

Tetraalkynyl calix[4]arenes with advanced NLO properties†

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Rigid, highly conjugated tetraalkynyl-calix[4]arenes synthesised via Sonogashira coupling give rise to improved second-order hyperpolarizability values as determined by hyper-Rayleigh scattering—a technique that in addition to X-ray crystallography also allows for the conformational analysis of the calixarene structures in solution.

Calixarenes, a benchmark in supramolecular chemistry,¹ have gained increasing attention over the years in the field of nonlinear optics (NLO).² The stable, cooperative orientation of NLO-active molecules in the bulk phase, essentially avoiding the antiparallel alignment of dipolar molecules, is a fundamental requirement for the successful construction of NLO materials. Increasing the bulkiness of the dipolar building blocks is a common approach to prevent the relaxational loss of an induced macroscopic order in *e.g.* a polymer matrix.³ In a first approximation,⁴ a suitably donor(D)–acceptor(A) functionalized calixarene can be considered as an ensemble of virtually independent chromophores held together in a well defined, rigid conformation.⁵

In particular, D–A-calixarenes with extended π -conjugation show superior NLO-performance in terms of high hyperpolarizability values.^{4,6} In spite of the general interest in rigid expanded deep cavitands,⁷ the usefulness of the Sonogashira coupling⁸ has been exploited in surprisingly few cases to access acetylene-extended calixarenes.⁹

The tetraalkynyl-calix[4]arenes **2–4** are obtained in good yields by coupling of tetraiodo-calix[4]arene **1**¹⁰ with three different ethynyl compounds (Scheme 1). The K_2CO_3 -promoted desilylation of **4** gives calixarene **5** in 77% yield. This tetraethynyl derivative constitutes an intriguing building block for the design of more

complex supramolecules, the synthesis of which is subject of ongoing research. For all calixarenes the cone-conformation in solution is clearly confirmed by ¹H and ¹³C NMR spectroscopy.

Furthermore, single-crystal X-ray structural analysis confirmed the expected structure of **2** with a pinched conical shape (Fig. 2). Compound **2** crystallized as a 2½ toluene solvate in the centrosymmetrical space group $C2/c$.[‡] The tetrahedral angle between a central axis z perpendicular to the calixarene rim and the two different toluene subunits in the 1,3- and 2,4-position is roughly 106° and 0°, respectively. The neighboring *p*-nitro aromatic rings are not completely face to face orientated having an approximate 60° twist angle and a shortest C–C distance of 3.7 Å. Neither in the single molecule nor in the crystal packing do we observe the typical distances indicative for attractive interactions such as π -stacking.

The linear and second-order nonlinear optical properties of the arylalkynyl derivatives **2** and **3**, and of toluene model compound **7**,¹¹ are studied by UV-VIS absorption spectroscopy and hyper-Rayleigh scattering (HRS),¹² respectively. To be able to assess the

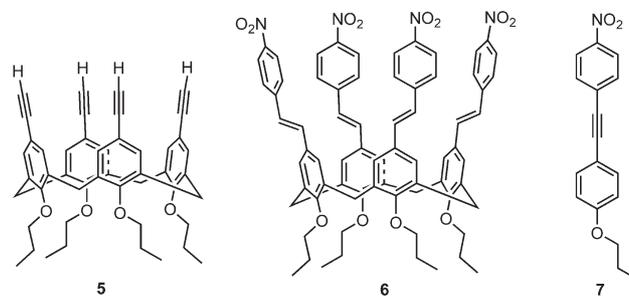
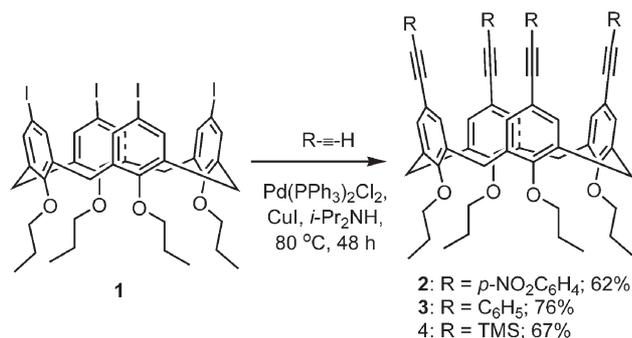


Fig. 1



Scheme 1

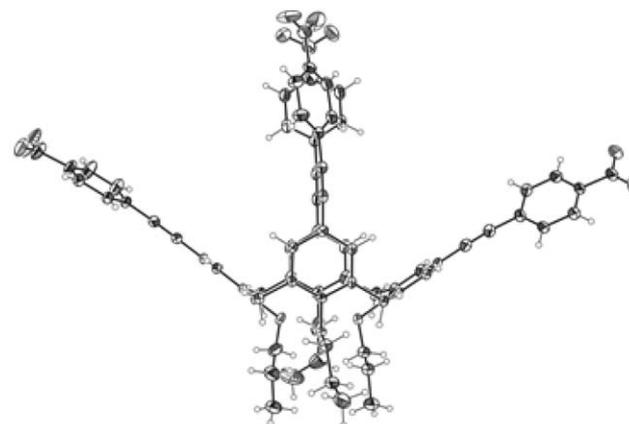


Fig. 2 Ortep plot of **2**.

† Electronic supplementary information (ESI) available: general methods, synthesis and characterization of **2–5**. See <http://www.rsc.org/suppdata/cc/b5/b502045j/>

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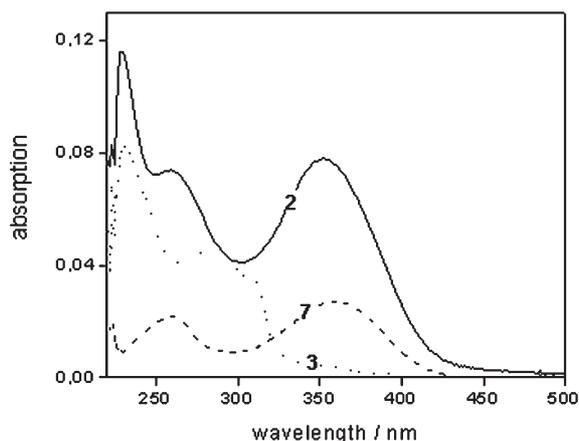


Fig. 3 UV-visible absorption spectra of **2**, **3**, and **7** in CH_2Cl_2 , $c = 1.0 \mu\text{mol L}^{-1}$.

solution phase molecular structure of these calixarene motives, total intensity HRS and HRS depolarization ratios have been determined on these compounds. The retrieved hyperpolarizability tensor components are compared with the hyperpolarizability as determined by Electric-Field-Induced Second-Harmonic Generation (EFISHG) for the analogous tetravinylcalix[4]arene **6**.⁴

The linear absorption spectra confirm the strong charge-transfer contribution to the optical properties in the nitro-substituted arylalkynyl compounds **2** and **7** (λ_{max} = at 348 and 357 nm, respectively). Without this strong electron-withdrawing moiety, as in calixarene **3**, the charge-transfer absorption band is at 290 nm (Fig. 3). From the small blue shift of the CT band for the calixarene *versus* the linear model compound, it can already be inferred that the dipolar axes of the chromophoric moieties in the cone are oriented in the same direction. The results of the HRS experiments (depolarization ratio ρ and major tensor component $\beta_{\text{zzz},800}$) are given in Table 1. Compound **3**, without the nitro substituents, exhibits significant (multiphoton) fluorescence. (quantum yield $\Phi_{\text{fluo}} = 0.005$). The nitro-substituted compounds **2** and **7** are practically non-fluorescent. With the femtosecond HRS setup with frequency-dependent amplitude and phase delay for the multiphoton fluorescence *versus* the nonlinear scattering, it is possible to retrieve an accurate fluorescence-free hyperpolarizability value together with the fluorescence lifetime (τ_{fluo}) for compound **3**. From the spectral position of the CT band and by applying the two-level model, we arrive at the static hyperpolarizability value $\beta_{\text{zzz},0}$ corrected for resonance enhancement.

The large depolarization ratios ρ for the nitro-substituted calixarenes, close to the value of 5 for pure dipolar compounds with only diagonal hyperpolarizability tensor components,¹³ allow for the analysis towards a single major β_{zzz} component. The low

Table 1 Data from absorption, fluorescence, and NLO spectroscopy

	λ_{max} (nm)	Φ_{fluo} (ns)	τ_{fluo}	ρ	$\beta_{\text{zzz},800}$ ($\times 10^{-30}$ esu)	$\beta_{\text{zzz},0}$ ($\times 10^{-30}$ esu)
2	348	^a	^a	4.96 ± 0.09	530 ± 20	105 ± 4
3	290	0.005	3	1.11 ± 0.01	80	33
7	257	^a	^a	4.02 ± 0.09	340 ± 40	55 ± 6

^a Not determinable.

value for ρ for the fluorescent compound **3** is due to the depolarization of the light emitted with a relaxation time of 3 nanoseconds. This very low value cannot be an indication of off-diagonal contributions. Our values for **2** and the model compound **7** are in good agreement with earlier reported EFISHG results for the corresponding vinyl versions,⁴ yet they combine this with an increased transparency window. The non-resonant $\beta_{\text{zzz},0}$ value for compound **6** is 116×10^{-30} esu, calculated from the reported β_{zzz} value of 142×10^{-30} at 1910 nm and the CT band at 377 nm, and is within experimental error identical with the $\beta_{\text{zzz},0}$ value for compound **2**. However, the CT band for **2** is blue shifted with respect to **6** and ensures better transparency in the blue.

From the value of 4.96 ± 0.09 for ρ for calixarene **2**, and the conclusion that there is only a single diagonal β_{zzz} tensor component present, a simple vector model permits the study of the orientation of the individual dipolar subunits in the cone. Based on the average C_{4v} symmetry as observed in NMR experiments, we take θ as the angle between the dipolar molecular axis z of **2** and the 4 constituting subunits. Then, $\beta_{\text{zzz,calixarene}} = 4\beta_{\text{zzz,subunit}} [\cos \theta]^3$. From this, we obtain, based on the HRS results, an average value of 43° for this angle θ . Note that if this value were 0° , then $\beta_{\text{zzz,calixarene}} = 4\beta_{\text{zzz,subunit}}$. Since the dipolar subunits are not completely parallel, there is partial cancellation along the non-dipolar molecular axes, resulting in an enhancement factor for the first hyperpolarizability smaller than 4.

In conclusion, compound **2** displays advanced NLO properties among the expanded calix[4]arenes studies. HRS is employed for the first time to elucidate the conformation of these highly dynamic systems. As a particularly interesting parameter, the dihedral “opening” angle can be determined in solution. The solution based value of 43° is in good agreement with an average angle of 53° in the solid state, attributing the difference of the two values to the crystal packing.

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Notes and references

‡ Crystal data for **2**: $\text{C}_{72}\text{H}_{60}\text{N}_4\text{O}_{12} \cdot 2\frac{1}{2} \text{C}_7\text{H}_8$, $M = 1403.58$, monoclinic, $a = 29.410(3)$, $b = 17.1574(19)$, $c = 31.210(4)$ Å, $\beta = 108.879(3)^\circ$, $V = 14902(3)$ Å³, $T = 100(2)$ K, space group $C2/c$ (no. 15), $Z = 8$, $\mu = 0.083 \text{ mm}^{-1}$, 70045 reflections collected, 15670 independent reflections ($R_{\text{int}} = 0.1017$) which were used in all calculations. Final $R_1 = 0.0879$ and $wR_2(F^2) = 0.2188$ (observed data). CCDC 264208. See <http://www.rsc.org/suppdata/cc/b5/b502045j/> for crystallographic data in CIF or other electronic format.

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