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## **Branching of substituted push-pull polyenes for enhanced two-photon absorption**

**Francesca Terenziani, Céline Le Droumaguet, Olivier Mongin, Claudine Katan and Mireille Blanchard-Desce**

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### **Abstract**

*The paper will focus on the branching of substituted push-pull polyenes in the weak to medium interaction limit. Branching of dipolar units of increasing length is achieved through connection via a central triphenylamine core, leading to three-branched structures. Linear and nonlinear optical properties of these octupolar chromophores are compared to those of their dipolar analogues. In particular, photophysical properties, solvatochromism and two-photon absorption (TPA) cross sections are investigated. Results confirm that the branching strategy leads to TPA activation in spectral regions where the dipolar units are almost transparent and that large TPA enhancement can be achieved on a very large spectral range. Localization of the emitting excited state on a single dipolar branch is also evidenced.*

**Keywords:** two-photon absorption, solvatochromism, excitonic coupling, multipolar systems.

### **1. INTRODUCTION**

Recent breakthroughs in the field of organic molecular materials for nonlinear optics (NLO) make it very promising for future technological impacts in a great variety of areas [1]. Among the many NLO effects, two-photon absorption (TPA) has attracted increasing interest over recent years. After dipolar [2-9] and more recently quadrupolar structures [3,5,7,9-22], attention has progressively moved toward branched molecular architectures [23-36], such as dendrimers, to ensure enhanced TPA figures-of-merit. As long as branched structures can be considered as assemblies of individual monomeric bricks assembled through chemical connectors, understanding can be gained by systematic comparison with the monomeric building block.

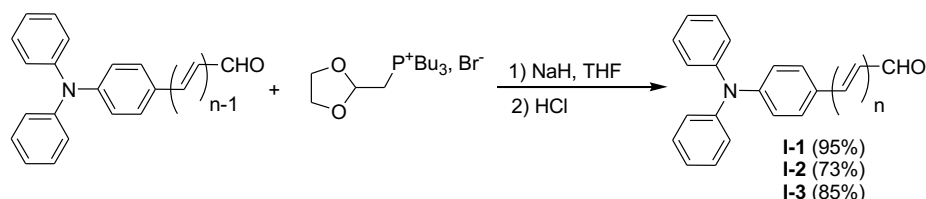
In this paper, photophysical and TPA properties of a novel series of chromophores based on asymmetrically substituted polyenic dipoles will be studied. Properties of octupolar derivatives,

F. Terenziani, C. Le Droumaguet, O. Mongin, C. Katan, M. Blanchard-Desce, *Branching of substituted push-pull polyenes for enhanced two-photon absorption*, **Nonlinear Optics, Quantum Optics** 35, 69-82 (2006) obtained by connecting three dipolar units through a central triphenylamine core, will be compared to their monomeric analogues. Experimental measurements include UV-Vis absorption spectra, fluorescence, solvatochromic behavior, as well as femtosecond two-photon-excited fluorescence (TPEF). Interpretation of experimental findings will benefit from comparison to related series [37,38] and from the use of the excitonic model [39].

## 2. METHODOLOGY

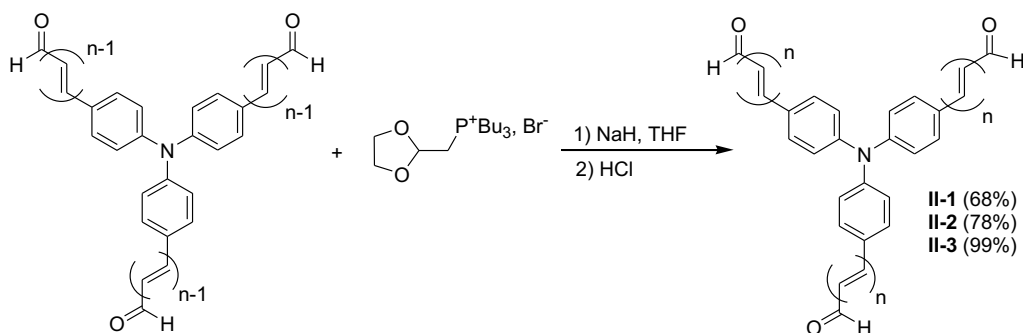
### 2.1 Synthesis of the chromophores

Two series of chromophores have been synthesized. Dipolar triphenylamine polyenals **I-1** to **I-3** were obtained stepwise by repetitive vinylic homologation from 4-formyltriphenylamine (Scheme 1). This involves reaction with tributyl-[(1,3-dioxolan-2-yl)methyl]phosphonium bromide [40] using solid-liquid phase transfer conditions [41] followed by hydrolysis in acidic conditions.



Scheme 1. Synthesis of dipolar aldehydes **I-1**, **I-2** and **I-3**.

Octupolar three-branch chromophores **II-1** to **II-3** were obtained in a similar way from tris(4-formylphenyl)amine [42], by successive triple vinylic homologations (Scheme 2). All compounds were obtained as pure all-E derivatives in good yield by column chromatography, as shown by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRMS.



Scheme 2. Synthesis of octupolar compounds **II-1**, **II-2** and **II-3**.

### 2.2 Photophysical methods

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UV/VIS spectra were recorded on a Jasco V-570 spectrophotometer. Fluorescence measurements were performed at room temperature in dilute solutions (*ca.*  $10^{-6}$  M) using an Edinburgh Instruments (FLS 920) spectrometer in photon-counting mode. Emission spectra were obtained, for each compound, at  $\lambda_{\text{ex}} = \lambda_{\text{max}}(\text{abs})$  with  $A \leq 0.1$  at  $\lambda_{\text{ex}}$  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 (quantum yield  $\Phi = 0.90$ ) [43].

Two-photon absorption cross-sections ( $\sigma_2$ ) were determined by the two-photon-excited fluorescence (TPEF) technique in solution (concentration *ca.*  $10^{-4}$  M) in the epifluorescence mode. These measurements provide the TPEF action cross-section  $\sigma_2 \Phi$ . The corresponding  $\sigma_2$  values were derived by determining the fluorescence quantum yield  $\Phi$  from standard fluorescence measurements. TPEF measurements were conducted using a mode-locked Ti:sapphire laser operating between 700 and 1000 nm and delivering 120-fs pulses at 76 MHz, following the experimental protocol described in detail by Xu and Webb [44]. The quadratic dependence of the fluorescence intensity on the excitation intensity was verified for each data point, indicating that the measurements were carried out in intensity regimes in which saturation or photodegradation do not occur. 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 690-1000 nm range [44,45]. Equations for relative determination of  $\sigma_2$  were adopted as reported in Ref. [46]. Experimental uncertainty does not exceed  $\pm 10\%$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Photophysical properties

The photophysical characteristics of the investigated chromophores are summarized in Table 1. All chromophores show an intense absorption band in the near UV–blue visible region (Figure 1). As expected, absorption and fluorescence spectra of both dipolar and octupolar compounds undergo a red-shift with increasing chain length (Figure 1 and Table 1). The molar extinction coefficient is roughly proportional to the number of branches, indicative of a nearly additive behavior. Gathering dipolar units (chromophores **I**) via a common electron-donating nitrogen within trigonal branched molecules (three-branched compounds **II**) leads to a slight red-shift of the absorption bands (Figure 2 and Table 1). This is indicative of sizeable coupling between the dipolar branches that can be estimated within the excitonic model [37]. The coupling constants  $V$  are estimated to be  $\sim 0.16$ ,  $0.19$  and  $0.15$  eV, respectively, for **II-1**, **II-2** and **II-3**. These values are comparable to previous estimates

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Table 1. Photophysical properties of the investigated compounds (in toluene): absorption wavelength ( $\lambda_{abs}$ ), fluorescence wavelength ( $\lambda_{em}$ ), Stokes-shift, molar extinction coefficient ( $\epsilon$ ).

Compound	$\lambda_{abs}$ [nm]	$\lambda_{em}$ [nm]	Stokes-shift [cm <sup>-1</sup> ]	$\epsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ]	$\Phi$
<b>I-1</b>	390	476	4633	20700	0.32
<b>I-2</b>	410	500	4390	20600	0.13
<b>I-3</b>	427	540	4901	20800	0.05
<b>II-1</b>	410	455	2412	49900	0.17
<b>II-2</b>	438	496	2670	60700	0.60
<b>II-3</b>	450	550	4040	48000	0.53

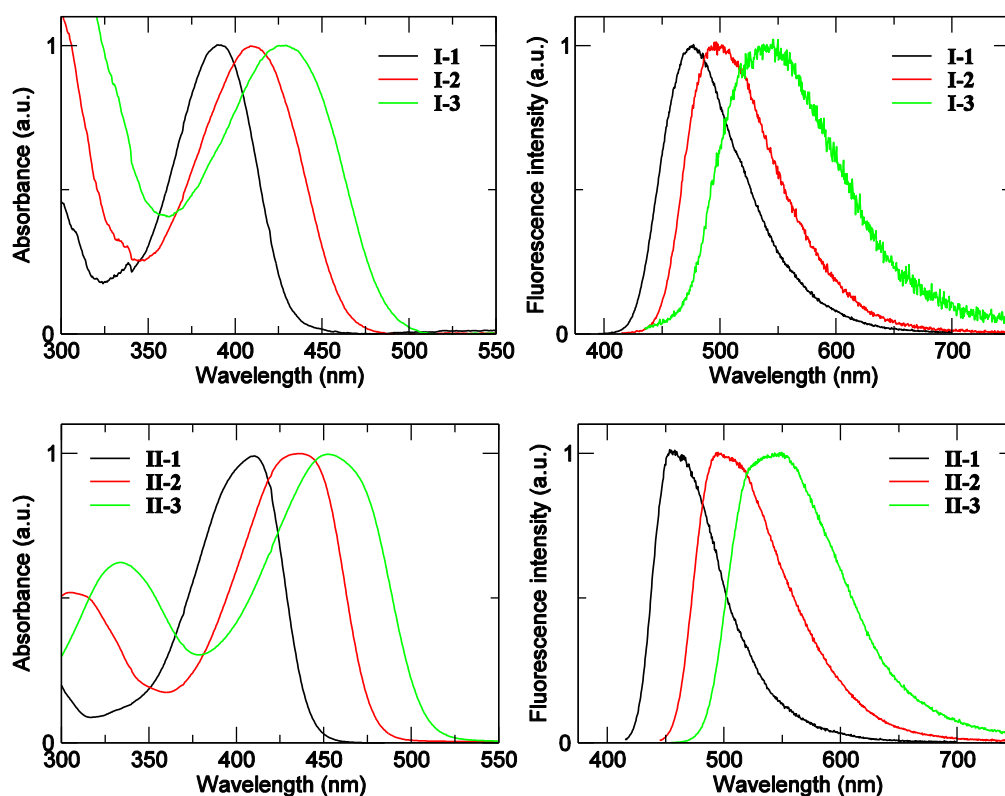


Figure 1. Absorption (left panels) and fluorescence (right panels) spectra of the investigated products in toluene.

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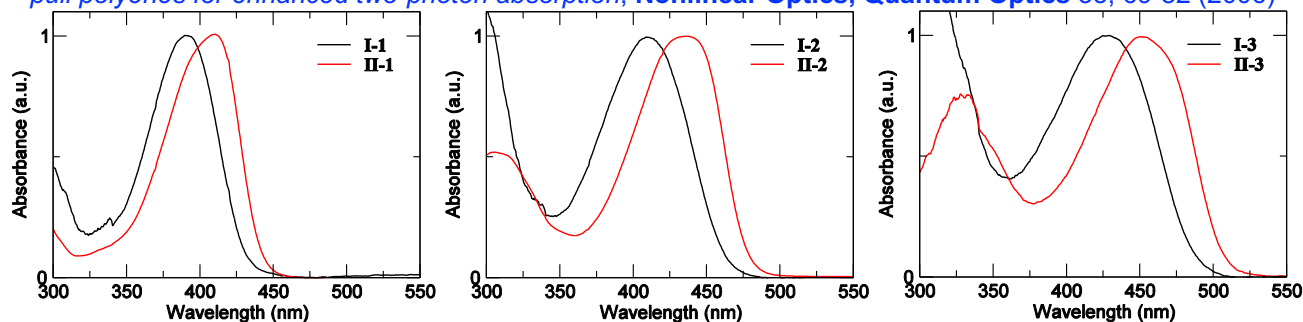


Figure 2. Absorption spectra (in toluene) of octupoles (red lines) compared with reference dipoles (black lines).

These results are consistent with those obtained for related branched structures [37,38] and arise from the significant dipolar character of the emitting excited state, which induces significant nuclear relaxation after photoexcitation and prior to emission. Interestingly, branched chromophores **II** exhibit smaller Stokes-shifts than their dipolar analogues **I**. This originates from the contrast in the absorption and emission behavior. Whereas octupolar chromophores show a noticeable red-shifted absorption band (Figure 2) with respect to their dipolar analogues (as a result of the coupling between dipolar branches), their emission spectra are either blue-shifted or only slightly red-shifted (Figure 1). This phenomenon is most probably related to the localization of the excitation on a single branch of the octupolar chromophores in the emitting excited-state.

### 3.2 Solvatochromism

All investigated octupolar chromophores show a marked positive emission solvatochromism. Increasing solvent polarity leads to a pronounced bathochromic shift of the fluorescence bands (Figure 3).

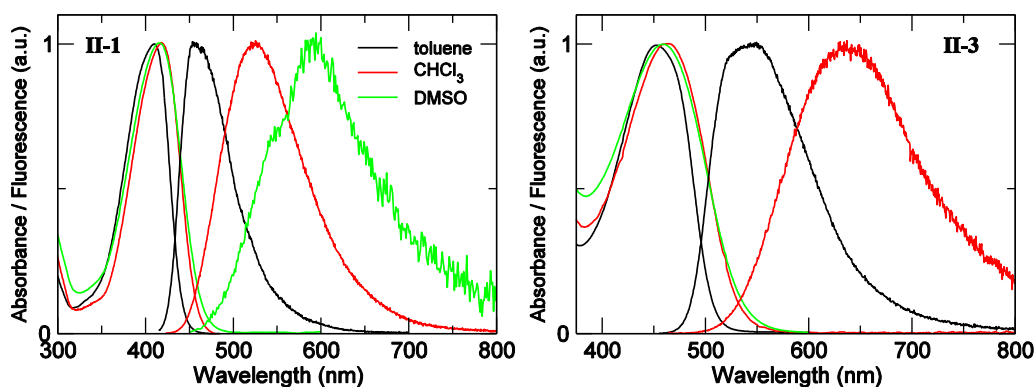


Figure 3. Absorption and fluorescence solvatochromism of compounds **II-1** and **II-3** (**II-3** is non fluorescent in DMSO).

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Solvent polarity allows tuning the photoluminescence in a significant way. In particular, the studied series allows covering the whole visible region. In contrast, only small shifts are observed for the absorption bands (Figure 3). Accordingly, the Stokes-shifts significantly increase with increasing solvent polarity. In addition, the solvatochromic behavior of all chromophores **II** follows the Lippert-Mataga relationship [47,48]. Such behavior is consistent with a slightly polar ground state and a highly polar emitting excited-state, the latter being largely stabilized by polar solvents. This is a clear indication that emission stems from one of the dipolar branches in these three-branched chromophores. This phenomenon of excited state localization was already reported in the literature for multipolar compounds obtained by branching dipolar units [37,38,49-53]. Our results thus confirm that the localization of the excitation on one of the branches after absorption and prior to emission is a common phenomenon for this class of branched structures.

### 3.2 Two-photon absorption

TPA spectra of the investigated chromophores are plotted in Figure 4, and corresponding results are summarized in Table 2.

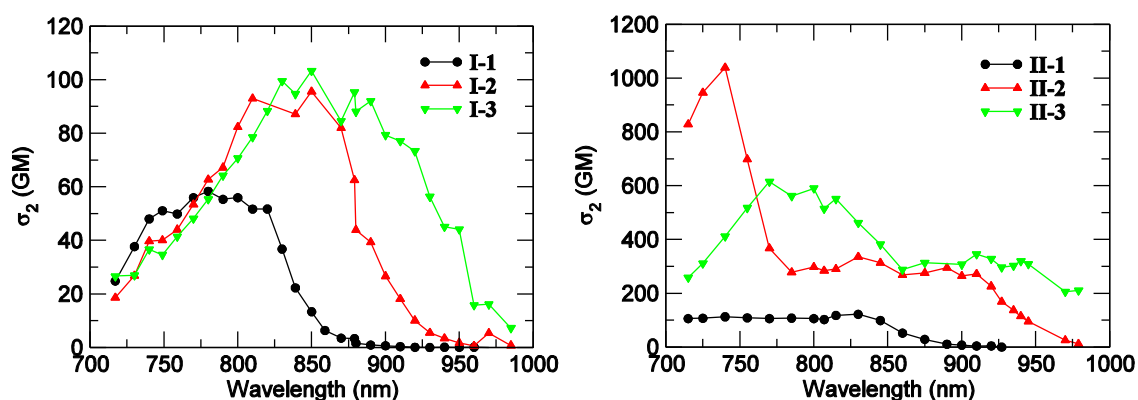


Figure 4. TPA cross section spectra of the investigated dipolar (left panel) and octupolar (right panel) chromophores in toluene. Notice that different scales have been used for the TPA cross section amplitudes.

Table 2: Two-photon absorption data of the investigated chromophores (in toluene).

Compound	$2 \lambda_{\text{abs}}$ (nm)	$\lambda_{\text{TPA}}^{\text{max1}}$ (nm)	$\lambda_{\text{TPA}}^{\text{max2}}$ (nm)	$\sigma_2^a$ (GM)		$\sigma_2/\text{MW}$ (GM g <sup>-1</sup> mol)	
				at $\lambda_{\text{TPA}}^{\text{max1}}$	at $\lambda_{\text{TPA}}^{\text{max2}}$	at $\lambda_{\text{TPA}}^{\text{max1}}$	at $\lambda_{\text{TPA}}^{\text{max2}}$
<b>I-1</b>	780	780	-	60	-	0.20	-
<b>I-2</b>	820	830	-	95	-	0.29	-
<b>I-3</b>	854	855	-	105	-	0.30	-
<b>II-1</b>	820	830	< 700	120	-	0.29	-
<b>II-2</b>	876	875	740	330	1040	0.70	2.14

<sup>a</sup> TPA cross-sections; 1 GM =  $10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>.

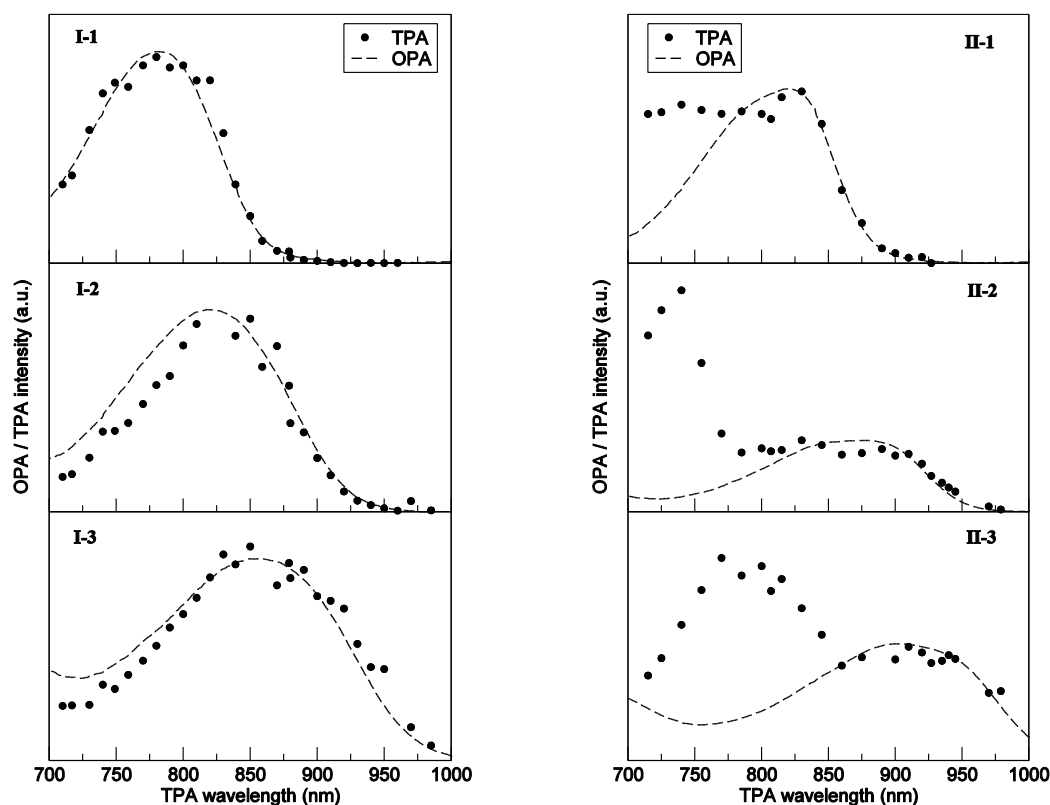


Figure 5. Comparison of two-photon absorption spectra and corresponding (rescaled) one-photon absorption spectra.

Figure 5 compares TPA spectra with rescaled linear absorption (OPA) spectra. Dipolar compounds display one TPA band at twice the OPA maximum, with a nice agreement of both position and bandshape. TPA spectra of octupolar systems can be figured out starting from the excitonic model. Within this model, interactions between branches lead to an energy separation between the (otherwise degenerate) excited states, so that final states of the three-branched chromophores are split toward higher ( $+2V$ ) and lower energies ( $-V$ ) with respect to their monomeric analogue [37-38]. Thus, the shoulder close to twice the OPA maximum wavelength indicates that the lowest energy excited-state is both one- and two-photon allowed. This local TPA maximum is red-shifted with respect to TPA maximum of the dipolar analogue of each branched chromophore due to interaction between branches. The TPA cross-section value is already larger than that of the corresponding dipolar analogue. But the most intense TPA band is that corresponding to the higher-energy excitonic state, which is only two-photon allowed. Using the coupling constants  $V$  deduced from the OPA spectra, positions of the main TPA maxima are predicted to show up at 710, 727 and 775 nm respectively for compound II-1, II-2 and II-3 (in reasonably good agreement with experimental findings). These new band is clearly visible for compounds II-2 and II-3, while for II-



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**1** it is outside the investigated spectral region (in agreement with the slight blue-shift of the maxima observed for compounds **II-2** and **II-3** as compared to the values derived from the excitonic coupling model). The corresponding absolute TPA maxima show a large enhancement when compared to those obtained for compounds **I-2** and **I-3** (Table 2). For instance, octupolar chromophore **II-2** shows a maximum TPA cross-section about ten times larger than that of its dipolar analogue **I-2**.

Further insight into the branching effect can be gained by setting some normalization criterion. A first normalization procedure is based on the molecular weight, as to obtain a relevant figure of merit for applications such as optical limiting. Examination of TPA values normalized following this criterion (i.e.  $\sigma_2/MW$ , where MW is the molecular weight) at the first local maxima shows that branched chromophores lead to larger normalized TPA cross sections than their corresponding branches (Table 2). This enhancement spreads over the whole investigated spectral range for all octupolar chromophores, thus indicating that the branching approach is a valid strategy for obtaining materials with increased TPA figures of merit. Normalized peak-TPA values lead to very high amplification factors for octupolar derivatives: of 7 and 4 respectively for compounds **II-2** and **II-3**.

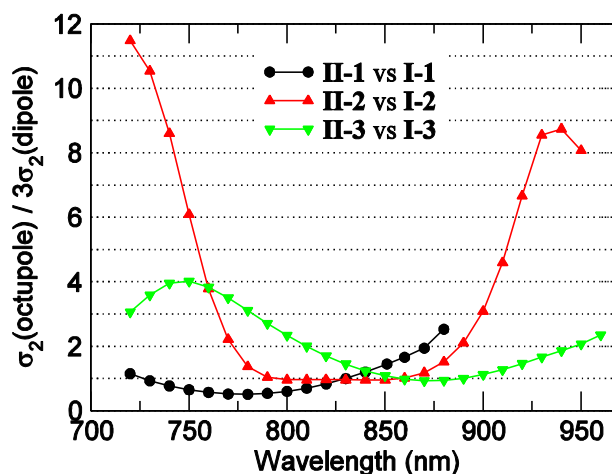


Figure 6. TPA enhancement factor for octupolar systems versus dipolar reference compounds.

Another normalization criterion can be chosen by simply rescaling the TPA response for the number of branches. This analysis yields better information on the intrinsic charge-symmetry and branching effect, allowing to distinguish additive behavior from cooperative effects. Figure 6 shows the enhancement factor for octupolar chromophores, calculated as the ratio between the TPA cross section of the three-branched structure and 3-times the TPA cross section of the corresponding dipole. This ratio is wavelength dependent, and the strongest enhancement for octupolar derivatives is observed on both sides of the TPA maximum wavelength of the corresponding dipolar

F. Terenziani, C. Le Droumaguet, O. Mongin, C. Katan, M. Blanchard-Desce, *Branching of substituted push-pull polyenes for enhanced two-photon absorption*, **Nonlinear Optics, Quantum Optics** 35, 69-82 (2006) compounds. This is a result of excited state splitting due to inter-branch coupling: two-photon active bands are obtained for branched compounds in spectral regions respectively blue- and red-shifted with respect to the monomeric reference, with a consequent TPA activation in regions where the monomeric model is almost two-photon transparent. These effects are particularly noticeable in Figure 6 for systems **II-2** and **II-3**, while **II-1** also shows a region of slightly reduced normalized TPA. Compound **II-2** presents the largest enhancement: about 12 and 9 times larger than **I-2** at 720 nm and 940 nm respectively.

The large amplification of TPA response shown by branched chromophores is directly related to the interaction between the dipolar units that are gathered via the common nitrogen core. This is also confirmed by the fact that the largest enhancement is obtained for the compound (**II-2**) for which the strongest excitonic coupling has been derived. Starting from cores providing larger inter-branch couplings may permit achieving even further TPA enhancement.

#### 4. CONCLUSIONS

A new series of dipolar and three-branched chromophores derived from a triphenylamine core has been designed and investigated. Chromophores containing a polyenic structure of different length (from 1 to 3 double bonds) have been selected to investigate the chain length's effect. Linear and nonlinear optical properties of the octupolar compounds have been explored and compared to those of their dipolar analogues. The one- and two-photon absorption properties of branched structures indicate that the dipolar branches significantly interact. Results have been interpreted in terms of the Frenkel exciton model allowing us to derive the corresponding coupling constants. This coupling not only induces shifts of the one- and two-photon absorption bands, but also results in strong TPA enhancement for the two longest derivatives ( $n = 2, 3$ ). The highest enhancement is observed for the branched compound characterized by the strongest excitonic coupling. Thus, appropriate tuning of this coupling should allow for achieving novel chromophores with efficient TPA responses in specific spectral regions. In addition, both fluorescence spectra and solvatochromic behavior corroborate previous findings showing that the emitting state of these branched molecules is localized on a single branch, leading to dipolar emitting excited-states. Combined with higher fluorescence quantum yields, branched derivatives thus show improved features for practical applications when compared to their dipolar analogues. This can be used for instance for the design of sensitive two-photon probes of micropolarity [54].

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