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### Article

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# Intramolecular Cooperative Effects in Multichromophoric Cavitands Exhibiting Nonlinear Optical Properties

Zsolt Csók,<sup>a</sup> Tímea Kégl,<sup>b,c</sup> Péter Szuroczki,<sup>b</sup> László Kollár,<sup>b,c</sup> Hoang Minh Ngo,<sup>d</sup> Isabelle Ledoux-Rak,<sup>d</sup> Naidel Caturello,<sup>a</sup> Rodrigo Q. Albuquerque<sup>a</sup>

<sup>a</sup>São Carlos Institute of Chemistry, University of São Paulo, Av. Trab. São-carlense 400, 13560-970 São Carlos (SP), Brazil; <sup>b</sup>Department of Inorganic Chemistry and MTA-PTE Research Group for Selective Chemical Syntheses, University of Pécs, Ifjúság 6, H-7624 Pécs, Hungary; <sup>c</sup>János Szentágothai Research Center, Ifjúság 20, H-7624 Pécs, Hungary; <sup>d</sup>Quantum and Molecular Photonics Laboratory (LPQM-ENS), 61. Avenue du Président Wilson, F-94230 Cachan, France

**KEYWORDS:** Cavitand; Hyperpolarizability; Multichromophores; Nonlinear Optics; Sonogashira-coupling; Molecular Modeling

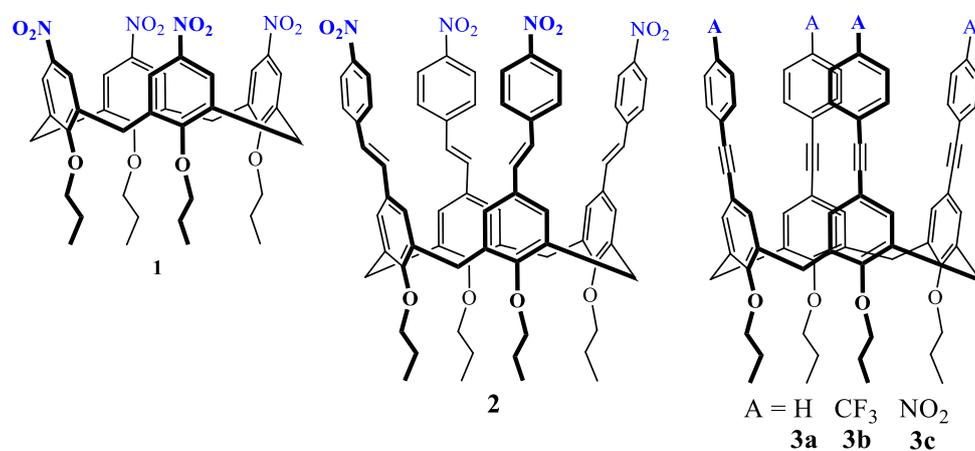
## ABSTRACT

We report on the design, synthesis and characterization of a new class of multichromophoric cavitands based on resorcin[4]arenes. The novel compounds have exhibited high values of second-order nonlinear optical (NLO) properties, as evidenced by electric field-induced second harmonic generation (EFISHG) measurements. We proved for the first time that the gain in the quadratic hyperpolarizabilities of multichromophoric NLO macrocycles, originating from the near parallel orientations of the subchromophores, can be partially suppressed if the distance between the dipolar subunits falls into a specific range, where intramolecular cooperative and/or collective effects are operative. Our findings may contribute to the smart design of new molecular materials with promising NLO properties.

## 1. INTRODUCTION

Organic molecules exhibiting high second-order nonlinear optical (NLO) properties contain both electron-donating and electron-withdrawing groups connected via a conjugated  $\pi$ -system (D- $\pi$ -A molecules).<sup>1</sup> These compounds are promising candidates for various NLO applications such as optical communication (signal processing, frequency generation), optical data storage, electronic and photonic devices and quantum machines.<sup>1a-c</sup> The key feature of second-order NLO-active molecules is a non-centrosymmetric, highly polarizable structure that is expressed by the second-order (quadratic) nonlinear polarizability or the *first hyperpolarizability* tensor ( $\beta$ ). Since the quadratic hyperpolarizability increases almost linearly with the number of chromophores,<sup>2</sup> the preparation of multichromophoric systems favoring an intramolecular non-centrosymmetric order is an attractive way to attain remarkable NLO activities.

Donor-acceptor functionalized calix[4]arenes, pioneered by Reinhoudt *et al.*,<sup>3</sup> gave rise to multichromophoric materials with advanced NLO properties.<sup>4</sup> Some illustrative examples are depicted in Chart 1: tetra(nitro)calix[4]arene (**1**), tetrakis(nitrostilbene)calix[4]arene (**2**), tetrakis(phenylethynyl)calix[4]arene (**3a**), tetrakis(4-trifluoromethylphenylethynyl)calix[4]arene (**3b**) and tetrakis(4-nitrophenylethynyl)calix[4]arene (**3c**).



**Chart 1.** Typical examples of conjugated calix[4]arenes displaying enhanced NLO activities.

Calixarenes display a certain degree of conformational mobility in solution, even if a relatively stable cone conformation is adopted.<sup>5</sup> The rotation around the methylene bridges generates a “breathing” motion that leads to a dynamic equilibrium between the two possible terminal positions of the phenolic subunits. Although large hyperpolarizabilities are expected from the intramolecular order exhibited by these compounds, the conformational mobility in solution causes non-parallel orientations of the dipolar subunits. Hence, the increase/decrease of the cone opening angle may cancel, at least partially, the increase of the  $\beta$  value of the multichromophoric molecule along the dipolar axis. Similarly, the relative orientation of the single NLO-active subunits was found to be the key factor for controlling the second-order NLO properties of cyclotetrasiloxane macrocycles decorated with four push-pull organic polar tails.<sup>1e</sup> Since these multichromophoric materials have been regarded as a collection of *isolated subchromophores*, their NLO behaviors were explained by the additive oriented-gas model, in which intramolecular interactions are fully neglected. In accordance with this approximation, the quadratic hyperpolarizability of a multichromophoric system ( $\mu\beta_{multi}$ ) in the direction of the dipole axis can be simply expressed as a vector summation of the individual contributions of all NLO activities of the *non-interacting* monochromophoric subunits ( $\mu\beta_{mono}$ ):<sup>1e, 3d</sup>

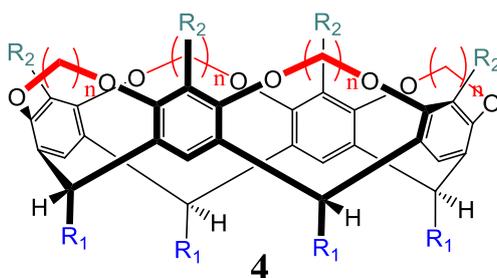
$$\mu\beta_{multi} = N^2 (\cos^4 \theta) \mu\beta_{mono} \quad (Eq. 1),$$

where  $N$  is the number of the chromophoric subunits;  $\theta$  is the *opening angle*, *i.e.*, the angle between the individual monochromophoric subunits and the dipole axis of the multichromophoric molecule.

In a seminal theoretical work,<sup>6</sup> Datta *et al.* critically investigated the validity of the oriented-gas behavior of **3c** using an essential-state model developed for *interacting* polarizable molecules of push-pull chromophores<sup>7</sup>, supported by density functional theory calculations. The NLO properties of these calixarenes were found to be far from additive: the

hyperpolarizabilities were suppressed with respect to the prediction of the oriented-gas model. The maximum damping in  $\beta$  was observed for the conformer in which the orientations of the dipolar subunits are completely parallel ( $\theta = 0^\circ$ ). For this conformation, the model predicted a reduction of up to 30% from the oriented-gas model. This non-additive NLO behavior was clearly explained by the effects of intramolecular electrostatic interactions between the dipolar subchromophores. Furthermore, previous theoretical investigations on each conformer of **1**<sup>8a</sup> as well as on the supramolecular dimers of *para*-nitroanilines<sup>8b</sup> have revealed that the hyperpolarizabilities decrease for the distances in the “*destructive*” range of 3.5-9.0 Å due to *face-to-face interactions* between the aromatic  $\pi$ -systems.

Resorcin[4]arenes, representing another fascinating class of molecular hosts, are acid-catalyzed condensation products of resorcinol and aldehydes.<sup>9</sup> The enhanced rigidity of cavitands (**4**) based on resorcin[4]arenes originates from an additional *intramolecular* covalent bridging ( $n = 1, 2, 3$ ) between the vicinal, phenolic OH groups (Chart 2).<sup>10</sup> The variation of the  $R_1$  group at the lower rim (‘feet’) and  $R_2$  at the upper rim of the cavitand enables one to access a wide range of interesting derivatives.



**Chart 2.** General molecular structure of cavitands based on resorcin[4]arenes, where  $n = 1, 2, 3$ .

It has been recently demonstrated that a tetraiodocavitand (**4**,  $n = 1$ ,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{CH}_2\text{O}-4\text{-I-C}_6\text{H}_4$ ) precursor has opened up new possibilities for the preparation of deep cavitands. For example, palladium-catalyzed cross-coupling and carbonylation reactions as

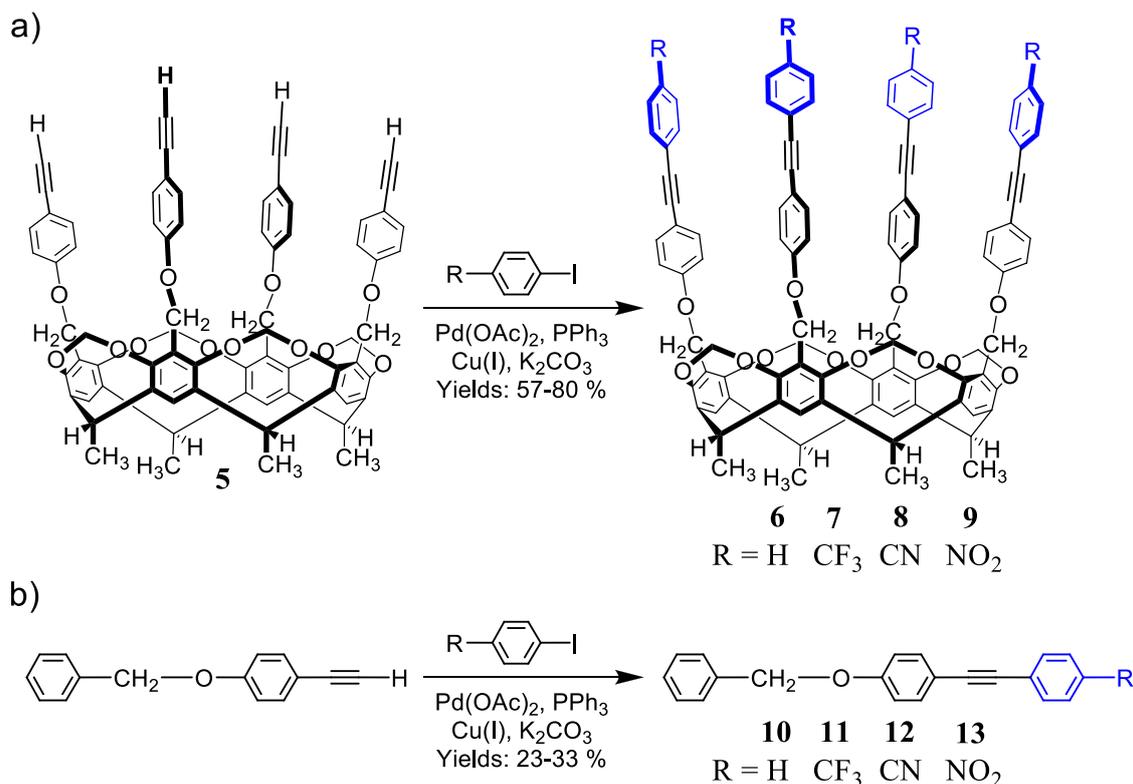
well as copper-catalyzed azide-alkyne cycloadditions (CuAAC) were shown to be excellent synthetic tools for the molecular enlargement of the cavitand scaffold.<sup>11</sup>

In this work, we aim at investigating quantitatively the validity of the theoretical gas-oriented model described in ref. 6 in the prediction of NLO properties of multichromophoric cavitands based on resorcin[4]arenes (Chart 2). For this reason we designed and synthesized a series of cavitands with four push-pull subchromophores aligned in a parallel fashion and bearing different electron-donor and electron-withdrawing substituents. The novel molecules are also characterized by molecular modeling techniques, and their NLO properties are evaluated by electric field-induced second harmonic generation (EFISHG) measurements. The synthesized cavitands are new alternatives to traditional calix[4]arenes since they are able to keep the relative alignment of the four subchromophoric building blocks nearly parallel to obtain multichromophoric systems exhibiting enhanced NLO properties. To the best of our knowledge, this work shows for the first time the design of NLO-active cavitands based on the optimization of both the intramolecular chromophore order and the interdipolar opening angle.

## 2. EXPERIMENTAL AND THEORETICAL METHODS

*Synthesis and Characterization.* In this study, tetra(ethynyl)cavitand (**5**)<sup>11d</sup> was used as substrate in fourfold Sonogashira-reactions to access multichromophoric NLO cavitands (**6-9**). Cavitand **5** was reacted with iodobenzene or *para*-substituted iodobenzenes (4-iodobenzotrifluoride, 4-iodobenzonitrile, 1-iodo-4-nitrobenzene) in the presence of copper(I)iodide, potassium carbonate and Pd(OAc)<sub>2</sub> + 2 PPh<sub>3</sub> *in situ* catalytic system (Scheme 1). to yield compounds 6-9. Reference compounds (**10-13**) were also synthesized, as shown in Scheme 1. The novel D- $\pi$ -A functionalized cavitands were fully characterized by state-of-the-art techniques, such as <sup>1</sup>H and <sup>13</sup>C NMR and high-resolution mass spectrometry. The

quadratic hyperpolarizabilities were measured using the electric-field induced second harmonic generation (EFISHG) technique, which is fully described in the Supporting Information (SI). The description of the detailed synthetic procedures and the full characterization of the novel compounds are also given in the SI.



**Scheme 1.** Synthesis of a) the multichromophoric cavitands **6-9** and b) the monochromophoric reference compounds **10-13** via Sonogashira-coupling reactions.

*Computational Details.* Optimized geometries of compounds **6-8** and **10-12** were obtained by carrying out a conformational search using the Schrödinger suite [] with the force field MM3, followed by the use of the semiempirical PM6 Hamiltonian method.<sup>12a</sup> The solvent effect was also considered in the semiempirical calculations by the application of the COSMO model (solvent = bla),<sup>12b</sup> and the first hyperpolarizabilities and dipole moments were predicted and compared with the experimental values. Further details about the theoretical procedure, together with all optimized structures are shown in the SI.

### 3. RESULTS AND DISCUSSION

All reactions afforded cleanly the expected products (**6-9**) in good yields (57-80 %). The synthetic strategy used here (Scheme 1) has enabled one to achieve a rapid diversification of this cavitand family by implementing electron-withdrawing groups (CF<sub>3</sub>, CN and NO<sub>2</sub>) at the upper edge of the conjugated  $\pi$ -system. In contrast to the calixarene-based compounds (**1-3**), the macrocyclic ring itself is not part of the extended multichromophoric system, but it simply provides a rigid molecular scaffold to which the four dipolar NLO subunits are directly attached. Using analogous synthetic protocols, the corresponding monochromophoric reference compounds (**10-13**) were also synthesized from the commercially available 4-ethynyl-1-benzyloxybenzene (Scheme 1). These model compounds have structural motives identical to those of the individual chromophoric subunits in each corresponding cavitand product.

The novel cavitands **7** and **8** show a small blue shift in their UV-Vis spectra when compared to their monomeric reference compounds **11** and **12** (Table 1 and SI), thus maintaining the transparency window in the visible spectral region and the possible applicability of these materials. This hypsochromic shift is indicative of intramolecular interactions or aggregation effects between the subchromophores within these multichromophoric systems.<sup>8a,13</sup> The quadratic hyperpolarizabilities ( $\mu\beta$ ) of both the macrocyclic chromophores and the reference model compounds were evaluated by EFISHG with a fundamental wavelength of 1910 nm.<sup>14</sup> The second harmonic response of the tetrakis(4-nitrophenylethynyl)cavitand (**9**), which accommodates groups with the strongest electron-withdrawing effect, could not be determined due to its limited solubility in organic solvents.

**Table 1. Maximum Absorption Wavelengths, Experimental and Theoretical (Gas-Oriented Model) Static Quadratic Hyperpolarizabilities, Calculated Dipole Moments and Average Opening Angles Obtained from MM.**

	Experimental		Molecular Modeling <sup>b</sup>				Gas-Oriented Model
Compound (R)	$\lambda_{max}$ (nm)	$\mu\beta_0^a$ ( $10^{-48}$ esu)	$\mu$ ( $10^{-18}$ esu)	$\beta_0$ ( $10^{-30}$ esu)	$\mu\beta_0$ ( $10^{-48}$ esu)	$\theta_{avg}$ (°)	$\mu\beta_0$ ( $10^{-48}$ esu)
<b>6</b> (H)	291	320	1.9	26	49	0.3	368
<b>7</b> (CF <sub>3</sub> )	298	320	17.6	20	352	4.5	479
<b>8</b> (CN)	315	360	21.2	37	784	17.2	799
<b>10</b> (H)	291	23	2.2	8	18	n.a.	n.a.
<b>11</b> (CF <sub>3</sub> )	300	30	1.6	18	29	n.a.	n.a.
<b>12</b> (CN)	319	60	3.8	17	65	n.a.	n.a.

<sup>a</sup>EFISHG with a fundamental wavelength of 1910 nm; all measurements were performed in CHCl<sub>3</sub> at room temperature; the relative experimental error for the  $\mu\beta_0$  values is 10%; n.a. = not applicable; <sup>b</sup> PM6 Method with solvent (COSMO).

The measured quadratic hyperpolarizabilities were corrected by a dispersion factor derived from a two-level model, which allows the determination of static quadratic hyperpolarizabilities.<sup>15</sup> The resonance-corrected  $\mu\beta_0$  values for compounds **6-8** and **10-12** are given in Table 1. Cavitand **6**, lacking acceptor groups at the end of its conjugated  $\pi$ -system, shows a  $\mu\beta_0$  value of  $320 \times 10^{-48}$  esu. The incorporation of neither trifluoromethyl nor nitrile groups increased significantly the quadratic hyperpolarizabilities:  $\mu\beta_0$  values of  $320 \times 10^{-48}$  esu and  $360 \times 10^{-48}$  esu were obtained for cavitands **7** and **8**, respectively. In contrast, the  $\mu\beta_0$

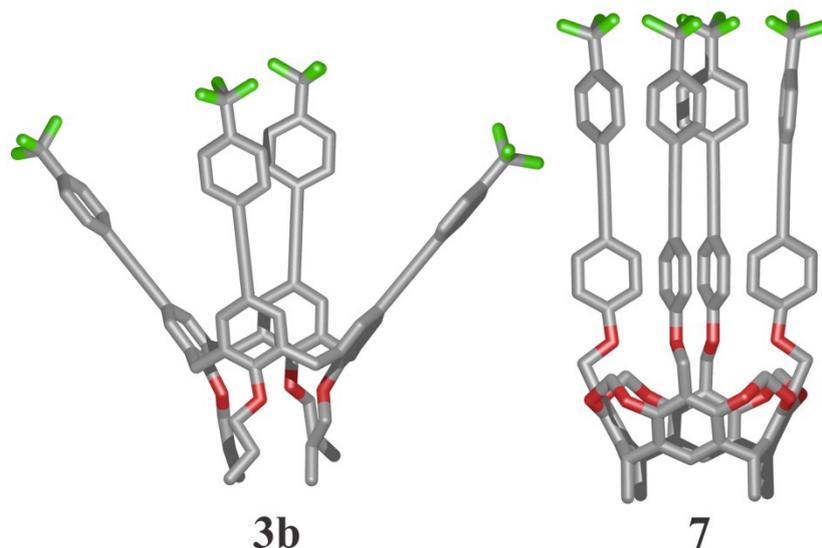
values of the corresponding reference compounds **10-12** increase with the inclusion of electron-withdrawing groups. An enhancement factor of 3.5 *per chromophore* was calculated for compound **6**, which is among the highest values observed for multichromophoric NLO macrocycles (the maximum theoretical enhancement is 4).

Semiempirical PM6 calculations were carried out for the new compounds as described in the Supporting Information. The calculations revealed that the average opening angle ( $\theta_{avg}$ ) is very small for compounds **6** ( $0.3^\circ$ ) and **7** ( $4.5^\circ$ ), which indicates a nearly parallel alignment of the four subchromophoric building blocks in these new derivatives. On the other hand, the aperture angle is somewhat higher ( $17.2^\circ$ ) for cavitand **8**, as shown in Table 1. The average dihedral angles between the various pairs of the neighboring rings are  $64^\circ$ ,  $76^\circ$  and  $79^\circ$  in the *middle* row, while  $71^\circ$ ,  $73^\circ$  and  $84^\circ$  in the *upper* row of phenyls for cavitands **6**, **7** and **8**, respectively. The average shortest distances between the aromatic carbon atoms of the neighboring subchromophores of the same cavitand were found to be 3.59, 3.60 and 4.39 Å for the *middle* row of aromatic rings of cavitands **6**, **7** and **8**, respectively. The same distances for the *upper* row of phenyl rings were 3.64, 3.71 and 6.87 Å for **6**, **7** and **8**, respectively. The side view and top view of middle-row aromatic rings obtained from the PM6-optimized structure of **7** are shown in Fig. blabla, from where the intramolecular interactions can be easily identified. Therefore, the observed short non-contact distances, which are combined with the nearly perpendicular arrangements of the neighboring aromatic rings, suggest that *edge-to-face T-shaped interactions* are the major forces that stabilize these new multichromophoric NLO cavitands in their conformations.<sup>16</sup> The self-organization of the aromatic building blocks on the different levels of the extended  $\pi$ -system results in highly ordered arrangements for these molecules. Similarly, both X-ray crystallographic studies and

gas-phase theoretical calculations revealed the presence of weak perpendicular T-shaped interactions between the upper phenyl rings of a related deepened cavitand.<sup>11a</sup>

The (PM6??)-calculated  $\beta_0$  values are similar for cavitands **6-8**, while the computed  $\mu$  values are significantly enhanced for **7** and **8** when compared to **6**, to which no electron-withdrawing groups are connected (Table 1). Therefore, the considerable improvement in the theoretical quadratic hyperpolarizabilities ( $\mu\beta_0$ ) obtained for **7** and **8** is predominantly due to a large increase in their dipole moments. It is important to note that, for the monochromophoric model compounds **10-12**, the calculated  $\mu\beta_0$  values are in very good agreement with the results of the experimental measurements.

For comparison, we also computed the energy-minimized structures for the calix[4]arenes analogues **3a-c** (see SI). In accordance with the reported X-ray structures, all these derivatives adopt a typical pinched cone conformer, where two opposite subunits in the 1,3-positions are almost parallel, while those in the 2,4-positions bend out with an approximate angle of 45°. The authors claimed that neither in the single molecule nor in the crystal packing the typical distances indicative for attractive interactions such as  $\pi$ - $\pi$  stacking were observed.<sup>4</sup> The energy-minimized structures of the trifluoromethyl derivatives **3b** and **7** are given in Figure 1, which shows marked differences between their structural geometries. For instance, the average opening angles were found to be 24° and 4.5° for calixarene **3b** and cavitand **7**, respectively. Therefore, the contribution of intramolecular interactions to the control of the NLO response may be more effective in the newly developed cavitands **6-9** than in classical calixarenes due to the more parallel orientations of the four monochromophoric subunits.



**Figure 1.** Energy-minimized structures of calixarene **3b** and cavitand **7**. Hydrogens are omitted for clarity.

Since the experimentally determined  $\mu\beta_{mono}$  values of the reference compounds were in excellent agreement with the (PM6??)-calculated ones, we can safely apply these values in *Eq. 1.*, together with the opening angles derived from the molecular modeling, in order to determine the quadratic hyperpolarizabilities of our multichromophoric cavitands based on the *gas-oriented model*.<sup>6</sup> According to this simple approximation, which neglects non-bonded electronic interactions between the individual NLO subunits,  $\mu\beta_{multi} = 368, 479$  and  $799 \times 10^{48}$  esu were calculated for compounds **6**, **7** and **8**, respectively (Table 1). The comparison of these values to the experimental ones revealed significant quenching (explain better...) in the quadratic hyperpolarizabilities for **7** (33 %) and **8** (55 %). On the contrary, cavitand **6** exhibiting much lower dipole moment showed a minor suppression (13 %) in its  $\mu\beta_0$  value.

Therefore, in full accordance with the prediction of the theoretical model in ref. 6, a decrease in the cone angle of the cavitand with respect to that of classical calixarenes is accompanied by an increase in the suppression of the quadratic hyperpolarizabilities. We show experimentally that this effect is particularly intensified when the monochromophoric

subunits are highly polar. The large deviation of the  $\mu\beta_0$  values from the simple additive oriented-gas model in compounds **7** and **8** may be attributed to intramolecular *cooperative* and/or *collective* effects. Due to repulsive interactions, the strongly polarizable monochromophoric subunits reduce their polarization ( $Z_{\text{solt}}$ , an electric field induces a polarization) in response to the electric field generated by other neighboring subchromophores in their close proximity.<sup>6,7,17</sup> In addition to this cooperative behavior, collective excitonic effects resulting from the interchromophoric delocalization of the excitation have also important consequences on the material properties. In the constrained geometry of cavitands, the delocalization of the exciton states gives rise to an increase of the optical gap, which is therefore responsible for the collective suppression of the NLO responses.<sup>6,7,17</sup>

#### 4. CONCLUSIONS

Highly conjugated, multichromophoric cavitand derivatives were synthesized via Sonogashira-coupling, whose constrained geometries were designed to decrease both the interchromophoric flexibility and the opening angle. Theoretical calculations based on the semiempirical PM6 model indicate the presence of edge-to-face T-shaped interactions between the aromatic building blocks within these multichromophoric systems, which is further supported by the detection of hypsochromic shifts. The quadratic hyperpolarizability values were experimentally determined by EFISHG for the novel donor-acceptor functionalized cavitands and for their corresponding monochromophoric reference compounds. We have proved for the first time that the gain in the quadratic hyperpolarizabilities of multichromophoric NLO macrocycles, originating from the near parallel orientations of the subchromophores, can be partially cancelled by damping effects. This non-additive behavior may arise from intramolecular cooperative and/or collective effects between the highly polar NLO tails. It is evident from this study that the elaborate

interplay of many different factors renders the rational design of new supramolecular NLO materials particularly difficult. Future designs will require not only the proper choice of dipolar building blocks and the smart optimization of structural geometries, *e.g.* the interdipolar opening angle, but it will also be essential to take into account the effect of through-space electrostatic and/or dispersion interactions between the monochromophoric subunits.

## ASSOCIATED CONTENT

### Supporting Information.

The description of the detailed synthetic procedures, the full characterization (including  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra) of the new compounds **7-13**, the details of the nonlinear optical measurements and the theoretical calculations as well as the optimized structures are available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

**Corresponding authors:** [zscsok@iqsc.usp.br](mailto:zscsok@iqsc.usp.br) (Z. Csók); [isabelle.ledoux@lpqm.ens-cachan.fr](mailto:isabelle.ledoux@lpqm.ens-cachan.fr) (I. Ledoux-Rak)

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