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Nanoscale multipolar chromophores for optical limiting in the visible-NIR range based on multiphoton absorption

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ABSTRACT

A series of structurally-related multipolar chromophores of different symmetry (dipolar, quadrupolar, octupolar, dendritic...), and shape (rod-like, Y-shaped...) propeller-shaped, were investigated for optical power limiting based on multiphoton absorption processes. Their design is based on the functionalization of nanoscale linear or branched conjugated backbones with electro-active (i.e. electron-releasing or electron-withdrawing) peripheral and core/node groups. Their two-photon absorption (TPA) spectra were determined by investigating their two-photon-excited fluorescence properties in the NIR region using pulsed excitation in the femtosecond regime. These studies provide evidence that the charge symmetry plays an important role, the quadrupolar chromophores leading to giant TPA cross-sections in the visible red. Furthermore, modulation of the nonlinear absorptivity/transparency/photostability trade-off can be achieved by playing on the nature of the electroactive groups and of the spacers. Interestingly, higher-order charge symmetries and branched structures provide an innovative route for TPA amplification and/or spectral broadening in the NIR region.

Keywords: Two-photon absorption, multipolar structures, nanoscale systems, branched-structures, optical limitation

1. INTRODUCTION

Multiphoton absorption has attracted considerable attention for optical power limiting applications.¹⁻⁴ This nonlinear process offers the possibility of maintaining high transparency in ambient light and achieving efficient and instantaneous protection against the high intensity delivered by high power lasers. Key ingredients for such purpose are a high transmission at low intensity (i.e. weak linear absorption) and high multiphoton absorption cross-sections (i.e. high nonlinear responses). In this context, we have focused on the design of chromophores showing very large two-photon absorption (TPA) cross-sections (σ_2) while maintaining wide transparency in the visible and/or NIR spectral range. Large one-photon excited-state cross-section (σ_e) and long excited-state lifetime are also desirable to allow two-photon induced excited-state absorption phenomenon to arise, leading to synergic effects of TPA and excited-state absorption and improved optical limitation behavior in the nanosecond regime.^{4,5}

Until recently, optimization of molecular TPA has focused mainly on one-dimensional dipolar,⁶⁻¹² or quadrupolar^{5,7,10,11,13-17} structures. However, it has been realized lately that two-dimensional,¹⁸⁻²⁰ branched²¹⁻³³ and dendritic^{29,32,34-37} structures could lead to highly effective multiphoton absorption. In this context, we have been interested in the elucidation of the role of dimensionality and charge-symmetry on molecular TPA. We have investigated a series of structurally-related chromophores of different symmetry (dipolar, quadrupolar, pseudo-dipolar, octupolar, dendritic...) and shape (rod-like, propeller-shaped, Y-shaped...). Their design is based on the functionalization of semi-rigid linear or branched conjugated backbones with electro-active (i.e. electron-releasing or electron-withdrawing) peripheral and core/node groups (Fig. 1). In addition to investigating structure-property relationships, our aim was to identify appropriate structural combinations to optimize the TPA/transparency/solubility/photostability trade-offs.

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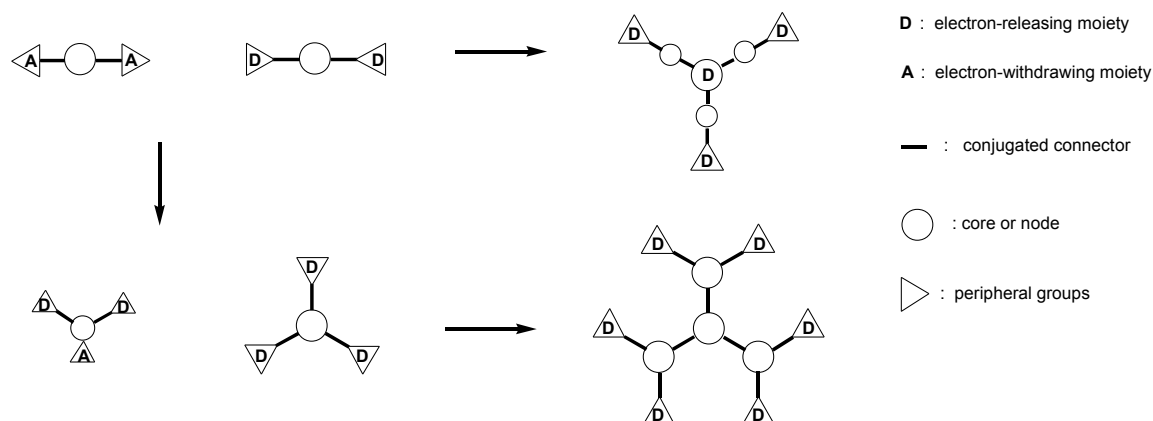


Fig. 1. Molecular engineering of multipolar chromophores for two-photon absorption and optical limitation.

The series includes quadrupolar molecules (Fig. 2) built from the symmetrical functionalization of a biphenyl core that is either free (Q_1, Q_2) or planarized when using dinonylfluorene (Q_3-Q_8). Quadrupolar chromophores bearing either electron-releasing (Q_1-Q_4) or electron-withdrawing (Q_5-Q_8) peripheral groups were investigated in order to assess the role of both end-groups on molecular two-photon absorptivity (Fig. 2). Arylene-vinylene and phenylene-ethynylene rods were used as connecting spacers between the core and the electroactive end-groups to ensure effective electronic conjugation while tuning the nonlinearity/transparency range.

All compounds show excellent solubility in apolar or weakly polar solvents (typically higher than 300 g.L⁻¹) due to the presence of the long alkyl chains on the core and/or the end-groups. This is of particular interest for optical limiting applications for which high concentrations are required. We also note that the linear nonyl chains ($n\text{-C}_9\text{H}_{19}$) grafted on the fluorenyl core not only provide excellent solubility but also hamper tight π -stacking between chromophores in concentrated solution.³⁸

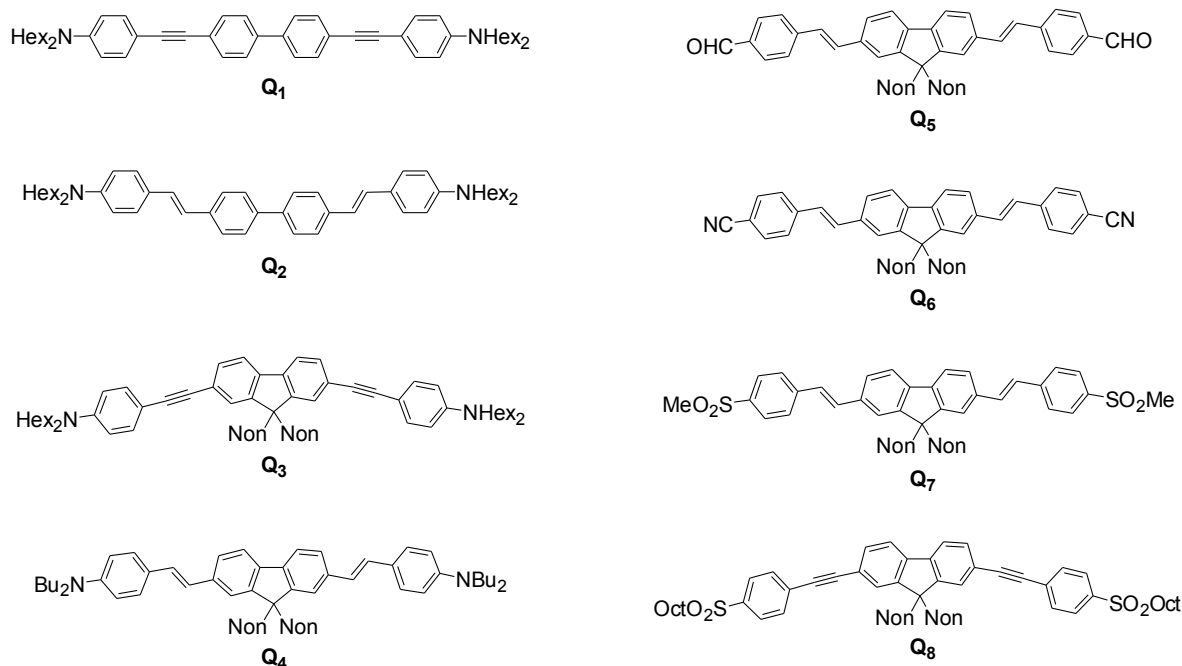


Fig. 2. Series of quadrupolar chromophores investigated in the present work.

Branched structures **TPB₁**-**TPB₃** where 1,3,5-triphenylbenzene (TPB) units (i.e. a trigonal analogue of the biphenyl core) are used as trigonal cores and nodes moieties (Fig. 3) have been studied in order to investigate branching and charge symmetry effects. In addition a branched structure **TPA(Q₄)** built from the assembly of three chromophores **Q₄** via a common donating nitrogen has been investigated (Fig. 3).

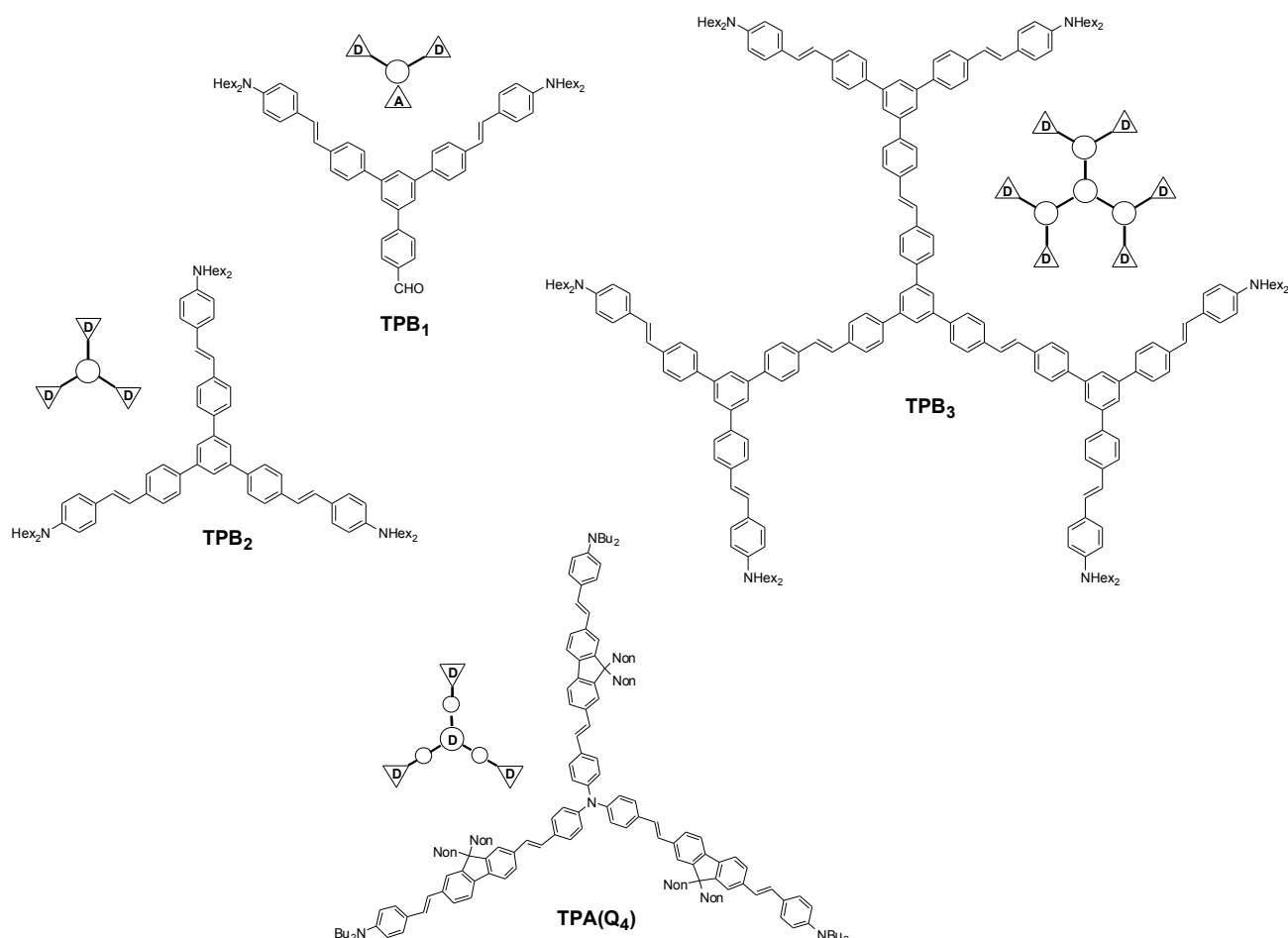


Fig. 3. Series of structurally-related branched chromophores built from triphenylbenzene (TPB) and triphenylamine (TPA) nodes.

2. METHODOLOGY

2.1. Optical measurements

UV/VIS spectra were recorded on a Jasco V-570 spectrophotometer.

Fluorescence measurements were performed at room temperature in diluted solutions (ca. 10^{-6} M) using a PTI spectrometer (LPS-220B) in photon counting mode. Emission spectra were obtained, for each compound, at $\lambda_{\text{ex}} = \lambda_{\text{max}}(\text{abs})$ with $A_{\text{ex}} = 0.1$ to minimize internal absorption. Fluorescence quantum yields were measured on degassed samples at room temperature; fluorescein in 0.1 N NaOH was used as a standard ($\Phi = 0.90$ at $\lambda_{\text{ex}} = 470$ nm) and refractive index correction was performed.³⁹ The lifetime values were obtained from the reconvolution fit analysis of the decay profiles with the F900 analysis software and the fitting results were judged by the reduced chi-square value.

2.2. TPEF measurements

The TPA cross-sections of the quadrupolar molecules were determined by investigating their TPEF properties. This procedure provides the TPEF action cross-sections $\sigma_2\Phi$ from which we can derive the corresponding σ_2 values. The TPEF excitation spectra of quadrupolar molecules were measured following the experimental protocol described in detail by Xu and Webb,⁴⁰ using a mode-locked Ti:sapphire laser operating between 700 and 990 nm and delivering 80 fs pulses at 80 MHz. TPEF measurements were calibrated relative to the absolute TPEF action cross-section determined by Xu and Webb for fluorescein in water (pH = 11) in the 690-1050 nm range.^{40,41} The quadratic dependence of the fluorescence intensity on the excitation intensity was verified for every data point, indicating that the measurements were carried out in intensity regimes in which saturation or photodegradation do not occur. The experimental uncertainty is estimated to $\pm 10\%$.

2.3. Calculations

Calculations and especially geometry optimization were conducted using the Gaussian 98 package⁴² with the B3LYP⁴³ density functional and the 6-31G* basis set. For the sake of simplicity, calculations have been conducted on chromophores where the alkyl solubilizing chains have been replaced by methyl substituents. Illustrations have been obtained with MOLEKEL.⁴⁴

3. RESULTS AND DISCUSSION

The photophysical data of the chromophores are collected in Table 1.

Table 1. One and two-photon absorption properties of multipolar chromophores

Compd	X	Connector	Core/node	$\lambda_{\max}^{\text{OPA}}$ (nm)	$\lambda_{\text{cut-off}}^a$ (nm)	τ^b (ns)	λ_{TPA} (nm)	σ_2^c (GM)	N^d	σ_2/N^2^e
Q₁	NHex ₂	PE	BP	374	422	0.70	705	890	28	1.14
Q₂	NHex ₂	PV	BP	401	455	0.82	730	1040	28	1.33
Q₃	NHex ₂	PE	FL	387	436	0.74	705	1200	28	1.53
Q₄	NBu ₂	PV	FL	415	465	0.87	740	1265	28	1.61
Q₅	CHO	PV	FL	397	447	0.86	705	575	32	0.56
Q₆	CN	PV	FL	389	434	0.84	705	395	32	0.39
Q₇	SO ₂ Me	PV	FL	387	429	0.87	705	215	32	0.21
Q₈	SO ₂ Oct	PE	FL	363	411	0.64	705	52	32	0.05
TPB₁	NHex ₂ /CHO	PV/-	TPB	385	436	0.79	755	365	24.25	0.62
TPB₂	NHex ₂	PV	TPB	384	433	0.63	735	530	28.14	0.67
TPB₃	NHex ₂ -PV	TPB-V	TPB	375	432	0.60	755	810	50.79	0.31
TPA(Q₄)	NBu ₂	V-FIV	TPA	428	480	0.85	735	4160	48.5	1.77

^a λ at which the transmittance is 95%. ^b Experimental fluorescence lifetime from time-correlated single photon counting experiments.

^c TPA cross-sections at λ_{TPA} ; 1 GM = 10^{-50} cm⁴.s.photon; TPEF measurements were performed using a mode-locked Ti:sapphire laser delivering 80 fs pulses at 80 MHz, calibrating with fluorescein. ^d Effective number N of π -electrons in the conjugated system.⁴⁵ ^e TPA cross-sections at λ_{TPA} normalized by N^2 .

3.1 Structure-property relationships in quadrupoles

3.1.1. End-groups' effect

As noted from Table 1 and illustrated in Fig. 4 (**Q₃**, **Q₈**) and Fig. 5 (**Q₄**, **Q₅**), push-push chromophores always show larger TPA cross-sections in the NIR region than corresponding pull-pull derivatives, in correlation with a definite

red shift of the one-photon absorption spectra. Push-push derivatives thus offer interesting potentialities for optical limitation in the red-near IR region.

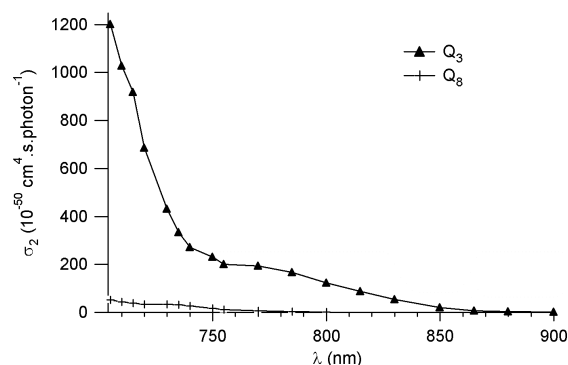


Fig. 4. TPA spectra of fluorophores **Q₃** and **Q₈** in toluene.

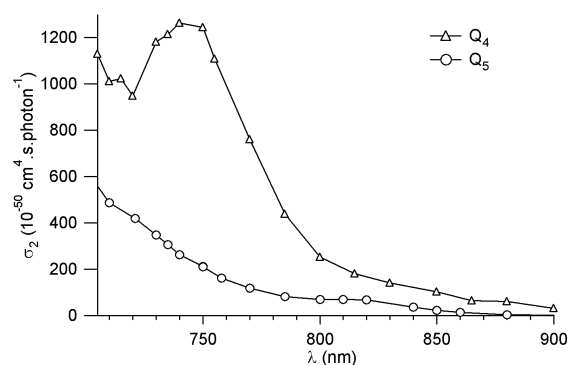


Fig. 5. TPA spectra of fluorophores **Q₄** and **Q₅** in toluene.

Indeed numerical simulations performed with compounds **Q₁** and **Q₂** (which also exhibit an intense excited-state absorption band overlapping the two-photon absorption band in the red-NIR region) demonstrate a strong nonlinear absorption behavior, suitable for optical limiting of nanosecond pulses (with threshold values down to $1.5 \times 10^{-2} \text{ J cm}^{-2}$ for 0.55 ns pulses).¹⁷

Comparison of pull-pull derivatives **Q₅-Q₇** (Fig. 6 and Table 1) indicates that increasing the electron-withdrawing strength of the end-groups (CHO: $\sigma_p = 0.42$, CN: $\sigma_p = 0.66$, SO₂Me: $\sigma_p = 0.72$)⁴⁶ results in a *decrease* of the TPA cross-section in the NIR region. Since pull-pull compounds are blue-shifted as compared to push-push derivatives, pull-pull derivatives offer a promising alternative for optical limiting in the visible blue region.

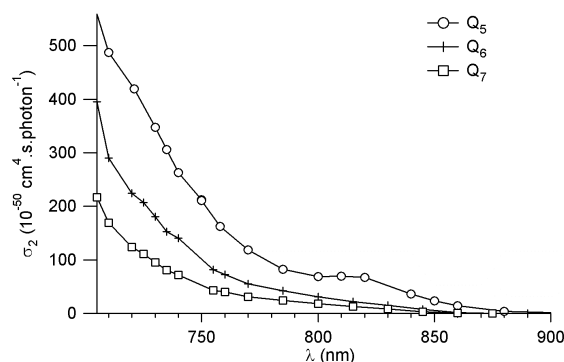


Fig. 6. TPA spectra of fluorophores **Q₅-Q₇** in toluene.

3.1.2. Core effect

Comparison of push-push derivatives built from different core moieties and bearing similar end-groups demonstrates that the nature of conjugated core significantly influences the TPA spectra.

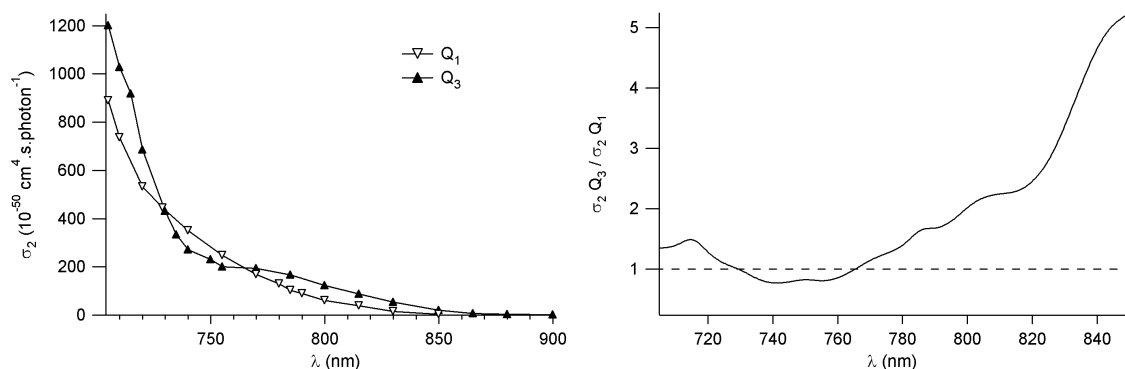


Fig. 7. TPA spectra of fluorophores **Q₁** and **Q₃** in toluene.

From Fig. 7 (left) and Table 1, we observe that replacing the twisted biphenyl core (BP) by the planarized fluorene unit (FI) results in both a red shift and a significant enhancement of the TPA cross-section close to the red region. In addition we observe that chromophore **Q₃** shows a low energy TPA maximum at 774 nm (*i.e.* at $2\lambda_{\text{max}}^{\text{OPA}}$). This indicates that the lowest excited state is both one-photon and two-photon allowed in the case of chromophore **Q₃**. Such phenomenon is not observed in the case of chromophore **Q₁** and is most probably related to the slight loss of symmetry caused by the fluorenyl moiety as compared to the symmetrical biphenyl unit. Such effect is responsible for the much more pronounced TPA efficiency in the NIR region (at $\lambda > 800$ nm) as illustrated in Fig. 7 (right).

3.1.3. Linker effect

As observed from the comparison of homologous push-push derivatives **Q₁** and **Q₂**, replacing a phenylene-ethynylene linker (PE) by a phenylene-vinylene one (PV) leads to larger TPA cross-sections in the 720-900 nm range (Fig. 8), in relation with a bathochromic shift of the TPA band. This effect is also visible when comparing the homologous PE and PV pull-pull derivatives **Q₈** and **Q₇** (Fig. 9). However, for push-push derivatives, the TPA cross-section become comparable close the red region (see for instance compounds **Q₃** and **Q₄** in Table 1).

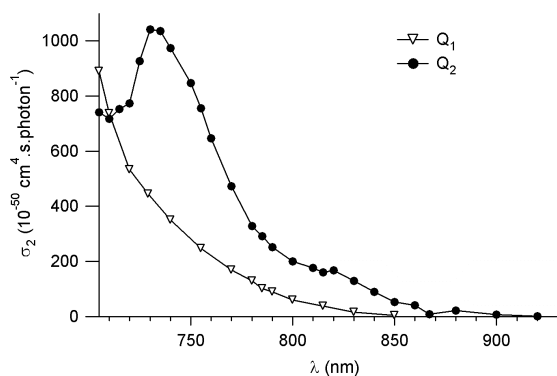


Fig. 8. TPA spectra of fluorophores **Q₁**-**Q₂** in toluene.

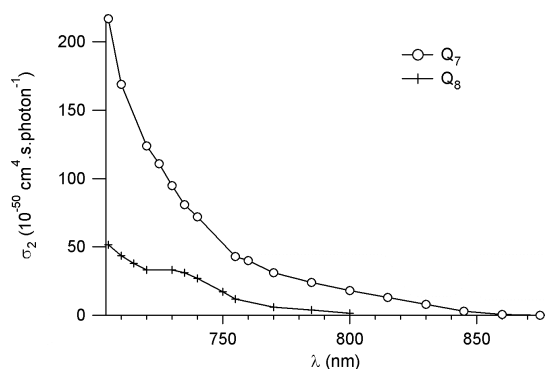


Fig. 9. TPA spectra of fluorophores **Q₇**-**Q₈** in toluene.

Moreover, the use of PE linkers lead to higher transparency in the visible range, as well as improved photostability (due to the lack of photoisomerization), as indicated by the absence of photodegradation either upon pulsed-laser or prolonged lamp irradiation.^{14,31} In view of their improved nonlinearity/transparency/stability trade-off, push-push derivatives with PE linkers thus represent interesting candidates for optical power limitation in the visible region.

3.2 Branching effect

Recently following pioneering work by P. N. Prasad and coll., several experimental and theoretical⁴⁷ studies have focused on the effect of branching on TPA. These studies lead to different outcomes: cooperative enhancement,^{22,28,35,36} additive behavior^{24,34} or even decrease of TPA.²² It should be emphasized that these results were obtained, in most cases, at one single wavelength, which might explain the different conclusions. In that context, we have been interested in investigating the wavelength dependence of the branching effect in various types of multipolar branched systems. Our goal was both to identify the origin of the discrepancies, and to assess the influence of charge symmetry. Indeed, a number of factors influence the TPA magnitude, such as electronic delocalization and intramolecular charge transfer phenomena, symmetry and dimensionality. A correlation between the square of the number of π -electrons in the conjugated systems (N) and the maximum TPA that can be reached has been reported recently.⁴⁵

3.2.1. Branching of quadrupoles

In this perspective, comparison of the TPA spectra of quadrupolar chromophores Q_4 and its three-branched analogue $TPA(Q_4)$ is quite informative. First of all, chromophore $TPA(Q_4)$ exhibits a *larger* normalized maximum TPA cross-sections (σ_2/N^2) than its quadrupolar branch Q_4 (Table 1) and one of the highest measured in the femtosecond regime for a branched structure.²⁸ In addition it maintains similar excited-state lifetime. These features are important for optical power limiting in the nanosecond regime since excited-state absorption subsequent to two-photon excitation is known to be responsible for the strongly nonlinear absorption behavior of quadrupolar chromophores.^{4,17}

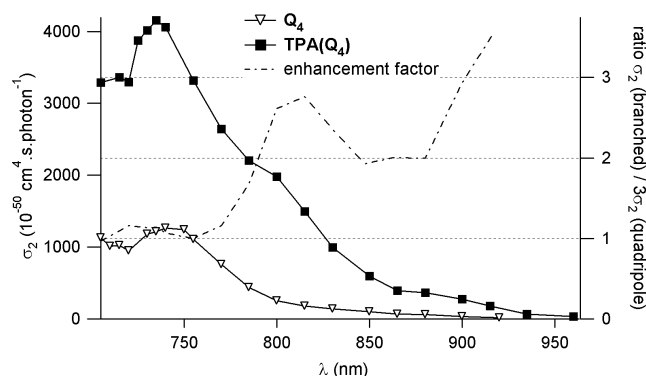


Fig. 10. Effect of branching of quadrupoles on TPA.

In addition, the ratio between the TPA cross-sections of quadrupolar chromophore Q_4 and its three-branched derivative $TPA(Q_4)$ significantly depends on the wavelength (Fig. 10). At lower wavelength, the contribution of the three quadrupolar branches to the TPA amplitude of $TPA(Q_4)$ seems roughly additive. The ratio significantly increases at higher wavelength, branched chromophore $TPA(Q_4)$ overcoming chromophore Q_4 . This effect is correlated with a definite TPA spectral broadening further to the NIR region where new TPA bands appear to emerge. Such phenomenon might be originating from an electronic coupling between the quadrupolar branches via the TPA core. In that respect, we note from Table 1 that the one-photon absorption band of $TPA(Q_4)$ is red-shifted with respect to that of chromophore Q_4 , suggesting that such coupling takes place.

3.2.1. Influence of charge symmetry and branched character

The series of structurally-related multipolar chromophores – Q_2 (quadrupolar), TPB_1 (pseudo-dipolar), TPB_2 (octupolar) and TPB_3 (dendritic) – built from the (linear) biphenyl or (trigonal) triphenylbenzene core/nodes was examined in order to investigate both the role of branching and charge symmetry. HOMO-LUMO calculations reveal that multipolar derivatives show pronounced *intramolecular charge transfer* phenomena upon excitation (Fig. 11-13). A charge density shift from the electron-releasing peripheral groups to the biphenyl (Q_2) or triphenylbenzene (TPB_2) core is observed both in 1-D quadrupolar chromophore Q_2 and in 2-D octupolar chromophore TPB_2 . For Y-shaped pseudo-

dipolar chromophore **TPB₁**, a directional intramolecular charge transfer from the donating end-groups towards the acceptor moiety is observed even though the donating and accepting moieties are not conjugated.

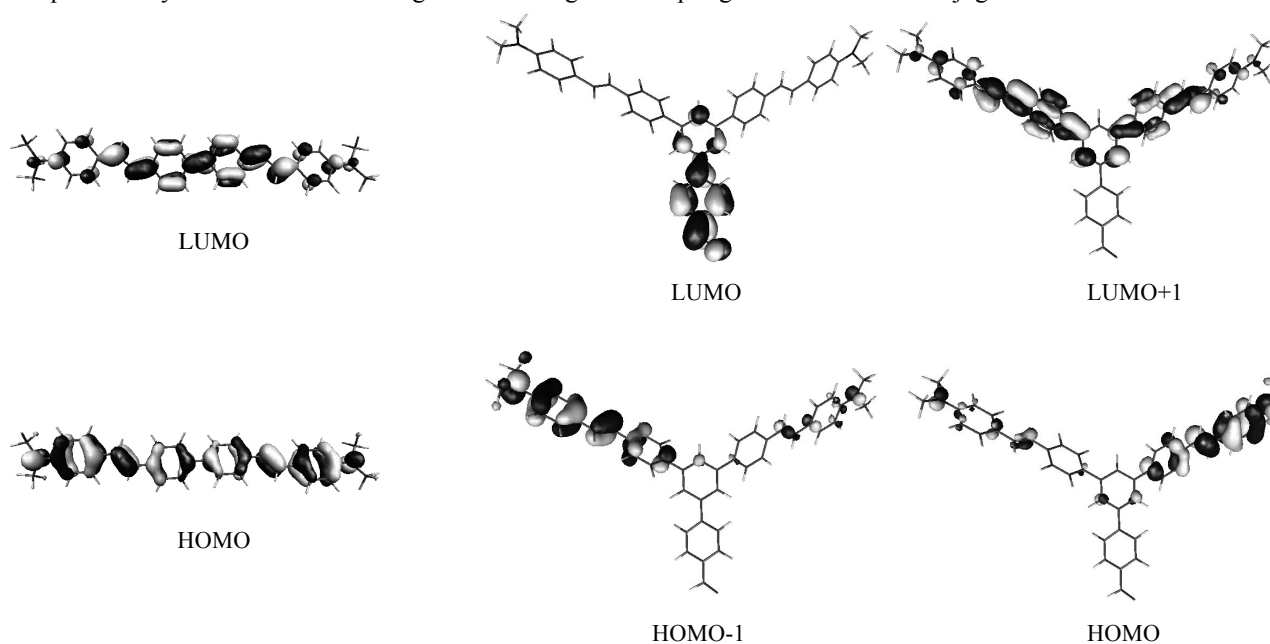


Fig. 11. Frontier orbitals of **Q₂**.

Fig.12. Frontier orbitals of **TPB₁**.

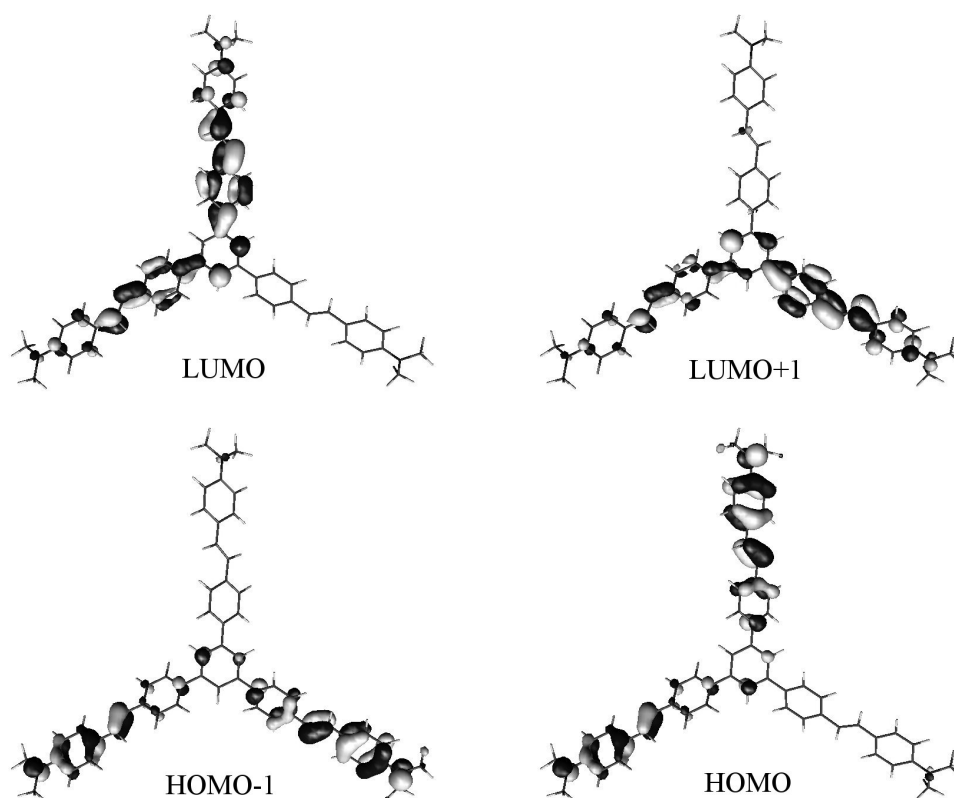


Fig.13. Frontier orbitals of **TPB₂**.

Interestingly, we observe from Table 1 and Fig. 14 that increasing the branched character leads to *improved transparency*: a clear blue-shift of the absorption band is observed with increasing number of branches in the chromophores. As a result branched chromophores **TPB₁**-**TPB₃** retain wide transparency in the visible region.

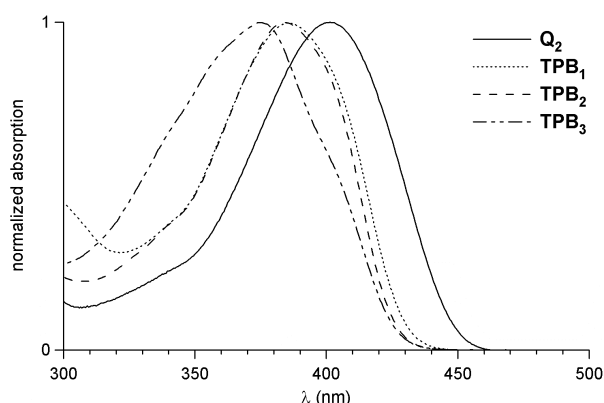


Fig. 14. Normalized absorption spectra of **Q₂** and **TPB₁**-**TPB₃** in toluene.

We observe from Fig. 15 that the 1-D quadrupolar chromophore **Q₂** shows the highest TPA cross-section close to the visible red while all 2-D branched structures become more efficient two-photon absorbers at $\lambda > 780$ nm. Indeed the branched structures show broader and red-shifted TPA band in the NIR region. Hence, the branched-structures exhibit both improved transparency in the visible region (as a result of a blue-shift of the OPA bands) and superior TPA efficiency further to the NIR region as compared their 1D-quadrupolar analogue (as a result of a red-shift of the TPA bands). For instance, the dendritic chromophore **TPB₃** shows a three times larger TPA cross-section at 800 nm than chromophore **Q₂** while being more transparent (Table 1). Hence increasing the branched character in multipolar structures built from the triphenylbenzene core seems to be a promising route for improving the TPA-transparency trade-off in the context of broadband optical limitation in the NIR region.

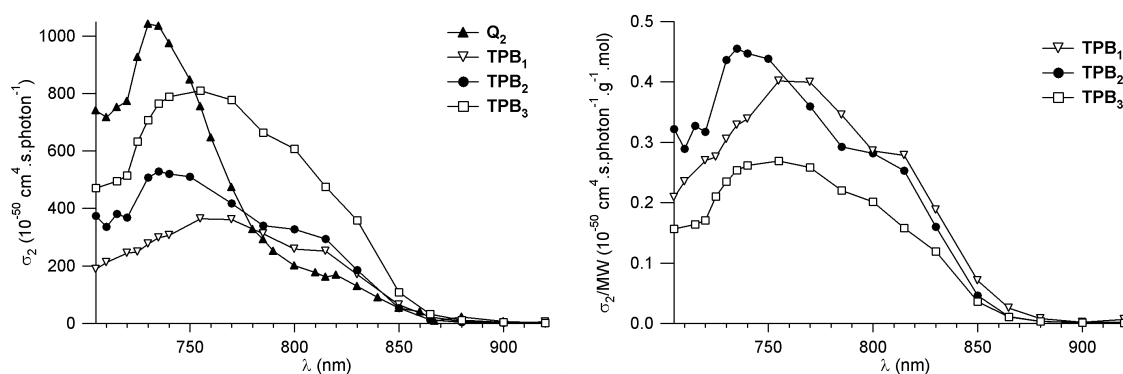


Fig. 15. Effect of branching on TPA in multipolar structures built from TPB core/nodes.

To compare the efficiency of the various branched structure in view of optical power limiting, it is helpful to consider the normalized TPA molecular efficiency σ_2/MW (Fig. 15 right). Interestingly, in the NIR region both the two-branched pseudo-dipolar chromophore **TPB₁** and the three-branched octupolar chromophore **TPB₂** appear as the best candidates in terms of normalized TPA-transparency trade-off. On the other hand, comparison of the normalized TPA efficiency of octupolar chromophore **TPB₂** and of its second-generation dendritic analogue **TPB₃** shows that in that particular case, increased branching character does not bring a net gain in normalized TPA efficiency (Fig. 15). This is most likely related to more confined intramolecular charge transfer phenomena in dendritic structures like **TPB₃**, as compared to pseudo-dipolar and octupolar structures (**TPB₁** and **TPB₂**).

4. CONCLUSION

The present work shows that modulation of the nonlinear absorptivity/transparency/photostability trade-off in 1D-quadupolar structures can be achieved by playing on both core and spacer structures. In particular, the replacement of the double bond by a triple bond in the conjugated spacers in *push-push* derivatives yields optimized TPA/transparency/photostability features for optical power limiting in the visible red region. In contrast, pull-pull derivatives are good candidates for optical power limiting in the visible blue. Both push-push and pull-pull quadrupolar chromophores also display very high solubility in apolar or weakly polar solvents. Such behavior is particularly attractive in the context of the search for optimizing multiphoton absorbers for broadband optical power limitation. Indeed nonlinear transmission experiments in the visible region conducted in solution in the nanosecond regime yield similar structure-TPA relationships as those derived from TPEF measurements in the NIR, and indicate that quadrupoles **Q₁-Q₄** show pronounced optical limiting properties.⁴⁸

The present study also demonstrates that the branching strategy provides a useful route for TPA enhancement and/or spectral broadening in the NIR region. In addition, by playing on the nature of the core/nodes and the charge symmetry, the transparency/nonlinearity trade-off can be tuned via control of the intramolecular charge transfer phenomena.

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