

# Optical limiting with soluble two-photon absorbing quadrupoles: Structure–property relationships

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## Abstract

The optical power limiting in the visible region of a series of two-photon absorbing quadrupoles built from conjugated backbones bearing electro-active peripheral groups was investigated. Nonlinear absorption experiments demonstrate that these molecules show marked nonlinear behaviour for short pulses (3 ns) in the ns regime. Structure–property relationships could be derived, emphasizing the role of the conjugated connectors and of the end-groups for improving the optical limiting efficiency. Push–push systems are more efficient than pull–pull systems, but at the expense of reduced transparency. Pyridine-*N*-oxides, terminal moieties which act in synergy as both donor and acceptor end-groups, lead to improved efficiency/transparency trade-off.

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## 1. Introduction

The fast development of frequency-agile pulsed lasers requires the design of new protecting systems. The development of efficient devices represents an important goal since it concerns eye but also NIR sensors protection. The challenge consists in elaborating systems both maintaining transparency in ambient light in order to preserve the detection function, and becoming strong absorbers under intense laser irradiation. The response time of the materials is an important parameter. The search for efficient optical limiting systems [1] has mainly focused on three classes of nonlinear optical systems: multiphoton absorbers [2–5], reverse saturable absorbers [6] and nonlinear scattering materials [7,8]. Among multiphoton absorbers, dipolar or quadrupolar derivatives have been shown to be of particular interest for optical limiting in the nanosecond re-

gime based on the combination of two-photon and excited-state absorptions for derivatives having excited-state lifetimes in the ns range.

In this work, we investigate the nonlinear optical limiting behaviour of a series of quadrupolar systems (compounds 1–10 shown in Fig. 1). Their design is based on the functionalization of semi-rigid linear conjugated backbones built from a biphenyl or fluorenyl core with electro-active (i.e., electron-releasing or electron-withdrawing) end-groups (Fig. 1). We have shown previously that such derivatives could have significant two-photon absorption (TPA) cross-sections in the NIR region [9,10]. In addition the experimental studies have revealed that the modular approach (modulation of the core, end-groups, increase of the connector length) in combination with quantum model-derived guidelines [11,12] could lead to significant enhancement in TPA. In addition the potentialities of some of these derivatives for optical limiting based on two-photon induced excited-state absorption (i.e., 2 + 1 absorption) have been demonstrated recently in the NIR region [13].

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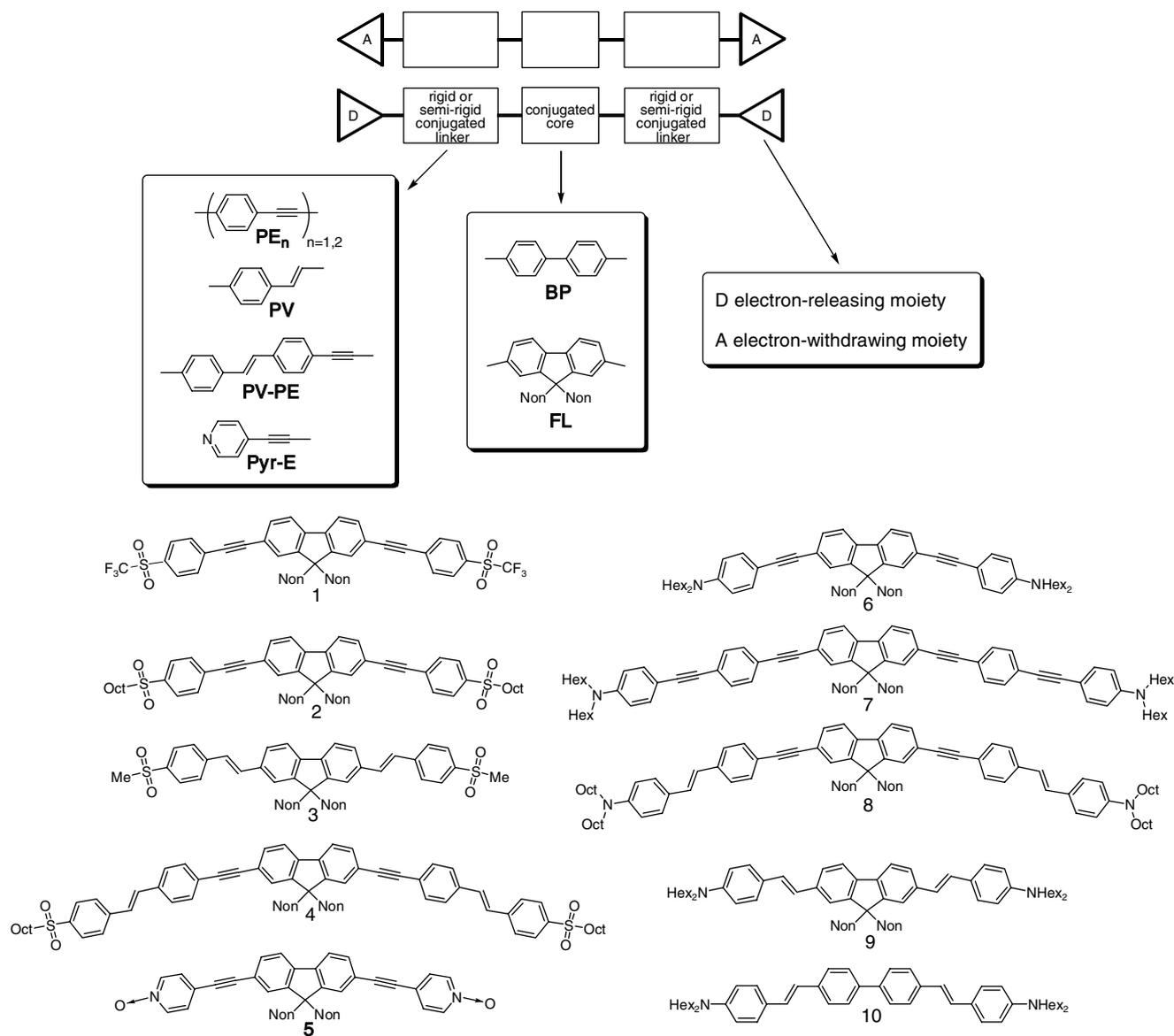


Fig. 1. Quadrupolar two-photon absorbers for optical limiting.

In the present Letter, we will focus on the nonlinear absorption in the *visible region* in the nanosecond regime and investigate the structural parameters that influence the nonlinear transmission behaviour in order to identify appropriate structural combinations for optimization of the optical limiting efficiency/transparency trade-off for broadband optical limiting in the visible.

## 2. Materials and methods

### 2.1. Two-photon absorbing molecules

The design of the two-photon absorbing molecules is based on the symmetrical functionalization of a conjugated core with conjugated arms bearing electron-withdrawing (1–4), electron-releasing (6–10) or both electron-donating and electron-withdrawing (5) end-groups

(Fig. 1). We selected cores derived from the biphenyl unit that may act as either *weak* acceptors or *weak* donors depending on the nature of the end-groups (and thus preserve transparency), and whose tilt angle controls the geometry and thus the extent of electronic conjugation along the conjugated backbone. The dinonylfluorene core (FL) is planar, whereas the free biphenyl one (BP) is twisted [14,15]. Phenylene–ethynylene (PE: 1–2, 6) and phenylene–vinylene (PV: 3, 9–10) connecting units were used as spacers between the core and the electro-active end-groups to ensure effective electronic conjugation while tuning the nonlinearity/transparency range. Finally elongated conjugated linkers made from the repetition of PE units (compound 7) or combination of PE and PV units (compounds 4 and 8) were used. By choosing PE units, we aimed at maintaining suitable transparency and photostability [9,16].

All compounds show excellent solubility in apolar or weakly polar solvents (typically up to  $500 \text{ g l}^{-1}$ ) due to the presence of the long alkyl chains on the core and/or the end-groups. We also stress that the linear nonyl chains ( $n\text{-C}_9\text{H}_{19}$ ) grafted on the fluorenyl core not only provide excellent solubility but also prevent tight  $\pi$ -stacking between chromophores in concentrated solution [17], thus hampering aggregation process that would possibly lead to reduced excited-state lifetimes.

## 2.2. Nonlinear transmission experiments

TPA molecules were dissolved in chloroform, and the concentration was fixed to  $50 \text{ g l}^{-1}$ . Nonlinear optical transmission measurements were performed on 2 mm thick cells using an optical parametric oscillator (OPO) with a pulse duration of 3 ns at 532 and 600 nm. The laser beam was only slightly focussed, in order to obtain a constant laser beam radius on the whole cell pathlength, the Rayleigh range being significantly larger (typically 1 cm) than cell thickness.

## 2.3. Excited-state lifetime measurements

Excited-state lifetimes were determined from fluorescence decays in toluene using time-correlated single-photon counting (TCSPC).

## 3. Results and discussion

The transparency characteristics (cut-off wavelengths) and the results of the nonlinear transmission experiments and lifetime measurements are summarized in Table 1. We note that the excited-state lifetimes are typically in the ns range, meaning that the excited-state population remains significant within the duration of the pulse. Nonlinear transmission data are represented on Figs. 2–5. In some cases, initial transmission is less than 100% indicating that

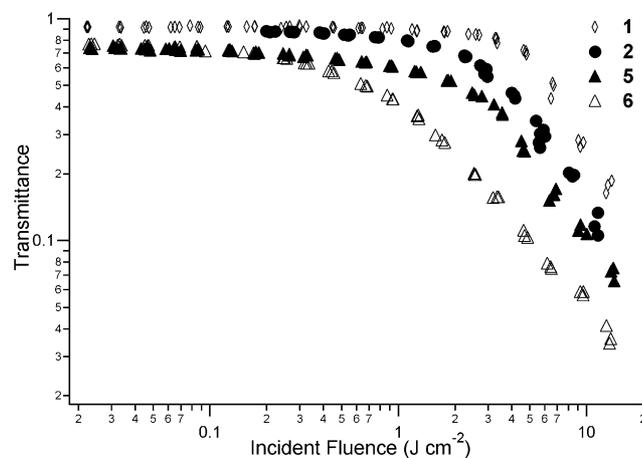


Fig. 2. Nonlinear transmission (at 532 nm, 3 ns pulses): end-group effect.

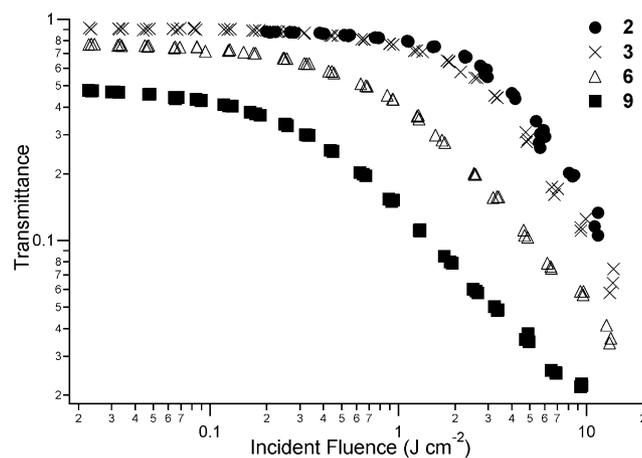


Fig. 3. Nonlinear transmission (at 532 nm, 3 ns pulses): linker effect.

for some compounds (particularly for compound 9) one-photon induced excited-state absorption (RSA) can contribute to the observed nonlinear absorption behaviour, leading to low threshold values (typically  $\ll 100 \text{ mJ cm}^{-2}$ ).

Table 1  
Nonlinear transmission characteristics of derivatives 1–10 in chloroform ( $50 \text{ g l}^{-1}$ )

Compound	X	Linker	Core	$\lambda_{\text{cut-off}}^{\text{a}}$ (nm)	$\text{Th}_{532}^{\text{b}}$ ( $\text{J cm}^{-2}$ )	$T_{532}^{\text{c}}$ (%)	$\text{Th}_{600}^{\text{d}}$ ( $\text{J cm}^{-2}$ )	$T_{600}^{\text{e}}$ (%)	$\tau^{\text{f}}$ (ns)
1	$\text{SO}_2\text{CF}_3$	PE	FL	417	1.2	25	2.3	26	0.79
2	$\text{SO}_2\text{Oct}$	PE	FL	421	0.40	17	0.51	18	0.64
3	$\text{SO}_2\text{Me}$	PV	FL	440	0.25	12	0.32	11	0.87
4	$\text{SO}_2\text{Oct}$	PV-PE	FL	438	0.14	6	0.2	5.5	0.56
5	O	Pyr-E	FL	427	0.13	11	0.24	10	0.54
6	$\text{NHex}_2$	PE	FL	451	0.10	5.5	0.15	5	0.74
7	$\text{NHex}_2$	$\text{PE}_2$	FL	461	0.12	6	0.17	5	0.80
8	$\text{NOct}_2$	PV-PE	FL	482	0.05	3.4	0.08	3.5	0.60
9	$\text{NHex}_2$	PV	FL	481	0.03	2.2	–	–	0.87
10	$\text{NHex}_2$	PV	BP	471	0.06	3.6	0.12	9.5	0.82

<sup>a</sup>  $\lambda$  at which the transmittance is 1%, with 2 mm optical length and  $50 \text{ g l}^{-1}$  concentration.

<sup>b</sup> Optical limiting threshold at 532 nm.

<sup>c</sup> Transmittance for incident fluence of  $10 \text{ J cm}^{-2}$  at 532 nm.

<sup>d</sup> Optical limiting threshold at 600 nm.

<sup>e</sup> Transmittance for incident fluence of  $10 \text{ J cm}^{-2}$  at 600 nm.

<sup>f</sup> Excited-state lifetime derived from TCSPC experiments in  $10^{-6} \text{ M}$  toluene solutions [20].

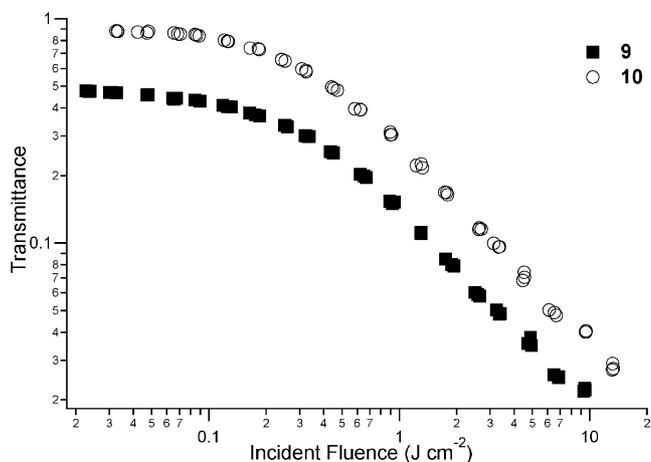


Fig. 4. Nonlinear transmission (at 532 nm, 3 ns pulses): core effect.

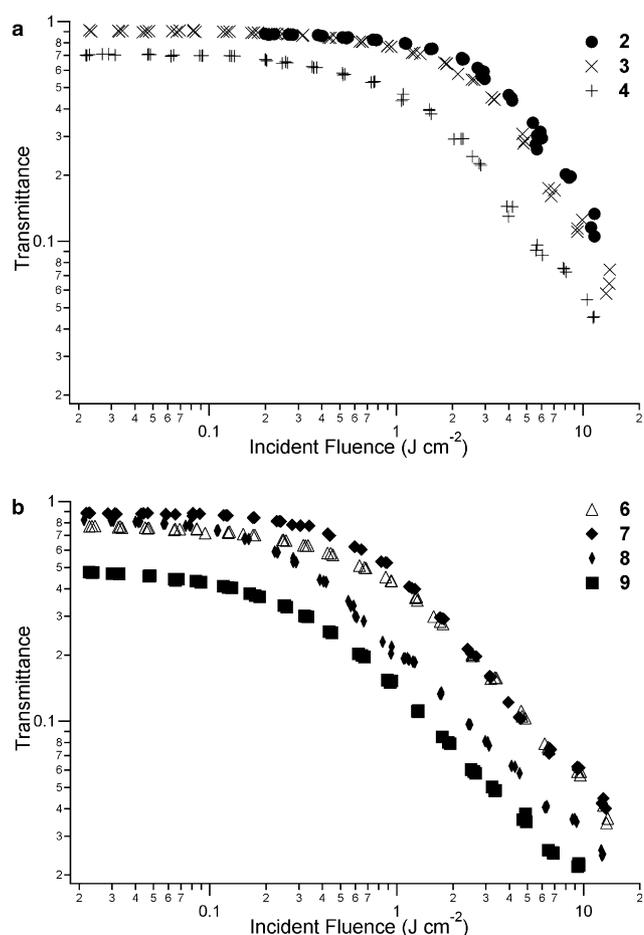


Fig. 5. Nonlinear transmission (at 532 nm, 3 ns pulses): length effect for (a) bis-acceptor and (b) bis-donor compounds.

Optical limiting threshold values were determined graphically (intersection of the linear and nonlinear parts of the transmittance curves as function of the incident laser fluence). We observe that all molecules show somewhat lower threshold values at 532 as compared to 600 nm.

However the reduction of transmission at high fluence (i.e.,  $10 \text{ J cm}^{-2}$ ) is similar at 532 nm and at 600 nm, indicating that most molecules show broadband optical limiting behaviour. The variation of the threshold values—which decrease by more than one order of magnitude by changing the molecular structure—provides evidence that significant improvement of the optical limiting behaviour can be achieved by playing on simple molecular parameters (nature of the end-groups and of the connectors).

### 3.1. Effect of end-groups

#### 3.1.1. Bis-donor vs bis-acceptor

Push–push systems (bis-donor) always show improved nonlinear behaviour as compared to analogous pull–pull (bis-acceptor) having the same core and connectors at the expense of a loss of transparency. This is clearly noted from Table 1 and illustrated in Fig. 2: bis-donor systems show lower optical limiting thresholds as well as lower transmission at high incident fluence. This remains valid for any type of connector (comparison of compounds 3 and 9 or 2 and 6) but the effect is more pronounced for the PV connector as compared to the PE connector: the optical limiting threshold decreases by a factor of 8 at 532 nm and by a factor of 6 at 600 nm for compound 9 as compared to compound 3, whereas it decreases by factors of 4 and 3 (at 532 and 600 nm, respectively) for compound 6 as compared to compound 2 (see also Fig. 3).

#### 3.1.2. Effect of acceptor strength

In addition, we observe by comparison of quadrupoles 1 and 2 that *stronger* acceptor end-groups (Hammett's  $\sigma_p = 0.96$  for  $\text{SO}_2\text{CF}_3$ ,  $0.77$  for  $\text{SO}_2\text{Oct}$  and  $0.72$  for  $\text{SO}_2\text{Me}$ ) lead to *lower* optical limiting efficiency (i.e., higher optical limiting threshold values and higher transmission at high fluence) as illustrated in Fig. 2.

#### 3.1.3. Pyridine-*N*-oxide end-groups

Among the various end-groups, the pyridine-*N*-oxide end-group (compound 5, Fig. 2) plays a particular role thanks to its *combined* electron-donating or electron-releasing character. As compared to pull–pull (molecules 1–4) or push–push derivatives (molecules 6–10) that allow core-to-periphery (or periphery-to-core) intramolecular charge transfer, a *periphery-to-periphery* charge transfer is allowed for molecule 5 only. Such phenomenon is expected to lead to higher TPA cross-sections due to the larger dipole moment of the zwitterionic forms [11,12,18]. Indeed chromophore 5 exhibits significantly improved optical limiting behaviour in the visible as compared to analogous pull–pull systems (i.e., compounds 1 and 2) while being only slightly red-shifted. Compound 5 shows an optical limiting threshold about 3 times smaller at 532 nm and 2 times smaller at 600 nm than pull–pull compound 2 while showing similar transparency (Table 1).

### 3.2. Linker effect

We observe from Table 1 (comparison of bis-acceptor quadrupoles **2** and **3** or bis-donor quadrupoles **6** and **9**, see Fig. 3) that whatever the end-groups, the PV linker leads to better optical limiting efficiency (lower optical threshold and lower transmitted intensity at high fluence), concomitantly with a loss of transparency. Interestingly, quadrupolar compounds built from PV linkers were also demonstrated to display higher TPA cross-sections in the near IR than analogous derivatives built from PE linkers [10].

The replacement of the PE linker by a PV linker leads to a larger bathochromic shift (Table 1) and a larger loss of transmission at low incident fluence (Fig. 3) for bis-donor compounds than for bis-acceptor ones. On the other hand, the gain in optical limiting efficiency is much larger for bis-donor derivatives. As observed from Table 1, the threshold values decrease by a factor of about 3 for bis-donors both at 532 and 600 nm, whereas the factor is only 1.6 for bis-acceptors at the same wavelengths. This emphasizes that bis-donor derivatives definitely overcome bis-acceptor derivatives in terms of optical limiting efficiency in the visible region.

### 3.3. Core effect

From comparison of analogous push–push derivatives bearing biphenyl (**10**) and fluorenyl (**9**) cores, we note that the optical limiting threshold value is reduced by a factor of 2 at 532 nm (Table 1) for compound **9**. We note a substantial loss of transmission at low incident fluence (Fig. 4), which indicates that the low optical limiting threshold is in that case most probably related to one-photon induced excited-state absorption (RSA). The transmittance at high incident fluence ( $10 \text{ J cm}^{-2}$ ) is reduced to 2.2% providing evidence of its excellent optical limiting ability.

### 3.4. Length effect

The nature and length of the conjugated linker significantly influences the optical limiting efficiency. Insertion of PV units in the conjugated arms based upon PE units (PE  $\rightarrow$  PV–PE) always leads to significantly enhanced optical limiting efficiency as observed from comparison of both bis-acceptor derivatives **2/4** (Fig. 5a) or bis-donor derivatives **6/8** (Fig. 5b), although the excited-state lifetimes decrease notably. Interestingly, this enhancement does not give rise to major loss of transparency (Table 1), providing an interesting route for optimization of the nonlinear absorption/transparency trade-off.

As shown from comparison of derivatives **3** and **4** (Table 1), insertion of PE moiety in the conjugated linkers containing a PV unit (PV  $\rightarrow$  PV–PE) has a favourable effect on the optical limiting behaviour (smaller threshold values) while maintaining similar transparency range (similar cut-off wavelengths). As a result, an improvement of the non-

linearity/transparency trade-off is achieved. For bis-donor compounds a net gain of transmittance at low incident fluence is obtained as indicated from the comparison of molecules **8** and **9** (Fig. 5b) with only slightly higher optical limiting threshold (Table 1).

Finally, insertion of a PE moiety in the conjugated linkers already containing a PE linker (comparison of compounds **6** and **7**) does not lead to improved optical limiting/transparency trade-off (Fig. 5b), resulting in both higher optical limiting thresholds and reduction of the transparency range (Table 1). This clearly indicates that the nature and topology of the conjugated arms are important structural parameters for optimizing the nonlinearity/transparency trade-off.

## 4. Conclusion

The present study, demonstrates that significant improvement of the optical limiting efficiency of quadrupolar derivatives in the nanosecond regime can be achieved by playing on simple structural parameters leading to particularly efficient derivatives for broadband optical limiting in the visible region in the nanosecond temporal range. In particular, bis-donor quadrupoles were found to be more efficient than bis-acceptor ones, however at the expense of non-negligible loss of transparency in the visible region. Pyridine-*N*-oxide end-groups, which can play both the role of donor and acceptor, lead to improved efficiency/transparency trade-off. Compounds with planarized core and PV linkers were also found to be more efficient than analogous derivatives built from twisted core or PE linkers. Interestingly, the optical limiting experiments in the visible region in the nanosecond range give rise to similar structure–property relationships as those derived from TPEF experiments conducted in the NIR region using femtosecond pulses.

The present study, also demonstrates that lengthening the conjugated system does not necessarily lead to improved optical limiting behaviour but that the nature of the conjugated connectors plays a significant role. The alternation of phenylene–vinylene and phenylene–ethynylene units allows to improve significantly the optical limiting efficiency/transparency trade-off for bis-acceptor compounds. This opens a route for further optimization of the optical limiting efficiency/transparency trade-off towards bis-acceptor compounds showing similar optical limiting thresholds than bis-donor compounds while being more transparent in the visible region. Finally, it would be quite interesting to combine the optimized quadrupolar molecules with grafted carbon SWNT in order to obtain efficient systems for broadband optical limiting in the picosecond to microsecond range [19].

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