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DFT study of two-photon absorption of octupolar molecules

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Abstract

The two-photon absorption (TPA) properties of octupolar molecules based on a triphenyl-isocyanurate cyclotrimer, a 1,3,5-triphenyl-benzene or a triphenyl-triazine core were theoretically investigated using DFT and TD-DFT computations. These compounds are very promising regarding their potential application especially for optical limitation. These systems, which exhibit a three-fold axis, contain three arms with a terminal electron donating group linked in 1, 3 and 5 positions to the central $C_3N_3O_3$ isocyanurate, benzene or triazine ring. The SAOP functional and a DZP basis set were selected for the TPA computations. The so-computed TPA energies and cross sections are in good agreement with the observed data. Increasing the strength of the donor terminal group enhances the TPA cross-section values. The compound with triazine core presents the highest two photon cross-section value compared to the values found for the isocyanurate or the 1,3,5-phenyl core as central ring. Furthermore, this study brings to light a cooperative enhancement of the TPA property between the three arms attached to the isocyanurate ring.

Keywords Two-photon absorption – DFT – TDDFT – SAOP – Triphenyl-isocyanurate.

1 Introduction

The process of simultaneous two-photon absorption (TPA) is a nonlinear optical (NLO) phenomenon predicted theoretically by Maria Göppert-Mayer in 1931[1] and the first experimental evidence was performed by W. Kaiser and C. G. B. Garret [2] 30 years later. The TPA process has attracted growing attention due to its potential applications, among them three-dimensional optical storage [3-5], two photon-fluorescence imaging [6-8], two-photon photodynamic therapy [9] and optical limitation [10-11].

Over the past decades, several theoretical studies have been carried out to understand the relation between chemical/electronic structures with TPA properties and to evaluate the reliability of TPA energies and cross-sections computations [12-23].

In this paper, we investigate TPA properties of some octupolar derivatives, namely triphenyl-isocyanurate, triphenyl-benzene and + (Scheme 1). In previous experimental studies, some of us reported on the linear and NLO properties of substituted triphenyl-isocyanurates, tristyryl-isocyanurates and triphenyl-benzene [24-28]. Triazinane-2,4,6-triones, more commonly known as isocyanurates are important cyclotrimeric molecules that attract considerable attention in polymer chemistry in regard to their numerous industrial applications, particularly in the field of foams, elastomers, paints, fibers, and surface coatings.[25] After proper functionalization, they can also give rise to anion receptors, drug-delivery agents or tensioactive building blocks. The recent realization that these molecules were also octupoles draw the attention of some of us toward their (nonlinear) optical properties and led to the discovery that some of them are highly fluorescent when peripherally functionalized by electron-donating arms and present intense nonlinear optical (NLO) responses, in particular fairly large two-photon absorption (2PA) cross-sections, a property of interest for various key developments in bioimaging, microfabrication or fields related to optical information storage and handling.[25] 1,3,5-Triphenylbenzenes and triphenyl-triazine are more ubiquitous octupolar derivatives, well studied for their two-photon absorption properties, which constitute interesting reference compounds.[3] The two first derivatives *i.e.* **1-NMe₂** and **2-NMe₂** [24-26] exhibit a good NLO activity/transparency trade-off, and, in terms of third-order activity, they were shown to possess high TPA cross-sections.
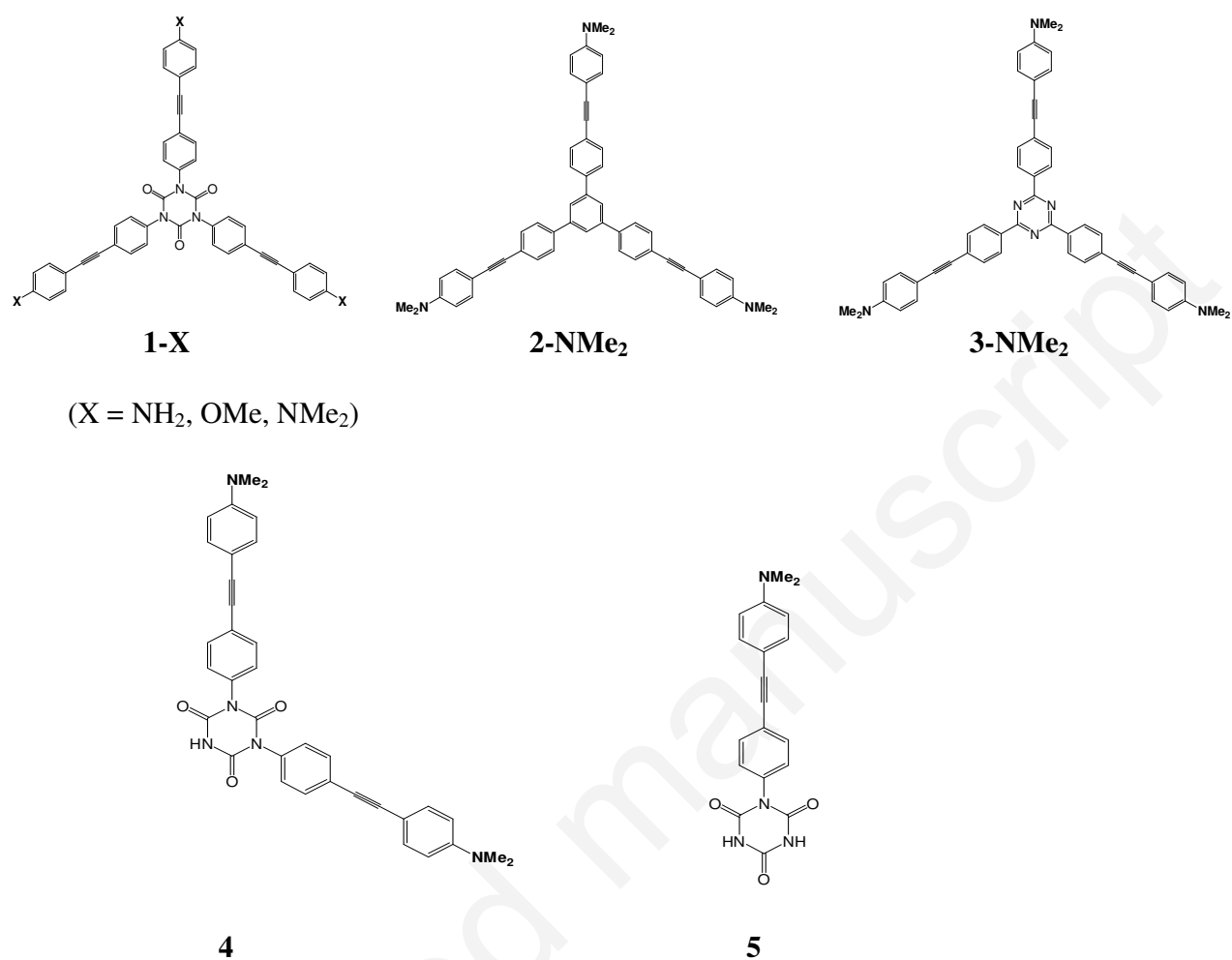
Scheme 1. Structures of the derivatives under study

The TPA properties of the studied compounds will be computed using DFT techniques. The aim of our work is (i) to compare the three considered cores regarding their TPA response; (ii) to investigate the influence of the strength of the terminal donating group on the considered property and (iii) to investigate if any cooperative effect between the three arms born by the isocyanurate core occurs or if only additivity of their own individual responses takes place.

2 Methods of calculation

2.1 Computational details

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All the TPA and one-photon absorption (OPA) calculations have been carried out using the Amsterdam Density Functional (ADF2017 and ADF2018) suite of programs [29]. These properties have been calculated using the SAOP model potential [30, 31] (statistical average of orbital model exchange-correlation potential) using the damped cubic response theory module of Lasse Jensen *and Coll.* [12] implemented in the ADF program package. The latter authors showed that SAOP leads to TPA results in satisfying agreement with experimental measurements. The geometries used in the calculations are those optimized at the MPW1PW91/6-31G* [32] level using the Gaussian09 suite of programs [33] taking into account the dichloromethane solvent used in the TPA experiments by the means of the PCM model [34]. We wish to remind here to the reader that the SAOP model potential cannot be used for geometry optimizations. It is also worth noting that the geometry considered has a non negligible effect on the computed TPA property. For this reason we decided to use for all systems the optimized geometry computed at the level of theory indicated above. In a previous work, this functional led us to very satisfying results regarding the ground state and OPA properties of these molecules [27]. Moreover, we checked that an extension of the DZP basis set used in our TPA and OPA calculations, *i.e.* to TZP and TZ2P, had only a small effect on the computed properties. The TPA computations have been carried out considering isolated molecules; it is expected that solvent effects should be the same for the series of homologous molecules considered in the present work.

The lifetime of the electronic excited states is included in the theory using a damping parameter

of 0.0034 au ($\sim$0.1 eV $\sim$ 800 cm^{-1}) value which was found suitable for TPA computations [12,

35, 36].

Finally, it must be recalled that, at our level of theory, the computation of the TPA properties for molecules of large size as ours necessitates a lot of computational time, and that the computation must be repeated for different laser energies in order to simulate the TPA spectra.

2.2 Two photon absorption cross section

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The TPA cross-section σ^{TPA} has been obtained from the imaginary part of the third-order hyperpolarizability γ using the following expressions [12,13,37]:

$$(1) \quad \sigma^{TPA} = \frac{N\pi^3\alpha^2\hbar^3\omega^2}{15e^4}\gamma^{TPA}$$

$$(2) \quad \gamma^{TPA} = \sum_{\alpha\beta}(\operatorname{Im}\gamma_{\alpha\alpha\beta\beta} + \operatorname{Im}\gamma_{\alpha\beta\beta\alpha} + \operatorname{Im}\gamma_{\alpha\beta\alpha\beta})$$

Where α is the fine structure constant (not to be confused with the α index of the summation in eq 2), e is the elementary charge, ω is the photon energy, $\hbar$ is the reduced Planck's constant whereas the integer value N=4 is used for all simulated TPA spectra [12,13]. The σ^{TPA} value is usually given in Göppert-Mayer units (1 GM = 10^{-50} cm^4 s photon^{-1}) [1]. We first evaluate σ^{TPA} in atomic units and then multiply it by $(0.529177 \times 10^{-8}$ cm/a.u.$)^4 \times (2.418884 \times 10^{-17}$ s/a.u.$)$ to obtain its value in the conventional units (cm^4 s photon^{-1}).

As said before, to simulate the TPA profiles, we calculated point by point the TPA cross-sections for different laser energies.

3 Results and discussion

As said before, the geometries of the studied species were optimized at the MPW1PW91/6-31G* level in dichloromethane (DCM) as solvent since this solvent has been used in most experimental measurements discussed here. The geometry plays an important role especially when it concerns possible conjugation paths between different moieties of the considering molecule thus influencing the HOMO-LUMO gap which is an important property considering optical and NLO properties.

As it can be seen from the optimized geometry of the isocyanurate **1-NMe$_2$** species (Fig.1), the three peripheral arms adopt a tilted conformation relatively to the central core, the average deviation from planarity being equal to 70° (table 1). In the case of the **1-NMe$_2$** derivatives with one and two arms, this deviation is higher and respectively equal to 81° and 89°.
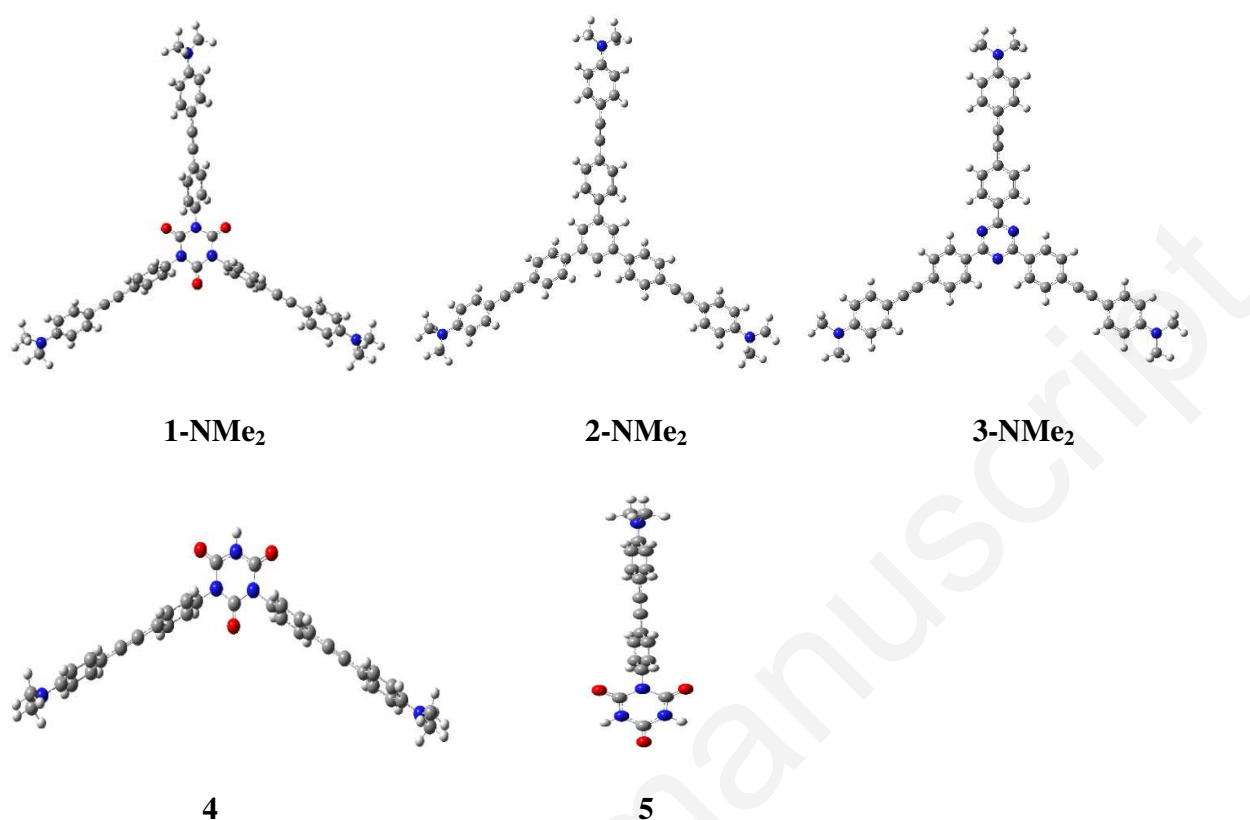
Fig. 1 Optimized geometries in CH_2Cl_2 of the derivatives under study.

Table 1 Calculated mean deviation from planarity of the studied systems

Cpds	Mean deviation (°)
4	81
5	89
1-NMe₂	70
2-NMe₂	37
3-NMe₂	0

We note also that the mean deviation from planarity for the phenyl core species **2-NMe₂** is less pronounced when compared to isocyanurate **1-NMe₂** , being equal to 37° for the former species

vs. 70° for **1-NMe₂**. Finally, the triazine system **3-NMe₂** adopts a planar structure between the three arms and the central core, so differs drastically from the two other systems.

As written before, the TPA properties for the studied systems, as well as the OPA spectra, were computed at the SAOP/DZP level in vacuum. The TPA-simulated profiles are represented in Fig. 2, the experimental and theoretical OPA, TPA maximum energies and cross-sections are summarized in Table 2.

Table 2 Experimental and calculated OPA, TPA energies ω (eV) and cross-sections σ^{TPA} (GM) of **1-X** (X = OMe, NH₂, NMe₂**), 2-NMe₂** and **3-NMe₂**

Cpds	Experimental[a]				Theoretical		
	ω (eV)		σ^{TPA} (GM)	Refs	ω (eV)		σ^{TPA} (GM)
	OPA	TPA			OPA	TPA	
1-OMe	-	-	-	-	2.93	1.85	860
1-NH₂	3.80	1.77	130	28	2.76	1.77	1071
1-NMe₂	3.52	1.72	360	25	2.63	1.55	4246
2-NMe₂	3.47	1.67	380	26	2.44	1.55	4322
3-NMe₂	3.06	1.51	1250	[b]	2.18	1.15	8701

[a]Experimental values for the TPA cross-sections have been obtained by two-photon excited fluorescence (TPEF) on a similar equipment for all compounds in dichloromethane using fs pulses except for **1-NH₂** for which the TPA cross-section has been derived by Z-scan (open aperture) measurements. See refs. [25] and [28] for typical TPEF and Z-scan conditions, respectively. [b] Work in progress (to be published).
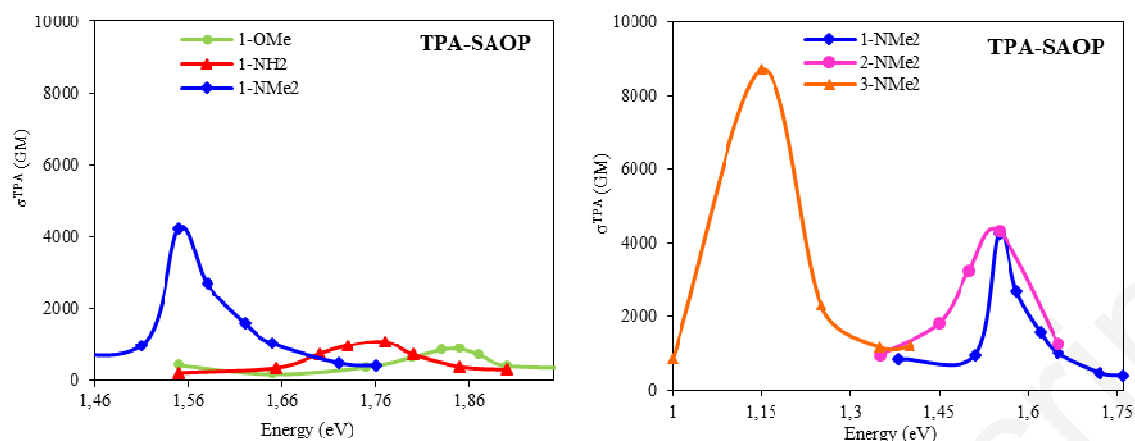
7

Fig. 2 Theoretical TPA profiles for **1-OMe** (green line), **1-NH₂** (red line), **1-NMe₂** (blue line), **2-NMe₂** (purple line) and **3-NMe₂** (orange line) computed at the SAOP/DZP level.

The computed σ^{TPA} cross-sections for the cyclotrimers using the SAOP model potential are higher than the measured ones, by a factor of the order of ten. Such deviations between measured and theoretical TPA cross-sections are not unusual and has been discussed by several authors [13,15]. The limitation of the non-linear response TD-DFT theory used for the TPA computations [38] is at least partly responsible for that, in particular the approximation done for the kernel. Obviously, the neglect of solvent effects is also responsible for a part of this deviation. Finally, we remind that we checked that in our case the extension of the basis set from the DZP to the TZ2P one has only a small effect on the computed TPA cross section.

However, our results reproduce the same trend as the experimental observations, *i.e.* that the 4 compounds **1-NH₂**, **1-OMe**, **1-NMe₂** and **2-NMe₂** are correctly ranked regarding σ^{TPA}. We must remind that our calculations consider isolated molecules whereas the measured TPA cross-sections are made in solution. Experimental data indicate that increasing the strength of the terminal donor group X namely replacing NH₂ by NMe₂ in the **1-X** cyclotrimers enhances the TPA cross-section, as experimentally observed; the theoretical computations indicate the same increase of σ^{TPA} when going from **1-NH₂** to **1-NMe₂**.

The enhancement of the maximum TPA cross-sections when increasing the strength of the electron-donating terminal groups *i.e.* going from **1-OMe** to **1-NH$_2$** and **1-NMe$_2$** correlates well with the decrease of the energy gap between HOMO and LUMO (Gap$_{H-L}$; see Fig. 3).
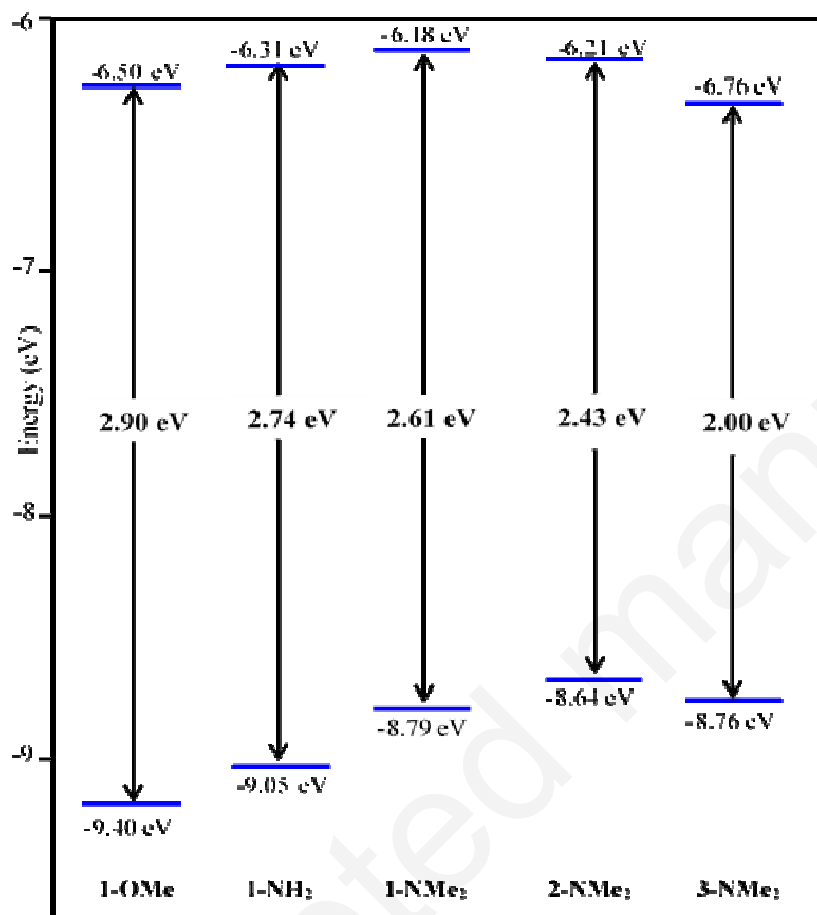

Fig. 3 SAOP/DZP HOMO-LUMO gaps for **1-X** (X = OMe, NH$_2$, NMe$_2$), **2-NMe$_2$** and **3-NMe$_2$**.

Experimentally, **1-NMe$_2$** and **2-NMe$_2$** molecules possess similar two-photon cross-sections; this result was not expected, because the central ring in the **1-X** (isocyanurate) derivatives was believed to be more electron-deficient than in the **2-X** (phenyl) compounds. The computations give also almost the same σ^{TPA} value, with a small increase of this property when passing from **1-NMe$_2$** to **2-NMe$_2$**, as also observed experimentally.

Our results indicate a significant enhancement on the σ^{TPA} with the triazine core compared to the isocyanurate and phenyl centers, in good agreement with experimental observations (work in progress). We note that the calculated value of **3-NMe$_2$** is two times higher than for **1-NMe$_2$** and

2-NMe$_2$, whereas, experimentally, this value is three times higher. The enhancement of the σ^{TPA} of **3-NMe$_2$**, which can be related to the significant decrease of Gap$_{H-L}$ when going from 1**-NMe$_2$** and **2-NMe$_2$** to **3-NMe$_2$** originates (at least in part) from the planarity of the entire π system in **3-NMe$_2$**.

On the other hand, the SAOP calculated TPA energies reproduce well the experimental TPA peak energies for the studied compounds. Our calculations provide the exact value of the TPA energy measured for the **1-NH$_2$** and deviates by 0.17 eV and 0.12 eV in the case of **1-NMe$_2$** and **2-NMe$_2$**.

The calculated TPA peak has the same energy for **1-NMe$_2$** and **2-NMe$_2$**, and that calculated for **3-NMe$_2$** is lower by 0.4 eV. Experimentally, this trend is verified, but the computed value is 0.36 eV lower this time. We note also that the SAOP calculated OPA energies are underestimated compared to the experimental OPA energies. Finally, the comparison of the TPA and OPA results (Table 2) shows that the TPA peak energies are calculated at approximately (but not exactly) twice the OPA energies for the studied cyclotrimers, due to the method of calculation.

To assess a possible cooperative effect *vs.* simple additivity regarding the σ^{TPA} property of each individual arm of the isocyanurate core, we considered two models derived from **1-NMe$_2$** bearing one or two arms attached to the isocyanurate core instead of three (scheme 1). The one-arm (**5**) is a D–π–A dipole with the isocyanurate core as acceptor and a dimethylamino substituent as donor group, while the two-arms (**4**) and the three-arms (**1-NMe$_2$**) contain respectively two and three of these D–π–A units (by sharing the acceptor group). First of all, it can be noted that these three species exhibit almost the same HOMO-LUMO gap (Fig. S1), in line with a weak electronic coupling between the various arms.[38] The OPA and TPA results obtained are given in Table 3 and Fig. 4.

Table 3 Calculated OPA, TPA energies ω (eV) and cross-sections σ^{TPA} of the **1-NMe$_2$**, one arm (compound **5**) and two arms (compound **4**).

Cpds	Experimental[a]	Theoretical	
	ω(eV)	ω(eV)	σ^{TPA} (GM)

	OPA	TPA	σ^{TPA} (GM)	OPA	TPA	
1-NMe$_2$	3.52	1.72	360	2.63	1.55	4246
4	3.44	1.70	(108)^{b}	3.14	1.62	1687
5	/	/		3.09	1.55	544

^{a} Experimental values for the TPA cross-sections have been obtained by two-photon excited fluorescence (TPEF) on a similar equipment for all compounds in dichloromethane using fs pulses. See ref. [25] for typical conditions. ^{b} Work in progress (to be published).
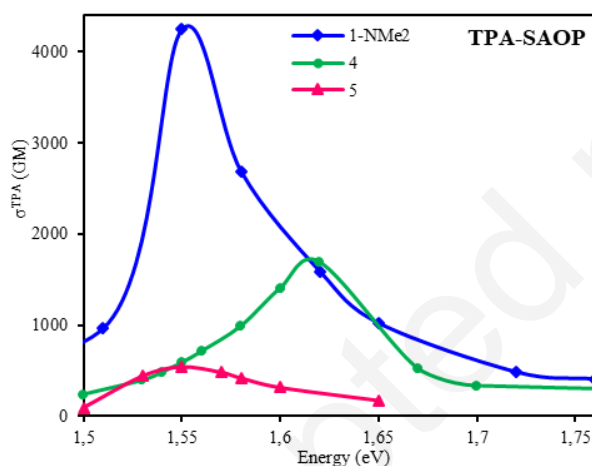

Fig. 4 Theoretical TPA profiles of **1-NMe$_2$** (blue line), **4** (green line) and **5** (red line) at SAOP/DZP level

We find that **1-NMe$_2$** displays a σ^{TPA} value which is 2.5 times larger than that of **4** which exhibits itself a value three times larger than that of **5.** This result is in good agreement with experiment which indicates that the measured σ^{TPA} of **1-NMe$_2$** is 3 times higher than the measured one for compound **4**.

We note that the TPA peak energy for **4** deviates by 0.07 eV compared to its congeners **5** and **1-NMe$_2$**. It appears then that the TPA cross-section increases significantly as the number of arms

increases, the two-photon absorption of one arm and the core (*i.e.* a single D–π–A unit) being modelled by **4**. As a result, simple additivity does not apply in our case for σ^{TPA} suggesting existence of a positive synergy between the arms. Such cooperative enhancement has already been observed experimentally in the case of planar triazine derivatives exhibiting one, two and three arms attached to the triazine core [39]. This issue has also been studied earlier theoretically by Beljonne *et al.* for related compounds having a C_3 symmetry axis [40]. It can be traced back to the octupolar symmetry of these derivatives.

4 Conclusions

In this work, we have reported a theoretical DFT study of the TPA properties of promising octupoles, namely triphenyl-isocyanurate, 1,3,5-triphenyl-benzene and triphenyl-triazine derivatives functionalized by extended conjugated arms at their peripheral *para*-positions. These compounds exhibit a three-fold axis and contain attached arms in 1, 3 and 5 positions, each of them bearing a terminal electron donating group.

The used SAOP functional provided a good qualitative estimate of the TPA cross-sections and energies. To our knowledge, it is the first time that such TPA computations are carried out for octupolar molecules at this level of theory. In agreement with experiment, it is found that an increase of the strength of the donor terminal group (replacing OMe and NH_2 by NMe_2) enhances the TPA cross-section. The calculated TPA properties bring to light a small difference for σ^{TPA} when replacing the isocyanurate ring by the phenyl one. In addition, the compound with the triazine core exhibits a much higher TPA cross-section value than the two other compounds with isocyanurate and phenyl cores. In all cases, the HOMO-LUMO gap is a determining factor. This property is for a large part related to the planarity of the considered systems, the triazine core system being perfectly planar contrary to the two other systems. We found also that the two-photon absorption cross-section increases more significantly than three time that of the model compound (**5**) with only one electron-releasing arm, indicating the existence of a cooperative enhancement of the TPA cross-sections and not a simple additivity of the σ^{TPA} of each arm.

5 Supplementary data

12

The HOMO-LUMO gaps for **1-NMe₂**, **4** and **5**, Cartesian coordinates of the optimized geometries of the studied systems.

Acknowledgements

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