43 mmol), *p*-nitrophenylacetic acid (1.04 g, 5.74 mmol) and piperidine (0.49 g, 5,74 mmol) in 10 ml of DMF was stirred at room temp. for 55 h. Subsequently, the reaction mixture was poured into ice water and filtered. The residue was taken up in CH_2Cl_2 (50 ml), washed with sat. NH_4Cl (3 × 20 ml), brine (1 × 30 ml) and dried with $MgSO_4$. After filtration, the solvent was evaporated and the crude product was purified by column chromatography (CH_2Cl_2/hexane 8:2) to afford **6d** as an orange powder in 24% yield. Mp > 300°C (CH_2Cl_2). − ^1H NMR ([D_6]acetone): δ = 8.71 (s, 2 H, OH), 8.07, 7.65 (dd, *J* = 8.8 Hz, 8 H, $ArHNO_2$), 7.42 (s, 4 H, ArH), 7.28, 7.11 (dd, *J* = 16.4 Hz, 4 H, CH=), 6.96 (d, *J* = 7.6 Hz, 4 H, ArH), 6.61 (t, *J* = 7.6 Hz, 2 H, ArH), 4.24, 3.42 (dd, $^2J_{AB}$ = 13.1 Hz, 8 H, $ArCH_2$), 3.95 (t, *J* = 6 Hz, 4 H, OCH_2), 1.98 (m, 4 H, CH_2CH_3), 1.27 (t, *J* = 7.3 Hz, 6 H, CH_3). − ^{13}C NMR: δ = 154.72, 151.90 (ArCO), 146.17, 144.67 (ArCCH=), 133.57, 129.14, 127.57, 126.28, 125.41, 124.17, 122.92 (CH=, ArCH), 133.02, 128.61 ($ArCCH_2$), 127.35 ($ArCNO_2$), 76.59 (OCH_2), 31.51 ($ArCH_2Ar$), 23.52 (CH_2CH_3), 10.93 (CH_3). − FAB MS; *m/z*: 802.2 $[M^+]$ (calcd. 802.3). − IR ($CHCl_3$): ν_{OH} = 3287 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 400 nm; ε = $15\cdot10^3\ l\cdot mol^{-1}\cdot cm^{-1}$. − $C_{46}H_{38}N_2O_8\cdot0.5\ H_2O$: calcd. C 73.10, H 5.20, N 3.70; found C 73.08, H 5.07, N 3.74.

Calix[4]arene **6e**: The residue was purified by column chromatography with Hex/CH_2Cl_2 2:1 as the eluent, slowly changing to Hex/CH_2Cl_2 4:1. Red crystals, yield 68%, mp 200−202°C (Hex/CH_2Cl_2). − ^{1}H NMR: δ = 8.85 (s, 2 H, OH), 7.27 (s, 2 H, ArH), 6.78−6.99 (m, 12 H, HC=, and ArH), 4.31, 3.43 (ABdd, $^2J_{AB}$ = 13 Hz, 2 × 4 H, $ArCH_2$), 4.01 (t, J = 6.1 Hz, 4 H, OCH_2), 2.58, 2.45 (2 s, 8 H, CH_2 iph), 2.05 (m, 4 H, CH_2CH_3), 1.33 (t, J = 7.3 Hz, 3 H, CH_3), 1.07 (s, 12 H, CH_3 iph). − ^{13}C NMR: δ = 169.35 [*C*=C(CN)$_2$], 155.82, 154.77, 151.79 (ArCOH, ArCOPr, R_2*C*CH=CH), 137.67, 129.19, 128.38 (*C*H=), 132.82, 128.93, 126.94 (Ar*C*CH=, Ar*C*CH_2), 125.97, 125.51, 122.21 (ArCH), 113.89, 113.20 (CN), 78.53 (OCH_2), 42.98, 39.20 (CH_2 iph), 32.02 [*C*(CH_3)$_2$], 31.48 (CH_2Ar), 28.04 (CH_3 iph), 23.48 (*C*H_2CH_3), 10.91 (CH_2*C*H_3). − FAB MS; *m/z*: 900.3 [M$^+$] (calcd. 900.5). − IR ($CHCl_3$): ν_{OH} = 3267 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 448 nm; ε = 76·10^3 l·mol^{-1}·cm^{-1}. − $C_{60}H_{60}N_4O_4$: calcd. C 79.97, H 6.71, N 6.22; found C 79.82, H 6.62, N 5.93.

Calix[4]arene **6f**: The residue was purified by column chromatography with Hex/CH_2Cl_2 1:1 as the eluent, slowly changing to pure CH_2Cl_2. Purple powder, yield 19%, mp 168−170°C (Hex/CH_2Cl_2). − ^{1}H NMR: δ = 8.82 (s, 2 H, OH), 8.43 (s, 1 H, HC=C iph), 7.30, 7.03 (2 s, 8 H, ArH, HC=CH), 6.98 (d, J = 7.4 Hz, 2 H, ArH), 6.81 (t, J = 7.3 Hz, 4 H, ArH), 4.57 (m, 8 H, CH_2N), 4.31, 3.42 (ABdd, $^2J_{AB}$ = 13 Hz, 2 × 4 H, $ArCH_2$), 4.01 (t, J = 6 Hz, 4 H, OCH_2), 3.11, 2.46 (2 s, 8 H, CH_2 iph), 2.0−2.2 (m, 4 H, CH_2CH_3), 1.2−1.4 (m, 18 H, CH_3CH_2N and CH_3), 1.06 (s, 6 H, CH_3 iph). − ^{13}C NMR: δ = 178.08, 171.04, 161.17, 160.91, 158.53, 155.79, 151.80, 112.10 (R_2C=, ArCOH, ArCOPr, C=O, C=S), 137.40, 129.24, 128.53, 128.31, 127.82, 125.51 (ArCH, CH=), 132.80, 128.82, 127.40 (Ar*C*CH=, Ar*C*CH_2), 78.52 (OCH_2), 44.79, 43.72, 43.61, 38.95 (CH_2N, CH_2 iph), 31.87 [*C*(CH_3)$_2$], 31.50 (CH_2Ar), 28.62 (CH_3 iph), 23.50 (*C*H_2CH_3), 12.61 (*C*H_3CH_2N), 10.92 (CH_2*C*H_3). − FAB MS; *m/z*: 1168.3 [M$^+$] (calcd. 1168.5). − IR ($CHCl_3$): ν_{OH} = 3260 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 516 nm; ε = 135·10^3 l·mol^{-1}·cm^{-1}. − $C_{70}H_{80}N_4O_8S$: calcd. C 71.89, H 6.89, N 4.79, S 5.48; found C 72.08, H 7.10, N 4.43, S 5.16.

5,11,17,23-Tetranitro-25,26,27,28-tetrapropoxycalix[4]arene (**9a**): A solution of 1 mmol of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene (**20**) in 15 ml of CH_2Cl_2 was cooled to 0°C, and 15 mmol of trifluoroacetic acid was added. Subsequently, 20 mmol of nitric acid (100%) was added in portions upon which the mixture turned purple-black. After 5−10 min or upon decoloration of the reaction mixture, it was poured into ice water and diluted with 50 ml of CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2 × 50 ml), and the combined organic layers were washed with sodium bicarbonate solution (2 × 20 ml) and brine (2 × 20 ml), dried with $MgSO_4$, and concentrated under reduced pressure. Subsequently, the crude product was purified by passing it through a short (2 cm) silica filter (CH_2Cl_2) followed by recrystallization from CH_2Cl_2/MeOH or trituration with MeOH. Compound **9a** was obtained as a white powder in 95% yield. Spectral data as in ref.[31a].

2,6-Dimethyl-4-nitrophenol (**10a**): Obtained from Aldrich (98%), purified by column chromatography with dichloromethane as the eluent. − ^{1}H NMR: δ = 9.77 (s, 1 H, OH), 7.88 (s, 2 H, ArH), 2.24 (s, 6 H, CH_3). − IR ($CHCl_3$): ν_{OH} = 3596 cm^{-1}. − UV/Vvis ($CHCl_3$) λ_{max} = 318 nm; ε = 2,3·10^3 l·mol^{-1}·cm^{-1}.

2,6-Dimethyl-4-[(E)-1-(nitro)ethenyl]phenol (**10b**): Orange crystals, yield 27%, mp 134°C (CH_2Cl_2). − ^{1}H NMR: δ = 5.12 (s, 1 H, OH), 7.91, 7.49 (dd, J = 13.6 Hz, 2 H, Ar*CH*=*CH*NO_2), 7.20 (s, 2 H, ArH), 2.27 (s, 6 H, CH_3). − ^{13}C NMR: δ = 156.17 (ArCOH), 139.51 (Ar*C*H=), 134.73 (Ar*C*CH=), 130.23 (ArCH), 124.22 (Ar*C*CH_3), 122.14 (=*C*HNO_2), 15.82 (CH_3). − EI MS; *m/z*: 193.1 [M$^+$] (calcd. 193.07). − IR ($CHCl_3$) ν_{OH} = 3599 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 362 nm; ε = 17·10^3 l·mol^{-1}·cm^{-1}. − $C_{10}H_{11}N_1O_3$: calcd. C 62.17, H 5.74, N 7.25; found C 62.17, H 5.98, N 7.29.

2,6-Dimethyl-4-(1,1,2-tricyanoethenyl)phenol (**10c**): The same procedure as used for the synthesis of compound **6c** was followed starting from 2,6-dimethylphenol (1.15 g, 8.19 mmol). Tetracyanoethylene (1.35 g, 9.00 mmol) in pyridine (20 ml) at 80°C. The crude product was recrystallized from EtOH/H_2O, filtered through 2 cm of silica gel (eluent CH_2Cl_2) and subsequently recrystallized from $CHCl_3$ to afford **10c** as orange crystals in 25% yield. Mp 182−184°C ($CHCl_3$). − ^{1}H NMR: δ = 7.81 (s, 2 H, ArH), 5.73 (s, 1 H, OH), 2.33 (s, 6 H, CH_3). − ^{13}C NMR: δ = 159.89 (ArCOH), 140.41 [Ar*C*C(CN)=], 134.73 [Ar*C*C(CN)=], 131.26 (ArCH), 125.42 (Ar*C*CH_3), 121.18 [Ar*C*(CN)=], 113.98, 112.12 (CN), 86.65 [=*C*(CN)$_2$], 15.93 (CH_3). − EI MS; *m/z*: 223.2 [M$^+$] (calcd. 223.1). − IR ($CHCl_3$): ν_{OH} = 3585 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 420 nm; ε = 23·10^3 l·mol^{-1}·cm^{-1}. − $C_{13}H_9N_3O\cdot0.1\ H_2O$: calcd. C 69.39, H 4.12, N 18.67; found C 69.04, H 3.97, N 18.53.

2,6-Dimethyl-4-[(E)-1-(4-nitrophenyl)ethenyl]phenol (**10d**): As **6d**, starting from 3,5-dimethyl-4-hydroxybenzaldehyde (**13**). The crude product was purified by recrystallization from CH_2Cl_2/MeOH. Orange crystals, yield 34%, mp 139−140°C (CH_2Cl_2/MeOH). − ^{1}H NMR: δ = 8.19, 7.58 (dd, J = 8.9 Hz, 4 H, $ArHNO_2$), 7.20 (s, 2 H, ArH), 7.16, 6.97 (dd, J = 16.2 Hz, 2 H, C*H*=), 4.80 (s, 1 H, OH), 2.28 (s, 6 H, CH_3). − ^{13}C NMR: δ = 153.18 (ArCOH), 146.30, 144.49 (Ar*C*CH=), 133.26, 127.63, 126.41, 124.16, 123.69 (ArCH, CH=), 128.45, 123.49 ($ArCNO_2$, Ar*C*CH_3), 15.96 (CH_3). − EI MS; *m/z*: 269.1 [M$^+$] (calcd. 269.1). − IR ($CHCl_3$): ν_{OH} = 3604 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 386 nm; ε = 7·10^3 l·mol^{-1}·cm^{-1}. − $C_{16}H_{15}N_1O_3$: calcd. C 71.36, H 5.61, N 5.20; found C 71.31, H 5.64, N 5.17.

Phenol **10e**: Red crystals, yield 83%, mp 208−209°C (Hex/CH_2Cl_2). − ^{1}H NMR: δ = 7.18 (s, 2 H, ArH), 6.91 (dd, 2 H, J = 6.1 and 14.8 Hz, HC=CH), 6.79 (s, 1 H, HC=C iph), 4.87 (s, 1 H, OH), 2.59, 2.44 (2 s, 4 H, CH_2 iph), 2.27 (s, 6 H, CH_3Ar), 1.07 (s, 6 H, CH_3 iph). − ^{13}C NMR ([D$_6$]acetone): δ = 170.55 [*C*=C(CN)$_2$], 156.84, 156.28 (ArCOH, R_2*C*CH=CH), 139.04, 129.47, 127.16 (*C*H=), 122.53 (ArCH), 128.69 (Ar*C*CH=), 125.35 (Ar*C*CH_3), 114.61, 123.81 (CN), 77.00 [*C*(CN)$_2$], 43.40, 39.43 (CH_2 iph), 32.54 [*C*(CH_3)$_2$], 28.01 (CH_3 iph), 16.60 (CH_3Ar). − FAB MS; *m/z*: 318.1 [M$^+$] (calcd. 318.2). − IR ($CHCl_3$) ν_{OH} = 3603 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 432 nm; ε = 54·10^3 l·mol^{-1}·cm^{-1}. − $C_{21}H_{22}N_2O$: calcd. C 79.21, H 6.96, N 8.80; found C 79.25, H 6.86, N 8.73.

Phenol **10f**: Purple crystals, yield 51%, mp 215−217°C (Hex/CH_2Cl_2). − ^{1}H NMR: δ = 8.38 (s, 1 H, HC=C iph), 7.20 (s, 2 H, ArH), 7.00 (s, 2 H, HC=CH), 4.87 (s, 1 H, OH), 4.53 (m, 4 H, CH_2N), 3.10, 2.44 (2 s, 4 H, CH_2 iph), 2.27 (s, 6 H, CH_3Ar), 1.31 (m, 6 H, C*H*$_3CH_2N$), 1.06 (s, 6 H, CH_3 iph). − ^{13}C NMR: δ = 178.11, 170.89, 161.15, 160.82, 158.00, 154.10, 112.47 (R_2C=, ArCOH, C=O, C=S), 136.77, 129.02, 128.46, 128.05 (ArCH, CH=), 128.85, 123.74 (Ar*C*CH=, Ar*C*CH_3), 44.68, 43.72, 43.61, 38.90 (CH_2N, CH_2 iph), 31.85 [*C*(CH_3)$_2$], 28.60 (CH_3 iph), 15.98 (CH_3Ar), 12.59 (*C*H_3CH_2N). − FAB MS; *m/z*: 453.2 [M + H]$^+$ (calcd. 453.2). − IR ($CHCl_3$): ν_{OH} = 3603 cm^{-1}. − UV/Vis ($CHCl_3$): λ_{max} = 494 nm; ε = 54·10^3 l·mol^{-1}·cm^{-1}. − $C_{26}H_{32}N_2O_3S\cdot0.5\ H_2O$: calcd. C 67.65, H 7.21, N 6.07, S 6.89; found C 67.73, H 7.14, N 5.80, S 6.94.

2,6-Dimethyl-4-nitro-n-propoxybenzene (**11a**): To a suspension of 2,6-dimethyl-4-nitrophenol (**10a**; 2.36 g, 14.12 mmol) and K_2CO_3 (1.36 g, 9.9 mmol) in acetonitrile (100 ml) was added *n*-propyl iodide (4.1 ml, 42.4 mmol). The mixture was refluxed for 18 h, cooled to room temp., and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2/1 N HCl (100 ml/50 ml), and after separation of the layers the organic layer was washed with 1 N HCl (3 × 50 ml), H_2O (50 ml), and brine (50 ml), dried with $MgSO_4$ and concentrated in vacuo. Freeze-drying gave the pure product **11a** (2.84 g) as slightly yellow crystals in 99% yield. Mp 24−25°C (CH_2Cl_2). − ^1H NMR: δ = 7.89 (s, 2 H, ArH), 3.77 (t, J = 5.6 Hz, 2 H, OCH_2), 2.33 (s, 6 H, CH_3Ar), 1.84 (m, 2 H, CH_2CH_3), 1.08 (t, J = 6.5 Hz, 3 H, CH_2CH_3). − ^{13}C NMR: δ = 161.40 (ArCO), 142.93 ($ArCNO_2$), 132.35 ($ArCCH_3$), 124.19 (ArCH), 74.22 (OCH_2), 23.60 (CH_2CH_3), 16.56 (CH_3Ar), 10.50 (CH_2CH_3). − EI MS; m/z: 209.2 [M^+] (calcd. 209.1). − UV/Vis ($CHCl_3$): λ_{max} = 296 nm; ε = $16 \cdot 10^3$ $l \cdot mol^{-1} \cdot cm^{-1}$. − $C_{11}H_{15}N_1O_3$: calcd. C 63.14, H 7.23, N 6.69; found C 63.33, H 7.37, N 6.78.

2,6-Dimethyl-4-[(E)-1-(4-nitrophenyl)ethenyl]-n-propoxybenzene (**11d**): As **6d**, starting from 3,5-dimethyl-4-*n*-propoxybenzaldehyde (**14**) but stirred at 80°C. The crude product was purified by column chromatography (CH_2Cl_2/hexane 20:80), to give the pure product as orange crystals in 34% yield. Mp 65−66°C (CH_2Cl_2/hexane). − ^1H NMR: δ = 8.03, 7.41 (dd, J = 8.9 Hz, 4 H, $ArHNO_2$), 7.06 (s, 2 H, ArH), 7.00, 6.85 (dd, J = 16.2 Hz, 2 H, CH=), 3.63 (t, J = 5.6 Hz, 2 H, OCH_2), 2.18 (s, 6 H, CH_3), 1.71 (m, 2 H, CH_2CH_3), 0.98 (t, J = 6.5 Hz, 3 H, CH_2CH_3). − ^{13}C NMR: = δ 156.95 (ArCO), 146.38, 144.21 (ArCCH=, $ArCNO_2$), 133.06, 127.64, 126.56, 124.88, 124.09 (ArCH, CH=), 131.50 ($ArCCH_3$), 73.95 (OCH_2), 23.70 (CH_2CH_3), 16.43 (CH_3Ar), 10.70 (CH_2CH_3). − EI MS; m/z: 312.0 [M + H]$^+$ (calcd. 311.1). − UV/Vis ($CHCl_3$): λ_{max} = 372 nm; ε = $3 \cdot 10^3$ $l \cdot mol^{-1} \cdot cm^{-1}$. − $C_{19}H_{21}N_1O_3 \cdot 0.29\ CH_2Cl_2$: calcd. C 68.95, H 6.47, N 4.17; found C 68.91, H 6.54, N 4.10.

Benzene **11e**: Red crystals, yield 32%, mp 184−186°C (Hex/CH_2Cl_2). − ^1H NMR: δ = 7.18 (s, 2 H, ArH), 6.92 (dd, 2 H, J = 9 and 16 Hz, HC=CH), 6.80 (s, 1 H, HC=C iph), 3.74 (t, J = 6.6 Hz, 2 H, OCH_2), 2.58, 2.44 (2 s, 4 H, CH_2 iph), 2.29 (s, 6 H, CH_3Ar), 1.83 (m, 2 H, CH_2CH_3), 1.07 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 1.06 (s, 6 H, CH_3 iph). − ^{13}C NMR: δ = 169.29 [C=$C(CN)_2$], 157.89, 154.25 (ArCOPr, R_2CCH=CH), 137.05, 128.32, 127.92 (CH=), 122.95 (ArCH), 131.77, 131.05 (ArCCH=, $ArCCH_3$), 113.65, 112.87 (CN), 78.01 [$C(CN)_2$], 74.05 (OCH_2), 43.01, 39.23 (CH_2 iph), 32.02 [$C(CH_3)_2$], 28.02 (CH_3 iph), 23.64 (CH_2CH_3), 16.40, 16.27 (CH_3Ar), 10.60 (CH_2CH_3). − FAB MS; m/z: 360.6 [M^+] (calcd. 360.2). − UV/Vis ($CHCl_3$): λ_{max} = 414 nm; ε = $40 \cdot 10^3$ $l \cdot mol^{-1} \cdot cm^{-1}$. − $C_{24}H_{28}N_2O$: calcd. C 79.96, H 7.83, N 7.77; found C 79.98, H 7.92, N 7.67.

Benzene **11f**: Purple crystals, yield 16%, mp 178−181°C (Hex/CH_2Cl_2). − ^1H NMR: δ = 8.36 (s, 1 H, HC=C iph), 7.20 (s, 2 H, ArH), 7.0 (dd, J = 4.4 and 15.8 Hz, 2 H, HC=CH), 4.53 (m, 4 H, CH_2N), 3.74 (t, J = 6.6 Hz, 2 H, OCH_2), 3.09, 2.42 (2 s, 4 H, CH_2 iph), 2.28 (s, 6 H, CH_3Ar), 1.83 (m, 2 H, CH_2CH_3), 1.31 (m, 6 H, CH_3CH_2N), 1.07 (t, J = 7.4 Hz, 3 H, CH_3), 1.05 (s, 6 H, CH_3 iph). − ^{13}C NMR: δ = 178.11, 170.48, 161.05, 160.70, 158.67, 157.23, 112.95 (R_2C=, ArCOPr, C=O, C=S), 136.18, 130.29, 128.42, 128.32 (ArCH, CH=), 131.62, 131.49, (ArCCH=, $ArCCH_3$), 74.00 (OCH_2), 44.53, 43.70, 43.57, 38.88 (CH_2N, CH_2 iph), 31.81 [$C(CH_3)_2$], 28.59 (CH_3 iph), 23.65 (CH_2CH_3), 16.40 (CH_3Ar), 12.59, 12.56 (CH_3CH_2N), 10.63 (CH_2CH_3). − FAB MS; m/z: 495.3 [M + H]$^+$ (calcd. 495.3). − UV/Vis ($CHCl_3$): λ_{max} = 476 nm; ε = $55 \cdot 10^3$ $l \cdot mol^{-1} \cdot cm^{-1}$. − $C_{26}H_{32}N_2O_3S$: calcd. C 70.41, H 7.74, N 5.66; found C 70.79, H 8.10, N 5.35.

3,5-Dimethyl-4-n-propoxybenzaldehyde (**14**): To a suspension of 3,5-dimethyl-4-*n*-hydroxybenzaldehyde (**13**; 5.0 g, 33.3 mmol) and K_2CO_3 (13.81 g, 99.9 mmol) in CH_3CN was added *n*-propyl iodide (9.74 ml, 99.9 mmol). The mixture was refluxed for 18 h, cooled to room temp., and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2/1 N HCl (100 ml/50 ml), and after separation of the layers the organic layer was washed with 1 N HCl (3 × 50 ml), H_2O (50 ml), and brine (50 ml), dried with Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography (CH_2Cl_2/hexane 1:1) to afford the pure product **14** (6.13 g) as a colorless oil in 96% yield. − ^1H NMR: δ = 9.79 (s, 1 H, HC=O), 7.46 (s, 2 H, ArH), 3.74 (t, J = 5.6 Hz, 2 H, OCH_2), 2.28 (s, 6 H, CH_3Ar), 1.80 (m, 2 H, CH_2CH_3), 1.08 (t, J = 6.5 Hz, 3 H, CH_2CH_3).

5,17-Diformyl-26,28-dipropoxycalix[4]arene (**18**):[24] To a solution of 25,27-dipropoxycalix[4]arene (**17**; 3 g, 5.9 mmol) and α,α-dichloromethyl methyl ether (5.4 g, 59 mmol) in CH_2Cl_2 (200 ml) was added dropwise a solution of $TiCl_4$ (6.5 g, 59 mmol) in CH_2Cl_2 (50 ml) at −10°C. After stirring for 30 min, the reaction was quenched with MeOH (15 ml) and 2 N HCl (100 ml). This mixture was stirred for 2 h and subsequently extracted with CH_2Cl_2 (3 × 50 ml). The combined organic layers were washed with 2 N HCl (4 × 50 ml), H_2O (2 × 50 ml), brine (1 × 50 ml) and dried with $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified by column chromatography (CH_2Cl_2/EtOAc 95:5) to afford **18** as a white powder in 80% (2.7 g) yield. Mp > 310°C (EtOAc/CH_2Cl_2). − ^1H NMR: δ = 9.79 (s, 2 H, HC=O), 9.25 (s, 2 H, OH), 7.63 (s, 4 H, ArH), 6.97 (d, J = 7.6 Hz, 4 H, ArH), 6.80 (t, J = 8.1 Hz, 2 H, ArH), 4.31, 3.51 (ABdd, $^2J_{AB}$ = 13.3 Hz, 2 × 4 H, $ArCH_2$), 4.02 (t, J = 6.2 Hz, 4 H, OCH_2), 2.1 (m, 4 H, CH_2CH_3), 1.33 (t, J = 7.3 Hz, 6 H, CH_3). − ^{13}C NMR: δ = 190.87 (C=O), 159.65 (ArCOH), 151.70 (ArCOPr), 132.40, 128.60 ($ArCCH_2$, ArCC=O), 130.93, 129.42, 125.67 (ArCH), 78.58 (OCH_2), 31.29 ($ArCH_2Ar$), 23.48 (CH_2CH_3), 10.91 (CH_3). − FAB MS; m/z: 563.6 [M − H]$^-$ (calcd. 563.3). − $C_{36}H_{36}O_6 \cdot 0.125\ CHCl_3$: calcd. C 74.86, H 6.28; found C 74.84, H 6.21.

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[37] By molecular mechanics calculations in vacuum at 0 K angles varying from 28 to 43° were found for the derivatives **6a−f** corresponding to enhancements factors of 1.2 to 0.6.

[38] Kelderman et al.[10] have determined μβ(0) values of 259 and 1767.10^{-48} esu for **9a** and **9d**, respectively. Since they used a different experimental configuration and a different fundamental wavelength both compounds were remeasured to allow good comparison.

[39] This is the averaged angle of the four angles of the four chromophoric units with the dipole axis of the molecule which is insensitive for pinched-*cone* to pinched-*cone* conformational motions.

[40] The SIR92 program is described in: M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, D. Viterbo, *J. Appl. Crystallogr.* **1989**, *22*, 389−393.

[41] [41a] C. K. Fair, *MolEN, An Interactive Intelligent System for Crystal Structure Analysis*, user manual, Enraf−Nonius, Delft, The Netherlands, **1990**. − [41b] *CAD4 Operations Manual*, Enraf−Nonius, Delft, The Netherlands, **1977**.

[42] *International Tables for Crystallography*, vol. C, Tables 4.2.6.8 and 6.1.1.4, **1992**.

[43] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100841. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + (1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

[44] [44a] Spectral data: K. Iwamoto, K. Araki, S. Shinkai, *J. Org. Chem.* **1991**, *56*, 4955−4962. − [44b] K. Iwamoto, K. Araki, S. Shinkai, *Tetrahedron* **1991**, *47*, 4325. − [44c] Procedure to obtain the the *cone* conformer selectively: see ref.[16a].

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