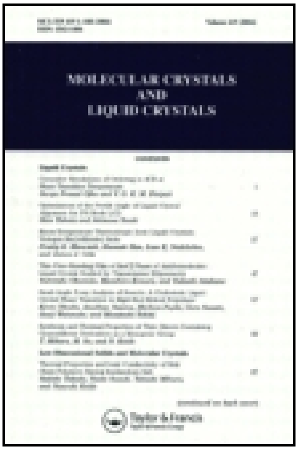

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Bifluorene Derivatives for Two-Photon Absorption in the Visible Range

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We report here linear and two-photon absorption (TPA) properties of bifluorene derivatives of different symmetries. C_{2v} and octupolar symmetries induce a significant enhancement of molecule TPA efficiency. These properties are interpreted in terms of coupling interactions between the different branches of molecules.

Keywords: bifluorene; excitonic coupling; fluorene; oligomer; two-photon absorption

INTRODUCTION

A lot of applications based on the two-photon absorption (TPA) process have already been reported *i.e.*, optical limiting, upconverted lasing, photodynamic cancer therapy, cells imaging, 3D microfabrication, 3D optical data storage [1]. Efficient two-photon absorbers were designed; the most frequent strategy used centrosymmetric molecules substituted by donor groups [2–8], while a new approach involving unsubstituted molecules, such as the Stilbene3 (a bistilbene) [9] or linear polyfluorenes derivatives [10–11] appears very promising in terms of TPA cross-sections. The origin of these promising properties was

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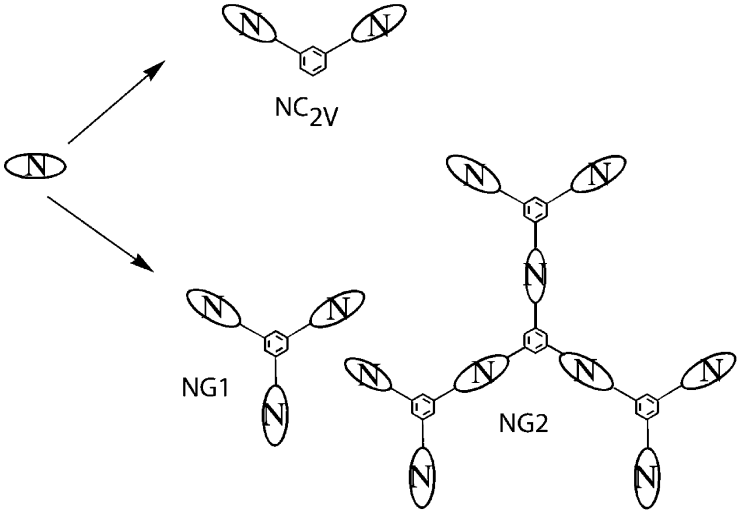

FIGURE 1 General structures of first and second generations dendritic systems of oligofluorenes of length N (N**G1** and N**G2** respectively).

ascribed to strong excitonic coupling interactions between monomers, enhancing strongly the TPA cross-sections of these linear oligomers molecules.

In order to induce further spatial interactions, a new approach to optimize oligomers TPA properties based on excitonic coupling was the introduction of oligomers in branched molecules such as C_{2v} and dendritic systems (Fig. 1). This strategy was shown to be efficient for nonlinear absorption based on TPA of 2D [12] and 3D dendritic fluorene derivatives [13].

In this article, we present and discuss linear and TPA properties of the bifluorene derivative **2** of C_{2v} symmetry and of the dendrimer of first generation **3** in comparison with data of the bifluorene **1** itself (Fig. 2); properties of molecules **2** and **3** will be also compared to those of linear oligofluorenes containing the total same number of fluorene units.

EXPERIMENTAL

The synthesis of the bifluorene **1** was already published [14], while the synthesis of molecules **2** and **3** will be described elsewhere.

TPA spectra were obtained by up-conversion fluorescence measurements using a Nd: YAG pumped optical parametric oscillator that produces 2.6 ns (FWHM) pulses in the 450–650 nm spectral range. The

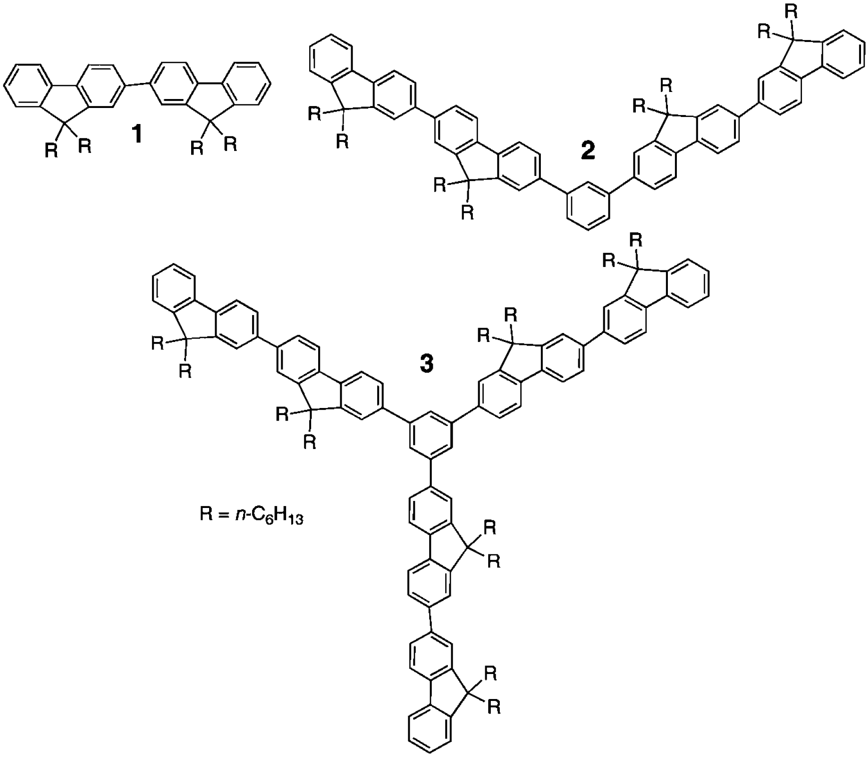

FIGURE 2 Molecular structures of molecules **1–3**.

excitation beam is collimated over the cell length (5 mm). The fluorescence, collected at 90° of the excitation beam, was focused into an optical fiber connected to a spectrometer. The incident beam intensity was adjusted to ensure an intensity squared dependence of the fluorescence over the whole spectral range. The TPA cross-section determined at 570 nm, using p-bis(o-methylstyryl) benzene as a reference standard for which $\sigma_{TPA} = 70 \cdot 10^{-50} \cdot cm^4 \cdot s$/photon-molecule [15], allows to scale the two-photon excited fluorescence spectrum.

RESULTS AND DISCUSSION

Linear absorption spectra of molecules **1–3** are displayed in Figure 3, while wavelengths maxima are reported in Table I. All molecules are colorless. Linear absorption spectra of these bifluorene derivatives present a main band lying between 330 and 350 nm. The effect of the molecules symmetry on linear absorption wavelengths can be

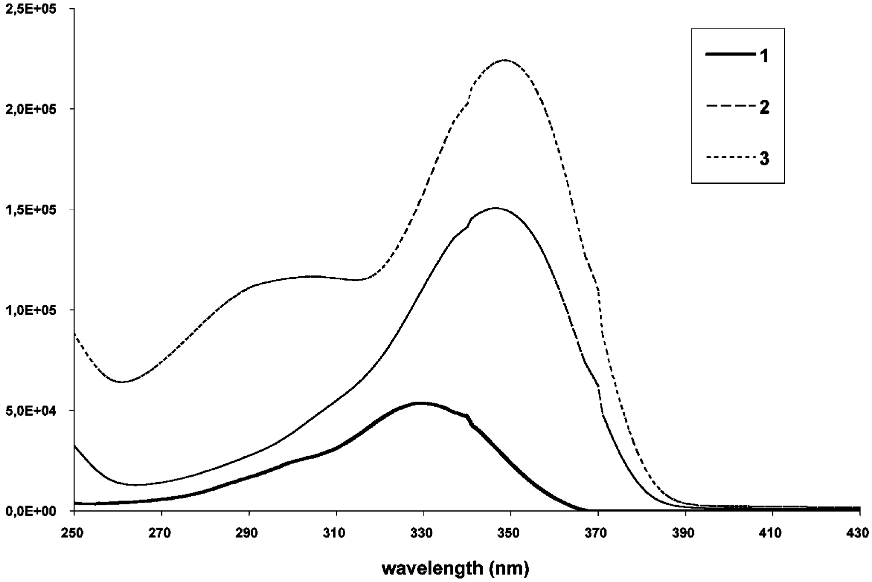

FIGURE 3 Linear absorption spectra of systems **1–3** in chloroform.

considered according to different approaches: (i) a bathochromic shift is observed in branched molecules **2** and **3** with respect to the absorption of the bifluorene **1** (347 and 349 nm for **2** and **3** respectively and 330 nm for **1**); (ii) spectral data of **2** and **3** can be compared to those of linear systems containing the same total number of fluorene units N' [14]: in this case, an hypochromic effect is observed for branched molecules **2** and **3** with respect to linear molecules with 4 and 6 fluorene units respectively (Fig. 4). The line fitting energy variations

TABLE 1 Spectroscopic Data of Systems **1–3**; Linear Absorption Maximum (λ_{abs}), Molar Extinction Coefficient ε, TPA Maximum (λ_{3PA}), TPA Cross-Section Density (σ_{TPA}/N')

Molecules	λ_{abs} (nm)	ε ($\mathrm{mol \cdot L^{-1} \cdot cm^{-1}}$)	λ_{TPA} (nm)	σ_{TPA}/N' (GM)
1	330	53370	525	37
2	347	150470 (tetrafluorene:124350)[a]	560	90 (tetrafluorene:196)[b]
3	349	224120 (hexafluorene:173870)[a]	550	65 (hexafluorene:263)[b]

[a] See Ref. [14].

[b] See Ref. [17].

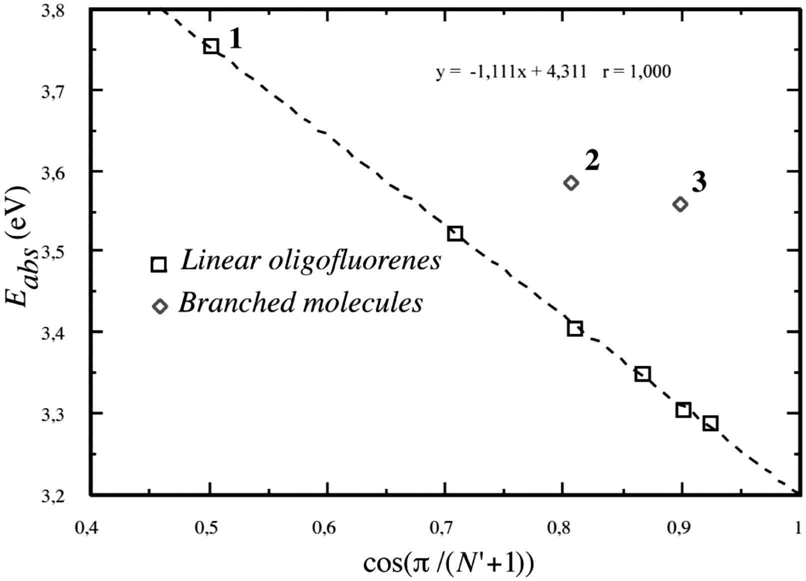

FIGURE 4 Variations with $\cos(\pi/(N'+1))$ of the linear absorption energy transition for linear oligofluorenes [14] and branched molecules **2** and **3** in chloroform (N' being the total number of fluorene units).

of linear molecules corresponds to the law (1) of Davidov, which takes into account coupling interactions between monomers. In this relationship, A represents the transition energy of the monofluorene and M the interaction elements matrix [16].

$$E_{abs} = A - 2|M| \cos \frac{\pi}{(N+1)} \tag{1}$$

A relevant result is the high intensity of the one-photon absorption band in branched molecules; molar extinction coefficients ε are reported in Table 1 (150470 and 224120 $\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$ for **2** and **3** respectively and 53370 $\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$ for **1**). Furthermore, the molar extinction coefficient ε of molecules **2** and **3** is close to that of linear molecules bearing the same number of fluorene units, *i.e.*, the tetra and the hexafluorene (124350 and 173870 $\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$ respectively [14]).

TPA spectra of molecules **1–3** are displayed in Figure 5. Broad bands were obtained between 450 and 650 nm with a bathochromic effect for branched molecules; TPA maxima were observed at 525 nm for **1** and 560 nm and 550 nm for **2** and **3** respectively (Table 1). As in the case of linear absorption properties, the comparison with linear

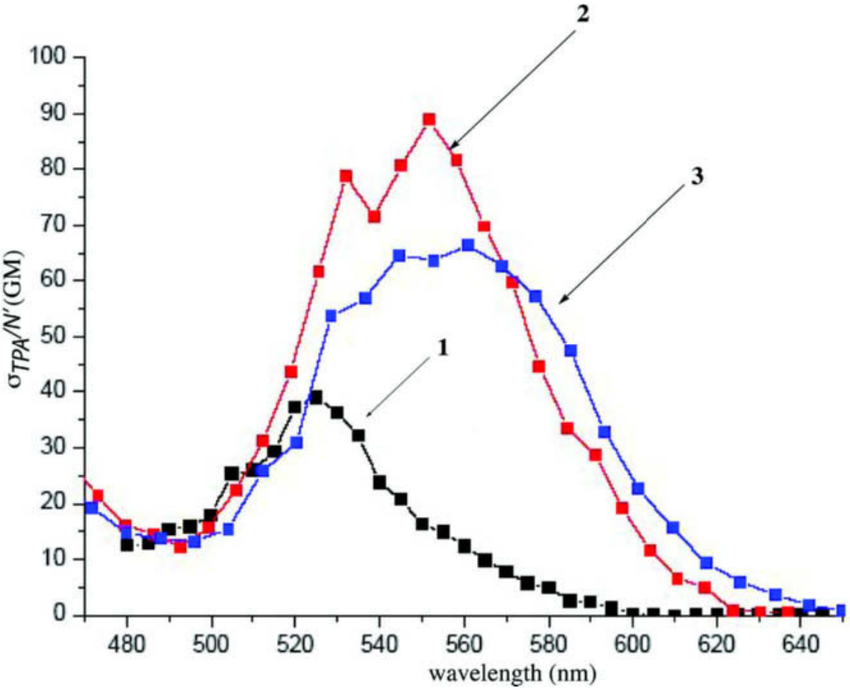

FIGURE 5 TPA spectra of systems **1–3** in chloroform.

oligomers with 4 and 6 fluorenes shows an hypochromic effect for molecules **2** and **3** respectively (Fig. 6). For a significant comparison of the TPA efficiency for molecules, the ratio σ_{TPA}/N' was used, in which σ_{TPA} represents the TPA cross-section. A large increase of this ratio was observed in branched molecules **2** and **3** with respect to that of the linear system **1** (90 and 65 GM respectively against 37 GM [18]) as shown in Figure 5 and Table 1. This trend could be related to the existence of coupling interactions between bifluorene units of the different branches in molecules **2** and **3**. On the other hand, these branched systems are less efficient than linear molecules for TPA properties, since molecules **2** and **3** present a weaker response than their linear analogs tetra and hexafluorenes (see Table 1 and Fig. 6).

CONCLUSION

Linear absorption and TPA properties of bifluorene derivatives (the bifluorene itself compared to C_{2v} and octupolar derivatives) were

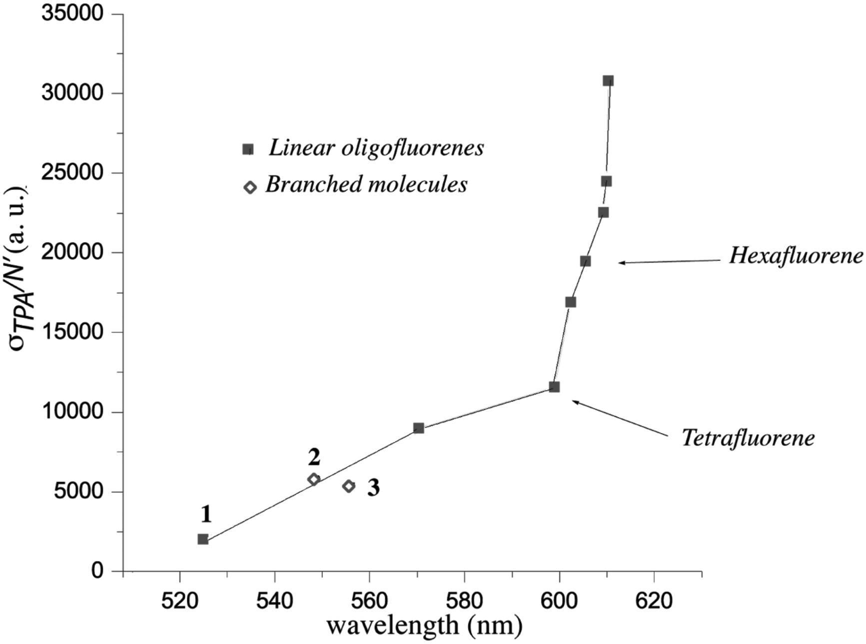

FIGURE 6 Variations with the maximum TPA wavelength of N' of σ_{TPA}/N' for linear oligofluorenes [17] and branched molecules **2** and **3** in chloroform.

studied. All molecules are colorless and transparent in the visible, while they present efficient TPA properties between 450 and 650 nm.

Branched molecules present linear absorption and TPA properties shifted towards the red range with respect to the linear bifluorene. Futhermore, branching bifluorene units in a 2D arrangement induces a significant enhancement of properties. This allows to conclude to the existence of further 2D excitonic interactions in branched molecules containing a bifluorene unit with respect to the bifluorene itself. This approach led to efficient nonlinear absorption properties based on TPA in 2D [12] and 3D [13] branched fluorene derivatives.

In order to rationalize and valid the excitonic interactions assumption, a theoretical model was built [19] and the study of longer branched molecules is in progress.

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[18] 1 GM = 10^{-50} $cm^4 s$/photon-molecule.

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