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Multichromophoric Calix[4]arenes: Effect of Interchromophore Distances on Linear and Nonlinear Optical Properties

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Multichromophoric calix[4]arenes with two or four disperse red one (DR1) moieties linked to the lower rim have been synthesized. The second-order nonlinear optical activity was measured by using the electric-field-induced second-harmonic generation technique and there was a nearly linear increase of the $\mu\beta$ value with the number of chromophores in the molecule without affecting the charge-transfer absorption wavelength. The effect that the number of DR1 units plays on the hyperpolarizability, the dipole moment, and the absorption maxima has been also studied by using quantum chemical calculations. It was found that it was necessary to synthesize multichromophores with distant chromophores to obtain large nonlinear optical responses.

1. Introduction

Organic molecules with second-order nonlinear optical (NLO) properties have generated great interest in the development of organic materials.[1] In general, such chromophores have an extended conjugated system, a low-energy transition with a high extinction coefficient, and a large dipole moment change between their ground and excited states.[2] It is well known that the extension of the conjugated system increases the hyperpolarizability, β, but unfortunately this is usually accompanied by a shift of the charge-transfer (CT) absorption band to a longer wavelength,[3] thereby restricting the use of these materials for certain applications, such as in frequency doubling.[4] This undesirable effect constitutes the transparence–efficiency trade-off.[5]

Multichromophore assemblies have been proposed[6] as a convenient way to increase the figure of merit, $\mu\beta$, overcoming the transparence–efficiency trade-off and this approach has led to a number of multichromophoric systems with enhanced NLO properties, such as V-shaped chromophores[7] or spirofluorene compounds.[8] Calix[4]arene was soon recognized as a suitable template to synthesize multichromophore assemblies with a controlled orientation of dipolar units. The NLO properties of the four conformers of tetranitrotetrapropoxycalix[4]arene were studied[9] and it was observed that the increase in molecular hyperpolarizability was sublinear with the number of chromophores, probably due to interchromophore interactions. Similarly, a joint experimental–theoretical study on tetrachromophores based on a cyclotetrasiloxane architecture[10] concluded that most of the increased $\mu\beta$ value, relative to monochromophores, was due to an increased dipole moment and the hyperpolarizability remained almost unchanged as a consequence of nonbonding electronic interactions between NLO chromophores.

The calix[4]arene structure has been used to preorganize chromophores in one single molecule,[11] but, up to now, its benzenic rings have been used as spacers in multichromophoric donor–π–acceptor assemblies; thus leading to low interchromophore distances that allow through-space interactions.[9,12,13]

Since it seems desirable to keep NLO-active units as isolated as possible to reach higher hyperpolarizabilities, we herein propose a different approach to multichromophore calix[4]arene derivatives in which the calixarene ring is not part of the chromophoric system. By using calix[4]arene as a template, multichromophoric systems are constructed by functionalization of the lower rim, giving rise to assemblies with more distant chromophores with the aim of avoiding (or at least minimizing) interchromophoric interactions.

2. Results and Discussion

2.1. Synthesis

Calix[4]arene is a versatile scaffold that can be readily functionalized.[14] Acids **1** and **3** were prepared by procedures described in the literature, involving the reaction of calix[4]arene with ethylbromoacetate under basic conditions[15] and subsequent hydrolysis of the resulting esters.[16]

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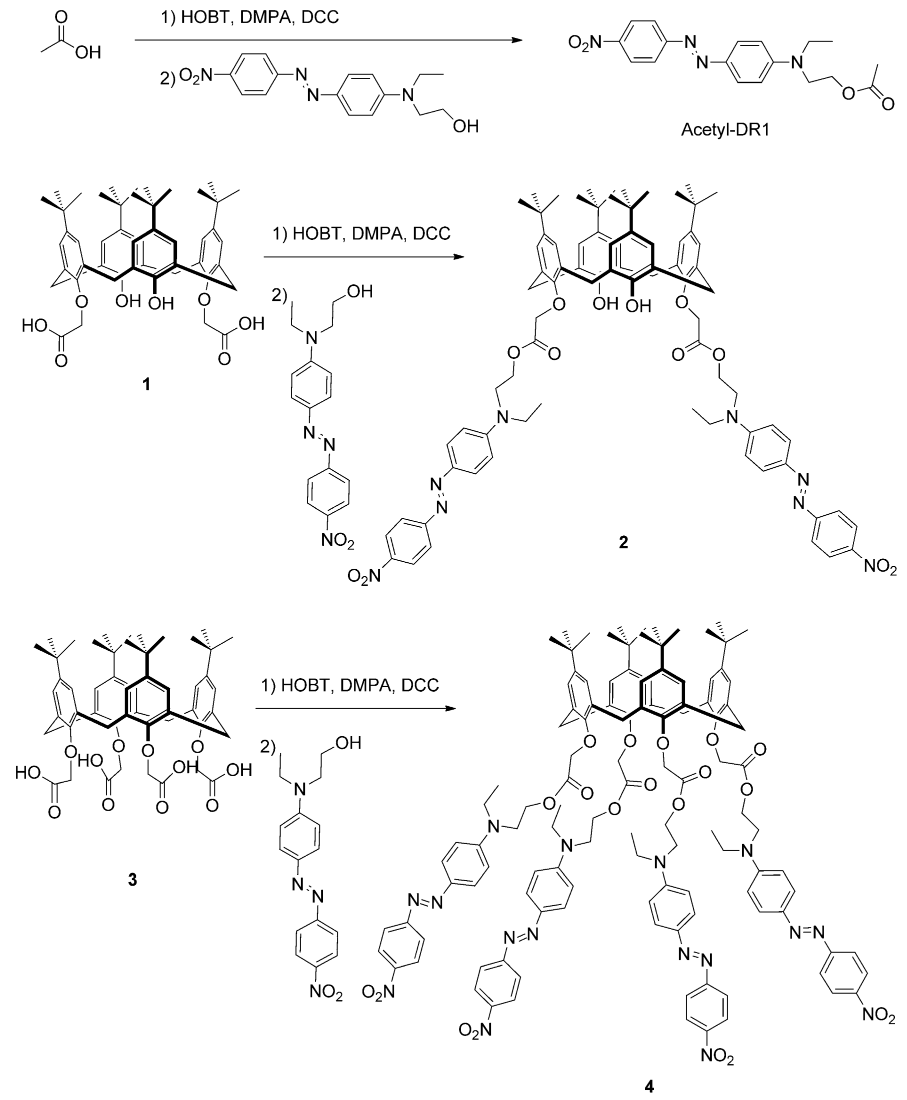
Following the experimental procedure described by Hudhomme et al.,[17] esterification of acetic acid, **1**,[18] and **3**[19] with disperse red one (DR1) in the presence of dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridine (DMAP), and 1-hydroxybenzotriazole (HOBT) afforded the corresponding Acetyl-DR1, diester **2**, and tetraester **4** in 58–80 % yield (Scheme 1). It is worth noting that, although Acetyl-DR1 has been previously prepared,[20] it was not completely characterized.



Scheme 1. Synthesis of Acetyl-DR1 and calixarenes **2** and **4**.

2.2. NMR Spectra

The calix[4]arene assemblies **1**, **2**, **3**, and **4** were characterized by NMR spectroscopy. The diastereotopic protons Ar–CH$_{exo}$H$_{endo}$–Ar of the aromatic cavity of these calix[4]arenes were studied. It is known that $\Delta\delta$ between the H$_{exo}$ and H$_{endo}$ in calix[4]arenes serves as a measure of the flattening: $\Delta\delta$ is generally 0.9 ppm for a system in the cone conformation, whereas in the flattened conformation $\Delta\delta$ is significantly decreased.[21] Thus, the calix[4]arene diacid **1** has $\Delta\delta = 1.23$[18a] and this value decreases to $\Delta\delta = 1.06$ for calix[4]arene diester **2**, which shows that the phenol units are more flattened because of steric crowding between the DR1 groups on the narrow, lower rim. An analogous variation in the $\Delta\delta$ values has been observed between tetrasubstituted calix[4]arenes **3** and **4** (with $\Delta\delta$ values of 1.66 and 1.55, respectively).

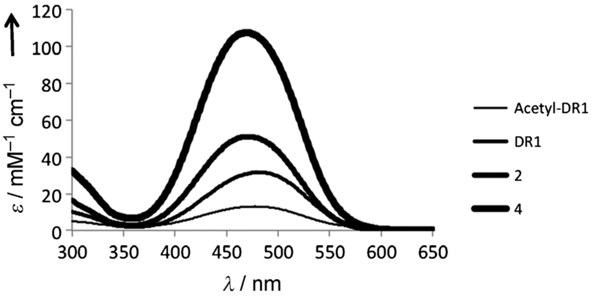


Figure 1. UV/Vis spectra of Acetyl-DR1, DR1, calixarene **2**, and calixarene **4** in CH_2Cl_2.

2.3. Electronic Absorption Spectra

The linear optical properties were studied by means of UV/Vis spectroscopy in dichloromethane and DMSO to follow the solvatochromic effect. Figure 1 shows the UV/Vis spectra of DR1 and calix[4]arenes **2** and **4**. The experimental parameters for the lowest energy absorptions are gathered in Table 1 along with the results of theoretical calculations. It can be seen that, in every case, there is a redshift of these absorptions on passing from CH_2Cl_2 to DMSO. This positive solvatochromic shift serves as an indicator of the increased dipole moment upon excitation;[22] thus confirming the CT character of these transitions[23] and indicating positive hyperpolarizability. The most noticeable feature of the UV/Vis spectra of these compounds is the blueshift of the CT band observed when linking the DR1 moiety to the calix[4]arene scaffold.

Considering that chromophores in molecules **2** and **4** are isolated, in other words, there is no electronic interaction

Table 1. Experimental and theoretically calculated UV/Vis absorption data.

	Experimental						Theoretical					Major
	CH_2Cl_2			DMSO			B3LYP/6-31G*					contributions[d]
	λ_{max}[a]	E_{01}[b]	$\log\varepsilon$	λ_{max}[a]	E_{01}[b]	$\log\varepsilon$	Symmetry	λ_{max}[a]	E_{01}[b]	$\Delta\mu_{01}$[c]	F	
DR1	480	2.59	4.50	508	2.44	4.52	–	445	2.78	11.85	0.95	H→L
Acetyl-DR1	476	2.61	4.26	498	2.49	4.13	–	441	2.81	11.94	0.98	H→L
2	469	2.40	4.71	493	2.52	4.71	B	438	2.83	9.39	0.84	H-3→L+1 H-2→L
							A	435	2.85	9.45	1.26	H-3→L H-2→L+1
4	470	2.64	5.03	491	2.53	4.99	A	442	2.81	16.04	0.16	H→L+2 H-1→L+3
							B	441	2.81	18.89	0.79	H→L+3 H-1→L+2
							B	440	2.82	31.53	0.54	H-2→L+3

[a] In nm. [b] In eV. [c] In Debye. [d] H = HOMO, L = LUMO.

among chromophores within the same molecule, these multichromophore systems can be studied in the framework of the exciton model.[24,25] If we consider molecule **2**, for composite double molecules with the two chromophores in an oblique arrangement, the exciton model predicts splitting of the lowest energy absorption into two perpendicularly polarized absorptions with that polarized perpendicularly to the symmetry axis (and hence, to the total dipole moment) shifted to lower energy and that polarized parallel to it shifted to higher energy. The absence of an experimentally observable energy splitting may be attributed to the large separation between the two chromophores in **2**, but the hypsochromic shift of **2** with respect to DR1 remains unexplained by this simple approach. To get a better understanding of the optical behavior of these chromophores, we performed DFT calculations using the hybrid B3LYP functional. The optimized geometry of **2** (Figure 2) reveals that the two amino nitrogen atoms are separated by 10.2 Å and the center-to-center distance between chromophores is more than 16 Å. These distances are large enough to allow any through-space electronic interactions to be neglected, since it has been reported[26] that above 7 Å chromophores behave as isolated moieties and molecular orbitals (MOs) of the dimeric chromophores are sums and differences of nearly unperturbed monomer MOs.

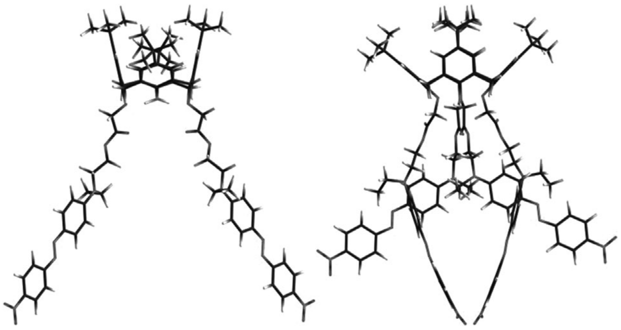


Figure 2. B3LYP/6-31G*-optimized geometries of **2** (left) and **4** (right).

The gas-phase excitation energies calculated by using the time-dependent (TD) DFT approach are approximately 0.2 and 0.3 eV higher than those measured in CH_2Cl_2 and DMSO, respectively, and are therefore in reasonable agreement with experimental results, taking into account the positive solvatochromism shown by these molecules. Furthermore, theoretical calculations reproduce the hypsochromic shift of **2** and **4** relative to that of DR1. According to these calculations, molecule **2** follows the exciton model and presents two orthogonally polarized excited states. However, the calculated energy separation for these excited states is only 0.02 eV; thus explaining the lack of an experimentally observable band splitting. The cause of the higher excitation energy of **2** relative to DR1 can be found in the increased energy gap from the occupied to the unoccupied MOs involved in these electronic transitions. Acylation of the OH group in DR1 causes the stabilization of both occupied and unoccupied MOs, but this stabilization is higher for occupied MOs, since they are closer to the acyl group, and therefore, the energy gap increases from 2.89 to 2.98 eV and the excitation energy from 2.78 to 2.83 eV on passing from DR1 to **2**. For the sake of comparison, we synthesized Acetyl-DR1, which seemed to be a more reliable monochromophoric model for **2** and **4**, and its measured absorption band was hypsochromically shifted with respect to DR1. Also, the calculated HOMO–LUMO gap (2.94 eV) and excitation energy (2.81 eV) for Acetyl-DR1 are similar to the values calculated for **2**.

The optimized B3LYP/6-31G* geometry of **4** (Figure 2) shows that, to accommodate the four DR1 units, this molecule adopts a pinched-cone conformation with interchromophore distances of about 5 Å between cone-cone and pinched-cone DR1 substituents. While we can expect some through-space electronic interactions between cone chromophores, giving rise to a modified UV/Vis spectrum, it has been described that energy changes in the lowest CT transitions are only observed at very low interchromophore distances (less than 3.3 Å).[26] TD-DFT calculations on **4** predict a HOMO–LUMO gap of 2.95 eV and a lowest excitation energy of 2.81 eV; this parallels the results obtained for Acetyl-DR1 and **2**.

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2.4. NLO Properties

The hyperpolarizabilities of multichromophores **2** and **4** and the reference compound DR1 were determined by electric-field-induced second harmonic (EFISH) with a fundamental wavelength of 1907 nm. Table 2 gives the $\mu\beta$ values obtained by EFISH measurements. The solvent used in these measurements was dichloromethane. It is observed that the $\mu\beta$ value is almost doubled when two DR1 units are linked to calix[4]arene **1** and almost quadrupled when four DR1 units are linked to calix[4]arene **3**.

Table 2. NLO properties of DR1 and compounds **2** and **4**.

Compound	Experimental[a]		CPHF/6-31G*[c]		
	$\mu\beta$[b]	$\mu\beta(0)$[b]	μ(D)	$\beta_{vec}(0)$[d]	$\mu\beta(0)$[b]
DR1	720(70)	490(50)	11.19	73	795
2	1270(130)	900(90)	12.73	105	1335
4	2700(300)	1900(200)	19.15	112	2141

[a] In CH_2Cl_2 at 1907 nm. [b] 10^{-48} esu. [c] Calculated for the B3LYP/6-31G*-optimized geometry. [d] 10^{-30} esu.

To get further insight into the NLO properties of these compounds, we have also calculated the molecular hyperpolarizabilities of these compounds using the coupled perturbed Hartree–Fock (CPHF) method, which yields the hyperpolarizability as the analytical second derivative of the dipole moment with respect to an electrical field. The CPHF method calculated on B3LYP/6-31G* geometries gave rise to the $\mu\beta(0)$ values shown in Table 2 and, while they were somewhat overestimated, they reproduced the experimental trend reasonably well, bearing in mind that conformational distribution and solvent effects were not considered in the calculations.

To rationalize the NLO behavior of **2**, this molecule must be considered as a V-shaped (or Λ-shaped) chromophore.[27] As discussed above, compound **2** presents two nearly degenerate excited states polarized orthogonally and these must contribute to the two major components of the hyperpolarizability tensor β_{zzz} and β_{zyy}, respectively. Assuming that there is no electronic interaction between chromophores, the total dipole moment and the hyperpolarizability[28] of **2** can be calculated by adding the contribution of each of the chromophores in the molecule [Eqs. (1) and (2)]:

$$\mu_z = 2\mu_1\cos\theta \tag{1}$$

$$\begin{aligned}\beta_{zzz} &= 2\beta_1\cos^3\theta \\ \beta_{zyy} &= 2\beta_1\cos\theta\sin^2\theta\end{aligned} \tag{2}$$

in which μ_1 and β_1 are the dipole moment and the hyperpolarizability of a single chromophore, respectively, and θ is the angle formed between the chromophore (defined herein by its ground-state dipole moment) and the symmetry conformations with axis (z). The electric-field-induced second harmonic generation (EFISHG) technique samples the product of the dipole moment and the vector component of the hyperpolarizability (β_{vec}).

For a V-shaped molecule displaying C_2 symmetry, β_{vec} can be calculated from Equation (3):

$$\begin{aligned}\beta_{vec} = \beta_z = \beta_{zzz} + \beta_{zyy} &= 2\beta_1(\cos^3\theta + \cos\theta\sin^2\theta) \\ &= 2\beta_1\cos\theta\end{aligned} \tag{3}$$

The angles were defined by the symmetry axis and the ground-state dipole moment of each subchromophore based on the calculated dipole moment of Acetyl-DR1. The angle (θ) formed between each chromophore and the z axis in the B3LYP/6-31G*-optimized geometry of **2** is 36.3°, and therefore, this simple additive model predicts $\mu_z = 2\mu_1\cos(36.3) = 1.61\mu_1$ and $\beta_{vec} = 2\beta_1\cos(36.3) = 1.61\beta_1$, giving rise to a measurable $\mu_z\beta_{vec} = 2.60\mu_1\beta_1$.

By comparing the $\mu\beta(0)$ values of DR1 and **2** obtained both experimentally and theoretically, it can be seen that there is almost a twofold increase, which is not far from the estimated value obtained with the simple addition model. Furthermore, a comparison with the calculated dipole moment and hyperpolarizability of Acetyl-DR1 ($\mu_0 = 8.93$ D, $\beta_{vec}(0) = 71\times10^{-30}$ esu, $\mu\beta(0) = 590\times10^{-48}$ esu) shows a much better fit to this model, indicating that Acetyl-DR1 is a better model for the chromophore units in **2** and that interchromophore interactions have a negligible influence on the molecular hyperpolarizability.

The B3LYP/6-31G*-optimized geometry of **4** showed a pinched-cone conformation with the two pinched chromophore groups forming an angle of $\theta = 54.1°$ with the symmetry axis, while the cone ones form an angle of $\phi = 19.0°$. By adding the contribution of each of the Acetyl-DR1 moieties in **4**, the resulting dipole moment and β_{vec} can be determined from Equations (4) and (5):

$$\begin{aligned}\mu &= 2\mu_1\cos\theta + 2\mu_1\cos\phi \\ &= 2\mu_1(\cos\theta + \cos\phi) = 3.06\mu_1\end{aligned} \tag{4}$$

$$\begin{aligned}\beta_{vec} &= 2\beta_1\cos\theta + 2\beta_1\cos\phi \\ &= 2\beta_1(\cos\theta + \cos\phi) = 3.06\beta_1\end{aligned} \tag{5}$$

Thus, by simply adding the contribution of the four chromophores in **4**, the measured $\mu\beta_{vec}$ should be around 9.36 ($=3.06^2$) times the $\mu_1\beta_1$ value of a single chromophore.

When comparing the experimental measurements, it can be seen that there is only a fourfold increase in the $\mu\beta(0)$ value when going from DR1 to **4**; this is well below the estimated increase obtained by adding the contribution of the four chromophores in the molecule.

It should be noted that to fit the "oriented gas" model to experimental results, a large angle between the symmetry axis and subchromophores must be assumed to explain the fourfold increase in $\mu\beta(0)$ measured by EFISH. It is well known that EFISH conditions with a large electric field favor conformations that have a larger dipole moment,[29] and therefore, such large angles between chromophores and the symmetry axis are not expected to contribute to the experimental results.

Results from CPHF calculations parallel the experimental trend, predicting that the NLO response of **4** is less than three times that of DR1 and less than four times that of Acetyl-DR1. As mentioned in the previous section, the interchromophore distance between DR1 substituents in calixarene **4** is 5 Å. According to Di Bella et al.,[26] below 7 Å, hyperpolarizability decreases with respect to the oriented gas estimation. Furthermore, Terenziani et al. demonstrated that, for oblique dimers at interchromophore distances between 5 and 9 Å, the hyperpolarizability never attained values expected in the oriented gas model, irrespective of the angle between chromophores.[12d] Analogous behavior has also been observed in tetrachromophoric calix[4]arenes.[12c]

When comparing the results obtained for **2** and **4**, increasing the number of chromophores in the molecules causes a large increase in the dipole moment, but has little influence on the hyperpolarizability, and therefore, increased $\mu\beta(0)$ is mainly a consequence of the larger dipole moment. Note that, while the interchromophore distances (Figure 2) in **4** are not short enough to modify the energy of the lowest electronic transitions, through space interactions give rise to lower transition dipoles and oscillator strengths with respect to **2**; this causes a decreased contribution of these transitions to the hyperpolarizability.

3. Conclusions

Lower-rim functionalization of calix[4]arene constitutes a new approach to the synthesis of multichromophoric, NLO-active molecules. The NLO activity of these new chromophores increases with the number of NLO-active units in the molecule without affecting the energy of the lowest absorption; thus overcoming the transparency–NLO efficiency trade-off. The undesirable nonbonding interchromophore interactions that cause a lowering of the molecular hyperpolarizability are avoided in the disubstituted derivative **2** by keeping large interchromophore distances, and therefore, the molecular hyperpolarizability results from the addition of the hyperpolarizabilities of single chromophores. However, due to its flexibility, tetrasubstituted **4** adopts a pinched-cone conformation, the cone chromophores of which are close enough to allow these interactions, and its hyperpolarizability remains almost unchanged compared to **2**. These results reinforce our initial approach of synthesizing multichromophores with distant chromophores to obtain large NLO responses. To minimize interchromophore interactions in tetrasubstituted calix[4]arenes, we propose the use of larger and more rigid spacers in the calix[4]arene scaffold and the chromophores linked to it to avoid conformations that could bring the chromophores together.

Experimental Section

General

IR spectra were recorded as Nujol mulls by using a Fourier transform IR spectrometer. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively; δ values are given in ppm [relative to tetramethylsilane (TMS)] and J values are in Hz. High-resolution electrospray (ESI) mass spectra were acquired on a Q-TOF instrument by using sodium formate clusters as a reference for accurate mass measurements. MALDI-TOF mass spectra were recorded by using dithranol as matrix and the sodium adducts of polyethylene glycol (PEG) as an internal reference for accurate mass measurements.

NLO Measurements

EFISHG measurements were performed by using the fundamental radiation at 1.9 μm obtained from an H_2 Raman cell excited by a Q-switched Nd:YAG laser (1064 nm). The repetition rate was 10 Hz and the pulse width was 8 ns. A computer-controlled NLO spectrometer completed the experimental setup. The 1.9 μm polarized light was split into two beams. The less intense one was directed to a *N*-(4-nitrophenyl)-L-prolinol (NPP) powder sample, the SH signal of which was used as a reference to correct laser fluctuations. The other beam was passed through a linear polarizer and focused into the wedge-shaped EFISHG liquid cell. The SH light from both the cell and the reference were measured with two photomultipliers. Interference filters were used to remove the residual excitation light beyond the sample and the NPP reference. Static $\mu\beta(0)$ values were deduced from the experimental values by using a two-level dispersion model. These experimental measurements were performed in CH_2Cl_2. Several solutions of each compound, with concentrations in the range 10^{-3}–10^{-4} M, were used in these measurements and gave rise to the same $\mu\beta$ values (within experimental uncertainties) and indicated that there were no noticeable aggregation effects.

Computational methods

All theoretical calculations were performed by using the Gaussian 09[30] program. Geometry optimizations started from structures with the alkyl groups in an all-staged *anti* arrangement and the C_2 symmetry of **2** and **4** was the only imposed restriction. The hybrid B3LYP[31] functional and the 6-31G(d)[32] basis set were used in both geometry optimizations and TD-DFT calculations and the excited-state dipole moments were calculated by using the CI density. Molecular hyperpolarizabilities at zero frequency were calculated by the CPHF method using HF/6-31G(d) model chemistry and the default parameters provided by the "polar" keyword on the B3LYP/6-31G*-optimized geometry. The default Gaussian 09 parameters were used in each case.

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Keywords: calixarenes · chromophores · nonlinear optics · quantum chemistry · transparency–efficiency tradeoff

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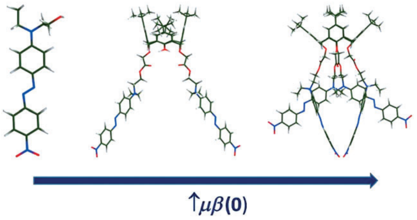
NLO response and effect: Multichromophoric calix[4]arenes with two or four disperse red one moieties linked to the lower rim have been synthesized. The second-order nonlinear optical activity was measured and there was a nearly linear increase of the $\mu\beta$ value with the number of chromophores in the molecule without affecting the charge-transfer absorption wavelength (see picture).



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Multichromophoric Calix[4]arenes: Effect of Interchromophore Distances on Linear and Nonlinear Optical Properties

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