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

Raquel Andreu,[a] Santiago Franco,[a] Javier Garín,[a] Judith Romero,[a] Belén Villacampa,[b] María Jesús Blesa*,[a] , Jesús Orduna*,[a]

((Dedication, optional))

Multichromophoric calix[4]arenes having two or four Disperse Red One (DR1) moieties linked to the lower rim are synthesized. The second order nonlinear optical activity was measured using the electric field induced second harmonic generation (EFISHG) technique and there is 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 using quantum chemical calculations.

Introduction

Organic molecules with second order nonlinear optical (NLO) properties have a 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 absorption band (CT band) to longer wavelength[3], thereby restricting the use of these materials for certain applications like frequency doubling.[4] This undesirable effect constitutes the so called 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 compared to monochromophores is due to an increased dipole moment, and the hyperpolarizability remains almost unchanged as a consequence of nonbonding electronic interactions between NLO chromophores.

The calix[4]arene structure has been used to pre-organize 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 in order to reach higher hyperpolarizabilities, we here 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 having more distant

[a] *Dr. R. Andreu, Dr. S. Franco, Prof. J. Garín, J. Romero, Dr. M.-J. Blesa*, Dr.J. Orduna**
Departamento de Química Orgánica, ICMA
Universidad de Zaragoza-CSIC
50009, Zaragoza, (Spain)
Fax: (+) 34 976 76 11 94
E-mail: jorduna@unizar.es

[b] *Dr. B. Villacampa*
Departamento de Física de la Materia Condensada, ICMA
Universidad de Zaragoza-CSIC
50009, Zaragoza, (Spain)

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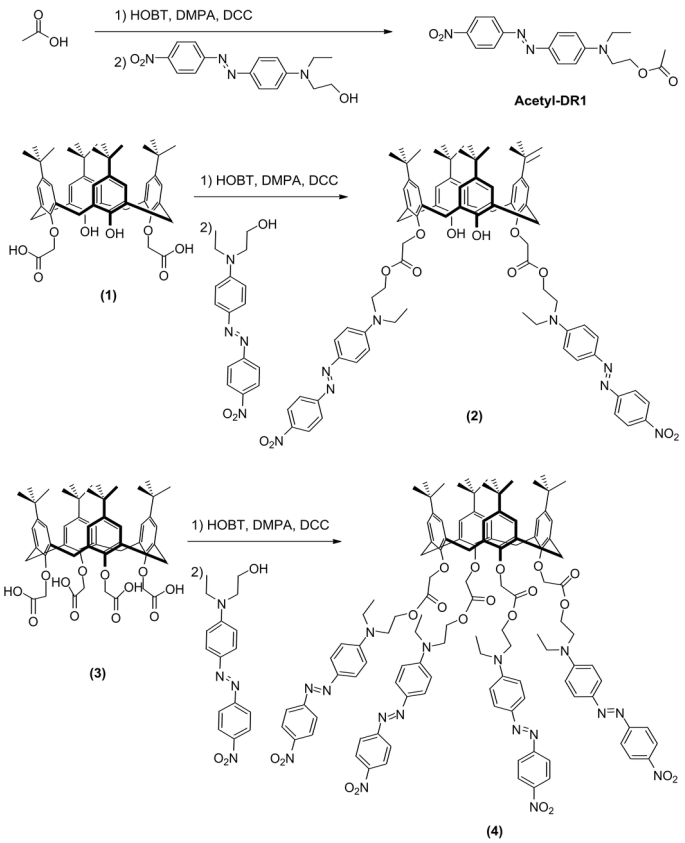
chromophores with the aim to avoid (or at least minimize) interchromophoric interactions.



((Insert Scheme here. **Note:** Please do **not** combine scheme and caption in a textbox or frame))

Scheme 1.

Results and Discussion

Synthesis

The calix[4]arene is a versatile scaffold which can be readily functionalized.[14] Acids **1** and **3** were prepared using described procedures that involve the reaction of calix[4]arene with ethylbromoacetate under basic conditions[15] and subsequent hydrolysis of the resulting esters.[16]

Following the experimental procedure described by Hudhomme, [17] esterification of acetic acid, **1**[18] and **3**[19] with **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 worthy to note that although **Acetyl-DR1** has been previously prepared[20] it was not completely characterized.

Nuclear Magnetic Resonance Spectra

The calix[4]arene assemblies **1**, **2**, **3** and **4** were characterized by NMR spectroscopy. The diasterotopic 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** shows a $\Delta\delta$ = 1.23[18a] and this value decreases for calix[4]arene diester **2** to $\Delta\delta$ = 1.06 which shows that the phenol units are more flattened because of the steric crowding among the DR1 groups on the narrow, lower rim. An analogous variation of 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).

Electronic absorption spectra

The linear optical properties of **DR1**, **Acetyl-DR1** and calix[4]arenes **2** and **4** were studied by means of Ultraviolet-Visible (UV-VIS) spectroscopy in dichloromethane (Figure 1) and DMSO. 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 red shift of these absorptions on passing from dichloromethane to DMSO. This positive solvatochromic shift serves as an indicator of the increased dipole moment on excitation,[22] thus confirming the charge-transfer character of these transitions[23] and pointing out to a positive hyperpolarizability. The most noticeable feature of the UV-VIS spectra of these compounds is the blue shift of the charge-transfer 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, that there is not electronic interaction among

chromophores within the same molecule, these multichromophore systems can be studied in the framework of the exciton model.[24, 25] If we pay attention to molecule **2**, for composite double molecules having 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 maybe attributed to the large separation between the two chromophores in **2**, but the hypsochromic shift of **2** with respect to **DR1** remains unexplained using this simple approach. In order to get a better understanding of the optical behavior of these chromophores, we have performed density functional theory 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 neglect any through-space electronic interaction, since it has been reported [26] that above 7 Å chromophores behave as isolated moieties and molecular orbitals of the dimeric chromophores are sums and differences of nearly unperturbed monomer molecular orbitals.

The gas phase excitation energies calculated using the TD-DFT (time dependent Density Functional Theory) approach are approximately 0.2 eV and 0.3 eV higher than those measured in dichloromethane and DMSO respectively and are therefore in a reasonable agreement with experiment, taking into account the positive solvatochromism shown by these molecules. Furthermore, theoretical calculations reproduce the hypsochromic shift of **2** and **4** compared to **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 for the higher excitation energy of **2** compared to **DR1** can be found in the increased energy gap from the occupied to the unoccupied molecular orbitals involved in these electronic transitions. Acylation of the OH group in **DR1** causes the stabilization of both occupied and unoccupied molecular orbitals, 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 have synthesized **Acetyl-DR1**, which seems to be a more reliable monochromophoric model for **2** and **4**, and its measured absorption band is 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 geometry of **4** (Figure 2) shows that, in order to accommodate the four **DR1** units, this molecule adopts a pinched-cone conformation with interchromophore distances of c.a. 5 Å between 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[26] that energy changes in the lowest charge-transfer transitions are only observed at very low interchromophore distances (less than 3.3 Å). TD-DFT calculations on **4** predict a HOMO-LUMO gap of 2.95 eV and a lowest excitation energy of 2.81 eV that parallels the results obtained for **Acetyl-DR1** and **2**.

Nonlinear optical properties

The hyperpolarizabilities of the multichromophores **2** and **4** and their reference compound **DR1** were determined by EFISH with a fundamental wavelength of 1907 nm. Table 2 gives the $\mu\beta$ values obtained by EFISH measurements. It is observed that the $\mu\beta$ value is almost doubled when two **DR1** units are linked to calix[4]are **1** and almost quadruplicated when four **DR1** units are linked to calix[4]arene **3**.

In order to get further insight into the nonlinear optical properties of these compounds, we have also calculated the molecular hyperpolarizabilities of these compounds using the coupled perturbed Hartree-Fock (CPHF) method that yields the hyperpolarizability as the analytical second derivative of the dipole moment with respect to an electrical field. These calculations give rise to the $\mu\beta(0)$ values shown in Table 2 and, while they are somewhat overestimated, they reproduce reasonably well the experimental trend having in mind that conformational distribution and solvent effects have not been considered in the calculations.

In order to rationalize the nonlinear optical behavior of **2**, this molecule must be considered as a V-shaped (or Λ–shaped) chromophore.[27] As we have already discussed above, **2** presents two nearly degenerated excited states polarized orthogonally and these must contribute respectively to the two major components of the hyperpolarizability tensor β_{zzz} and β_{zyy}. 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:

$$\mu_z = 2\,\mu_1\,\cos\theta \qquad (\mathbf{1})$$

$$\beta_{zzz} = 2\,\beta_1\cos^3\theta,\ \beta_{zyy} = 2\,\beta_1\cos\theta\sin^2\theta \qquad (\mathbf{2})$$

Being μ_1 and β_1 the dipole moment and the hyperpolarizability of a single chromophore, respectively and θ the angle formed between the chromophore and the symmetry axis (z). The 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 as:

$$\beta_{vec} = \beta_z = \beta_{zzz} + \beta_{zyy} = 2\beta_1\,(\cos^3\theta + \cos\theta\sin^2\theta) = 2\beta_1\cos\theta \qquad (\mathbf{3})$$

The angle (θ) formed between each chromophore and the z axis in the optimized geometry of **2** is 41.4º, and therefore this simple additive model predicts $\mu_z = 2\,\mu_1\cos(41.4) = 1.5\,\mu_1$ and $\beta_{vec} = 2\,\beta_1\cos(41.4) = 1.5\,\beta_1$ giving rise to a measurable $\mu_z\beta_{vec} = 2.25\mu_1\beta_1$.

Comparing the $\mu\beta(0)$ values of **DR1** and **2** obtained both experimentally and theoretically, it can be seen that there is almost a two-fold increase that is not far from the estimated value obtained with the simple addition model; furthermore a comparison to the calculated dipole moment and hyperpolarizability of **Acetyl-DR1** (μ_0 = 8.93 D, $\beta_{vec}(0) = 71\cdot10^{-30}$ esu, $\mu\beta(0) = 590\cdot10^{-48}$ esu) show a nearly perfect 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 in the molecular hyperpolarizability.

The optimized geometry of **4** shows a pinched-cone conformation with the two cone chromophore groups forming an angle of θ = 59.4º with the symmetry axis, while the pinched ones form an angle φ = 24.8º. Adding the contribution of each of the **Acetyl-**

DR1 moieties in **4**, the resulting dipole moment and β_{vec} should be:

$\mu = 2\mu_1 \cos\theta + 2\mu_1 \cos\varphi = 2\mu_1 (\cos\theta + \cos\varphi) = 2.84\mu_1$. (**4**)
$\beta_{vec} = 2\beta_1 \cos\theta + 2\beta_1 \cos\varphi = 2\beta_1 (\cos\theta + \cos\varphi) = 2.84\beta_1$. (**5**)

Thus, by simply adding the contribution of the four chromophores in 4, the measured $\mu\beta$ should be around 8 (=2.84^2) times the $\mu\beta$ value of a single chromophore.
Comparing the experimental measurements, it can be seen that there is only a four-fold increase in the $\mu\beta(0)$ value on passing from **DR1** to **4** which is half the estimated increase adding the contribution of the four chromophores in the molecule. And similar results are obtained from CPHF calculations predicting that the NLO response of 4 is less than three times that of **DR1** and less than four times that of **Acetyl-DR1**. 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 in the hyperpolarizability and therefore, the increased $\mu\beta(0)$ is mainly a consequence of the larger dipole moment. It is worthy to note that while the interchromophore distances 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** that cause a decreased contribution of these transitions to the hyperpolarizability.

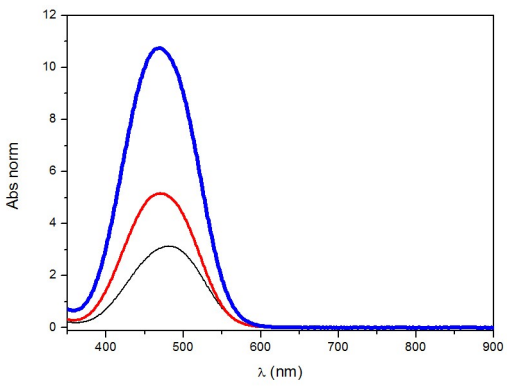
Scheme 1.

Table 1. Experimental and theoretically calculated UV-VIS absorption data

	experimental							theoretical				
	CH_2Cl_2			DMSO				B3LYP/6-31G*				
	λ_{max}[a]	E_{01}[b]	log ε	λ_{max}[a]	E_{01}[b]	log ε	symmetry	λ_{max}[a]	E_{01}[b]	$\Delta\mu_{01}$[c]	f	major contributions[d]
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] nm [b] eV [c] Debye [d] H:HOMO, L:LUMO

Figure 1. UV/VIS spectra of —Disperse Red 1 (**DR1**), –calixarene **2** and –calixarene **4** in CH_2Cl_2



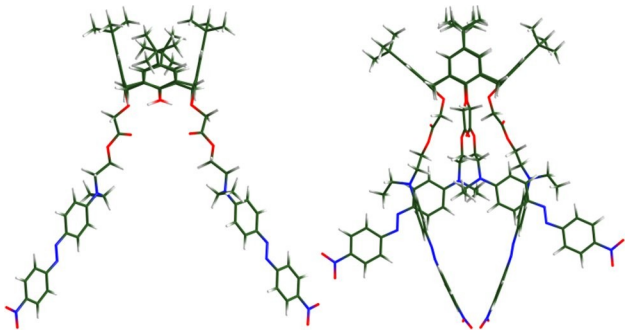


Figure 2. B3LYP/6-31G* Optimized geometries of **2** (left) and **4** (right).

Table 2. NLO Properties

	Experimental[a]		CPHF/6-31G*		
Compound	**μβ**[b]	**μβ(0)**[b]	**μ(D)**	**$\beta_{vec}(0)$**[c]	**μβ(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] 10^{-30} esu.

Conclusion

To sum up, lower rim functionalization of calix[4]arene constitutes a new approach to the synthesis of multichromophoric NLO active molecules. The nonlinear optical 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 have been avoided in the disubstituted derivative **2** by keeping large interchromophore distances, and therefore, the molecular hyperpolarizability resulted from the addition of the hyperpolarizabilities of single chromophores. However, due to its flexibility, tetrasubstituted compound **4** adopts a pinched-cone conformation whose cone chromophores 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. In order to minimize interchromophore interactions in tetrasubstituted calix[4]arenes, we propose the use of larger and more rigid spacers among the calix[4]arene scaffold and the chromophores linked to it to avoid conformations that could bring the chromophores together.

Experimental Section

General Experimental Methods. Infrared spectra were carried out in nujol mulls using a Fourier Transform Infrared spectrometer. Melting points are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded at 400 MHz and 100 MHz, respectively; δ values are given in ppm (relative to TMS) and *J* values in Hz. High resolution electrospray (ESI) mass spectra were acquired on a Q-ToF instrument using sodium formate clusters as a reference for accurate mass measurements. MALDI-ToF Mass spectra were recorded using dithranol as matrix and the sodium adducts of Polyethylene glycol (PEG) as internal reference for accurate mass measurements.

NLO measurements. Electric Field Induced Second Harmonic (EFISHG) measurements were performed using the fundamental radiation at 1.9 μm obtained from a H_2 Raman cell excited by a Q-switched Nd:YAG laser (1064 nm). The repetition rate was 10Hz and the pulse width 8 ns. A computer controlled NLO spectrometer completes the SHG experimental set-up. The 1.9 μm polarized light is split in two beams. The less intense one is directed to a N-(4-nitrophenyl)-(L)-prolinol (NPP) powder sample whose SH signal is used as 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 are measured with two photomultipliers. Interference filters are used to remove the residual excitation light beyond the sample and the NPP reference. Static $\mu\beta(0)$ values are deduced from the experimental values using a two level dispersion model.

Computational methods. All theoretical calculations were performed by using the Gaussian 09[29] program. The molecular geometries were optimized using the hybrid B3LYP[30] functional and the 6-31G(d)[31] basis set. The same model chemistry was used in 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 Coupled Perturbed Hartree Fock Method (CPHF) using the HF/6-31G(d) model chemistry and the default parameters provided by the "polar" keyword. The default Gaussian 09 parameters were used in every case.

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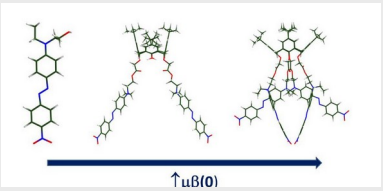

Raquel Andreu,[a] Santiago Franco,[a] Javier Garín, [a] Judith Romero,[a] Belén Villacampa,[b] María Jesús Blesa,[a] Jesús Orduna*,[a]*

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

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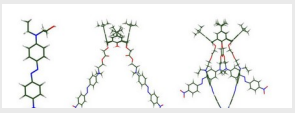

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