



The photophysics and two-photon absorption of a series of quadrupolar and tribranched molecules: The role of the edge substituent

M. Fakis^{a,*}, I. Fitis^a, S. Stefanatos^a, P. Vellis^b, J. Mikroyannidis^b, V. Giannetas^a, P. Persephonis^a

^a Department of Physics, University of Patras, Patras 26504, Greece

^b Department of Chemistry, University of Patras, Patras 26504, Greece

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ABSTRACT

A series of quadrupolar and tribranched molecules were synthesized in order to examine the role of the edge substituents on their photophysical and two-photon absorption properties. Two-photon absorption cross sections, δ , of the molecules were determined in THF solution using a two-photon excited fluorescence technique with femtosecond pulsed excitation. The quadrupolar molecules contained a fluorene or alkoxy-substituted phenylene central core together with various electron accepting edge substituents such as pyridine, terpyridine, phthalimide and naphthalimide. The tribranched molecules contained triphenylamine at the center and terpyridine or phthalimide substituents at the periphery. It was found that edge phthalimide substituent favour high δ values. δ Values as high as 1660 GM and 1500 GM were obtained from the phthalimide-fluorene-phthalimide and phthalimide-phenylene-phthalimide molecules, respectively; in the case of the tribranched molecule with a phthalimide substituent, a δ -value of 1200 GM was found.

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1. Introduction

Two-photon absorption (TPA) has received great scientific interest over the last years due to its potential use in various applications in physics, biology and chemistry like TPA pumped lasing, TPA microscopy and TPA polymerization [1–3]. Although, a huge amount of research has been devoted to the design and study of organic materials with enhanced TPA properties, this field remains highly attractive as it is obvious by the large number of recent reports [4–11]. The ultimate goal of the research efforts is to understand how the chemical structure affects the TPA properties and to find chemically stable, inexpensive organic materials with large TPA cross sections, δ [12,13].

It is nowadays well known that the incorporation of electron donating groups, D, (like amino and alkoxy) and electron accepting groups, A, (like cyano, pyridine and benzothiazole) in π -conjugated organic molecules can lead to a great enhancement of δ . Thus, dipolar, D- π -A and quadrupolar molecules, D- π -A- π -D or A- π -D- π -A, have been synthesized and studied experimentally [5,8,10,14–17] and theoretically [18]. Another strategy to obtain large δ values is the design of multibranched molecules. In these molecules, the coupling between the building blocks (branches) plays a crucial role. This coupling can be achieved, for example, by a triphenylbenzene core,

used as a π -linkage [7], by a triphenylamine core, used as an electron donating core [19,20], or by a tricyano phenylene and a triazine core, used as electron accepting cores [21,22]. In multibranched molecules, intramolecular electron transfer from the center to the periphery or vice versa occurs depending on the structure of the core and the substituents. Additionally, it has been theoretically found by Macak et al. that not only the electronic coupling between the branches but also the vibronic contributions of the tribranched molecules can play an important role towards enhancing the TPA properties over their single branch structures [23].

For the measurement of δ , various experimental techniques have been implemented including non-linear transmission [24], open z-scan [25] as well as TPA fluorescence techniques [26]. The parameters of the experiment strongly influence the values of δ [8]. The use of high excitation fluences obtained by nanosecond, picosecond and sometimes even by femtosecond pulses can give rise to excited state absorption following the TPA [27,28]. These two phenomena are difficultly discriminated and can lead to false δ values. The most suitable way of measuring the pure TPA cross section is by means of a two-photon excited fluorescence (TPEF) technique using low power excitation with femtosecond pulses. In this technique, the order of the non-linearity can be determined through the dependence of the two-photon excited fluorescence intensity on the excitation intensity. In a TPA effect, this dependence should follow the square-power law.

The use of organic molecules in TPA applications like TPA pumped lasing requires not only a large TPA cross section but also

* Corresponding author.

E-mail address: fakis@upatras.gr (M. Fakis).

a high fluorescence quantum yield. With this in mind, we report, in this paper, the photophysical and TPA properties of a series of new quadrupolar and tribranched molecules. The quadrupolar molecules bear various electron accepting edge substituents and two different central cores namely fluorene- and alkoxy-substituted phenylene. The tribranched molecules are based on a triphenylamine central core and electron accepting substituents at the periphery. The TPA cross sections have been determined through a TPEF technique with femtosecond pulsed excitation. The results are discussed in order to determine the role of the substituents for achieving both high TPA cross section and quantum yield.

2. Experimental

2.1. Molecules

The molecules studied in this work, together with their abbreviations are shown in Fig. 1. Molecules F(Pyr)₂, F(Terpyr)₂,

F(Pht)₂ and F(Npht)₂ bear fluorene central core which acts as a π -conjugated link. Fluorene has been found to be an excellent central link in quadrupolar or dipolar molecules because it provides planarity and extended overlap of π orbitals. Molecules P(Pyr)₂, P(Terpyr)₂, P(Pht)₂ and P(Npht)₂ contain an alkoxy-substituted phenylene ring as central core. Apart from a π -conjugated link, this core is also used as an electron-donating group because of its alkoxy substituents. All fluorene- and phenylene-core molecules bear various electron accepting edge substituents which are triphenylpyridine (F(Pyr)₂ and P(Pyr)₂), terpyridine (F(Terpyr)₂ and P(Terpyr)₂), phthalimide (F(Pht)₂ and P(Pht)₂) and naphthalimide (F(Npht)₂ and P(Npht)₂). The two tribranched molecules bear triphenylamine central core acting as a coupling core between the branches as well as an electron donor. The periphery of the tribranched molecules is constituted of terpyridine (TPA(Terpyr)₃) and phthalimide substituents (TPA(Pht)₃) which are used as electron acceptors. Therefore, our design strategy for the tribranched molecules aims at an intra-molecular charge transfer from the core to the periphery.

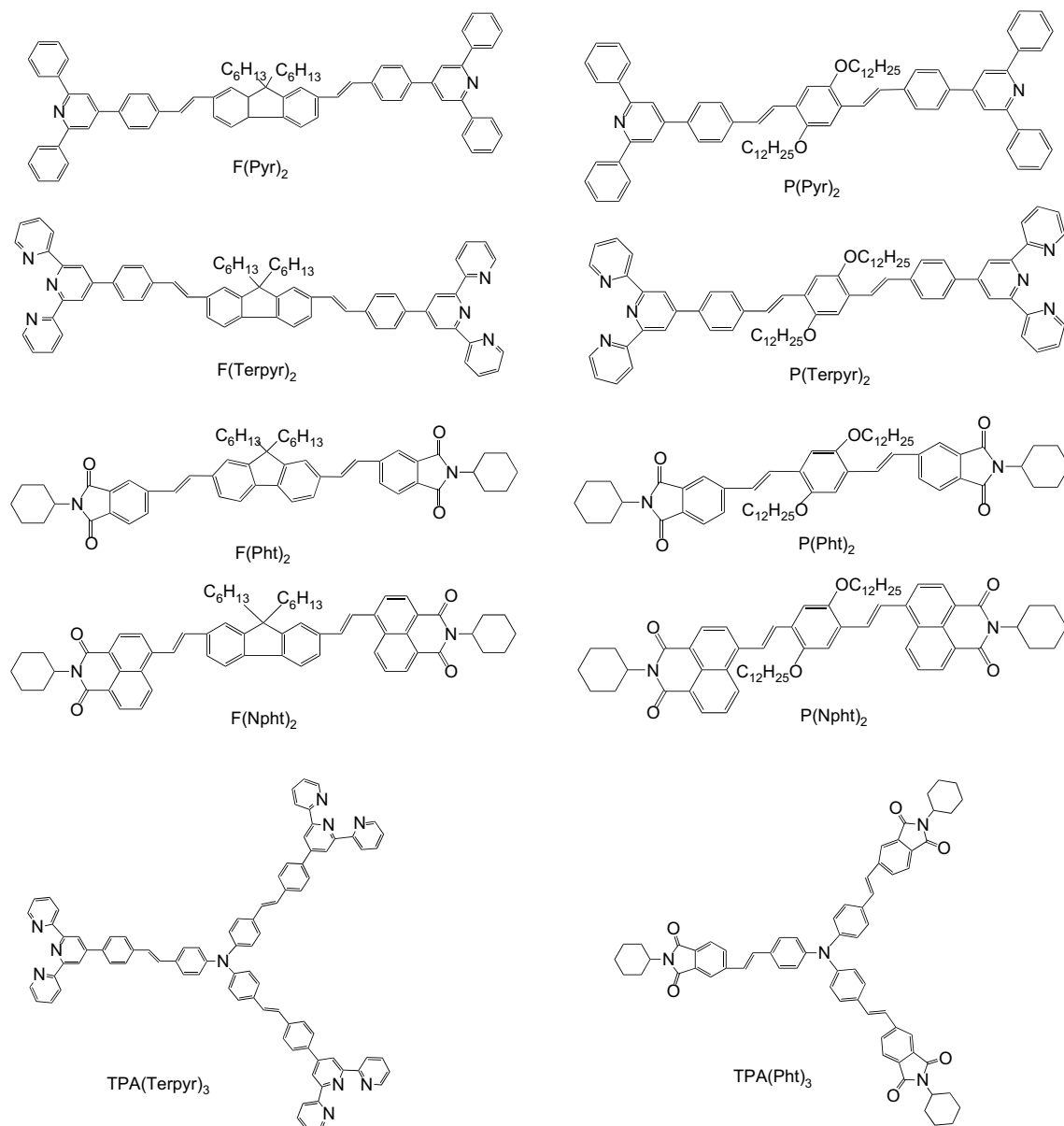


Fig. 1. The chemical structures of the molecules studied in this work together with their abbreviations.

2.2. Synthesis

All compounds were prepared by Heck coupling [29]. In particular, F(Pyr)₂, F(Terpyr)₂, F(Pht)₂ and F(Npht)₂, were synthesized from the reactions of 9,9-dihexyl-2,7-divinylfluorene with appropriate aromatic bromides in a molar ratio 1:2. The molecules P(Pyr)₂, P(Terpyr)₂, P(Pht)₂ and P(Npht)₂ were similarly synthesized from the reactions of 1,4-divinyl-2,5-didodecyloxyphenylene with the same bromides. The tribranched compounds TPA(Terpyr)₃ and TPA(Pht)₃ were prepared by reacting tris(4-bromophenyl)amine with appropriate aromatic vinyls in a molar ratio 1:3. All preparation reactions took place in *N,N*-dimethylformamide utilizing triethylamine and palladium acetate as acid acceptor and catalyst, respectively [30].

The preparation of P(Pyr)₂ is given as a typical example for the preparation of the compounds by Heck coupling: a flask was charged with a mixture of 4(4-bromophenyl)-2,6-diphenylpyridine (0.6200 g, 1.605 mmol), 2,5-didodecyloxy-1,4-divinylbenzene (0.4000 g, 0.803 mmol), Pd(OAc)₂ (0.0077 g, 0.034 mmol), P(*o*-tolyl)₃ (0.0580 g, 0.191 mmol), DMF (8 mL) and triethylamine (2 mL). The flask was degassed and purged with N₂. The mixture was heated at 90 °C for 24 h under N₂. Then, it was filtered and the filtrate was poured into methanol. The yellow precipitate was filtered and washed with methanol. The crude product was purified by dissolving in THF and precipitating into methanol (yield: 61%).

The spectroscopic characterization of the compounds was performed by FT-IR and ¹H NMR. The spectroscopic data and the preparation yields of the compounds are the following:

F(Pyr)₂: yield: 60%. FT-IR (KBr, cm⁻¹): 3028, 2922, 2852, 1594, 1458, 960, 820, 770, 734. ¹H NMR (CDCl₃, ppm): 7.94 (m, 8H); 7.79 (m, 2H); 7.72 (m, 4H); 7.54 (m, 8H); 7.30 (m, 16H); 7.30–7.21 (m, 4H); 2.03 (m, 4H); 1.11 (m, 16H); 0.77 (t, 6H).

F(Terpyr)₂: yield: 46%. FT-IR (KBr, cm⁻¹): 3052, 2926, 2854, 1602, 1584, 1566, 1466, 962, 824, 792, 740. ¹H NMR (CDCl₃, ppm): 8.80–8.71 (m, 12H); 7.92–7.98 (m, 10H); 7.21 (m, 12H); 2.02 (m, 4H); 1.12 (m, 16H); 0.87 (t, 6H).

F(Pht)₂: yield: 60%. FT-IR (KBr, cm⁻¹): 3026, 2926, 2854, 1766, 1706, 1610, 1436, 1368, 1090, 962, 746. ¹H NMR (CDCl₃, ppm): 8.01 (s, 4H); 7.79 (m, 8H); 7.22–7.16 (m, 4H); 2.24–2.21 (m, 4H); 4.13, 1.90–1.73 and 1.40–1.25 (m, 22H); 1.24–1.07 (m, 16H); 0.67 (t, 6H).

F(Npht)₂: yield: 52%. FT-IR (KBr, cm⁻¹): 3030, 2926, 2854, 1774, 1698, 1658, 1584, 1466, 1398, 1356, 1234, 1188, 1110, 1038, 960, 898, 820, 780, 754. ¹H NMR (CDCl₃, ppm): 8.62 (m, 6H); 8.06 (m, 4H); 7.99 (s, 2H); 7.81–7.78 (m, 4H); 7.48–7.45 (m, 4H); 2.09 (m, 4H); 4.13, 1.89–1.25 (m, 22H); 1.11 (m, 16H); 0.77 (t, 6H).

P(Pyr)₂: yield: 61%. FT-IR (KBr, cm⁻¹): 3036, 2922, 2852, 1594, 1492, 1460, 1388, 1198, 1024, 966, 768, 730, 690. ¹H NMR (CDCl₃, ppm): 7.96–6.82 (m, 34H); 7.26 (m, 4H); 3.94 (m, 4H); 1.71 (m, 4H); 1.33–1.29 (m, 36H); 0.96 (t, 6H).

P(Terpyr)₂: yield: 54%. FT-IR (KBr, cm⁻¹): 3050, 2922, 2850, 1600, 1584, 1566, 1466, 966, 819, 792. ¹H NMR (CDCl₃, ppm): 8.51–8.83 (m, 12H); 8.01 (m, 4H); 7.52–7.70 (m, 8H); 7.48 (m, 4H); 6.99 (m, 4H); 3.75–3.94 (m, 4H); 1.63 (m, 4H); 1.25 (m, 36H); 0.89 (m, 6H).

P(Pht)₂: yield: 58%. FT-IR (KBr, cm⁻¹): 3058, 2922, 2852, 2358, 2340, 1766, 1700, 1610, 1468, 1430, 1372, 1204, 1094, 962, 746. ¹H NMR (CDCl₃, ppm): 8.04 (s, 4H); 7.84 (m, 2H); 7.21–7.19 (m, 4H); 6.82 (m, 2H); 3.98 (m, 4H); 4.13, 1.90–1.73 and 1.40–1.25 (m, 22H); 1.71 (m, 4H); 1.29 (m, 32H); 1.33 (m, 4H); 0.96 (t, 6H).

P(Npht)₂: yield: 48%. FT-IR (KBr, cm⁻¹): 3084, 2924, 2852, 1768, 1698, 1658, 1586, 1496, 1466, 1424, 1394, 1358, 1234, 1206, 1188, 1110, 1040, 980, 910, 862, 778, 748. ¹H NMR (CDCl₃, ppm): 8.63–8.10 (m, 10H); 7.34–7.19 (m, 4H); 6.82 (m, 2H); 3.94 (t, 4H); 4.13, 1.90–1.24 (m, 22H); 1.72 (m, 4H); 1.30 (m, 32H); 1.33 (m, 4H); 0.96 (t, 6H).

TPA(Terpyr)₃: yield: 71%. FT-IR (KBr, cm⁻¹): 3050, 2922, 2850, 1600, 1584, 1544, 1460, 966, 792, 740, 822. ¹H NMR (CDCl₃, ppm): 8.84–8.51 (m, 12H); 8.02 (m, 6H); 7.65–7.46 (m, 12H); 7.31–7.34 (m, 6H); 6.97 (m, 6H); 6.79–6.82 (m, 6H).

TPA(Pht)₃: yield: 45%. FT-IR (KBr, cm⁻¹): 3030, 2930, 2856, 1766, 1706, 1592, 1486, 1438, 1368, 1314, 1282, 1174, 1092, 1014, 964, 818, 748. ¹H NMR (CDCl₃, ppm): 7.95–7.73 (m, 9H); 7.28–7.21 (m, 6H); 7.11–6.96 (m, 12H); 4.13, 1.89–1.26 (m, 33H).

2.3. Experimental techniques

Absorption and fluorescence spectra were taken with a Beckman DU-640 and a Perkin-Elmer LS55B spectrometer, respectively. The fluorescence quantum yields, Φ , were measured using a solution of quinine sulphate in 1 N H₂SO₄, having a fluorescence quantum yield of 0.546, as a reference [31].

Two-photon absorption cross sections were determined via a TPEF method with femtosecond pulsed excitation [26,31,32]. The excitation source was a mode-locked Ti:Sapphire laser operating in the femtosecond regime (100 fs, 80 MHz) tunable from 750 to 840 nm. The samples were 10⁻⁴ M solutions of the molecules in THF. Before exciting the samples, the laser beam was expanded through a 5-fold expanding telescope in order to obtain a top-hat excitation beam profile. An objective lens (NA = 0.32) was used for the excitation of the samples. The TPA-induced fluorescence was collected backwards by the same lens and was separated from the excitation beam by using a dichroic mirror and a series of short-pass filters. Finally, it was detected by a photomultiplier connected to photon counting electronics. The TPA fluorescence was measured as a function of the excitation power every 10 nm within the wavelength range of the excitation laser. In all cases, the calculations of δ were made within the power regime where the fluorescence was proportional to the square of the excitation power, in order to ensure that effects like saturation, excited state absorption etc., are negligible. A THF sample was used to measure the background signal which was subtracted from the TPA fluorescence signal of the samples. The values of δ were determined using rhodamine B (10⁻⁴ M in methanol) as a reference which has a well known TPA spectrum. For the calculation of δ , it was assumed that the fluorescence quantum yield is the same under two-photon or one-photon excitation following the analysis of Xu and Webb [26].

3. Results and discussion

The absorption and fluorescence spectra of the molecules studied are shown in Figs. 2 and 3, respectively. All spectroscopic results together with fluorescence quantum yields, Φ , are summarized in Table 1. A first conclusion drawn from the spectra is that the alkoxy-phenylene molecules exhibit red-shifted fluorescence spectra compared to the corresponding fluorene molecules. Specifically, this red-shift is equal to 55 nm from F(Terpyr)₂ to P(Terpyr)₂ while for the other molecules it ranges from 26 to 40 nm. The red-shift is due to the alkoxy side substituents in the central core of the phenylene molecules which act as electron donors shifting the spectra to longer wavelengths. It is also seen in Figs. 2 and 3 that the spectra of the molecules with phthalimide and naphthalimide substituents are red-shifted compared to the spectra of the molecules with pyridine and terpyridine substituents. This is due to the conformation adopted by the molecules in solutions. The edge pyridine and terpyridine substituents adopt a twisted conformation relative to the central core, shortening the conjugation length of the molecule. On the other hand, the branches with phthalimide and naphthalimide substituents are planar leading to an elongation of the conjugation length.

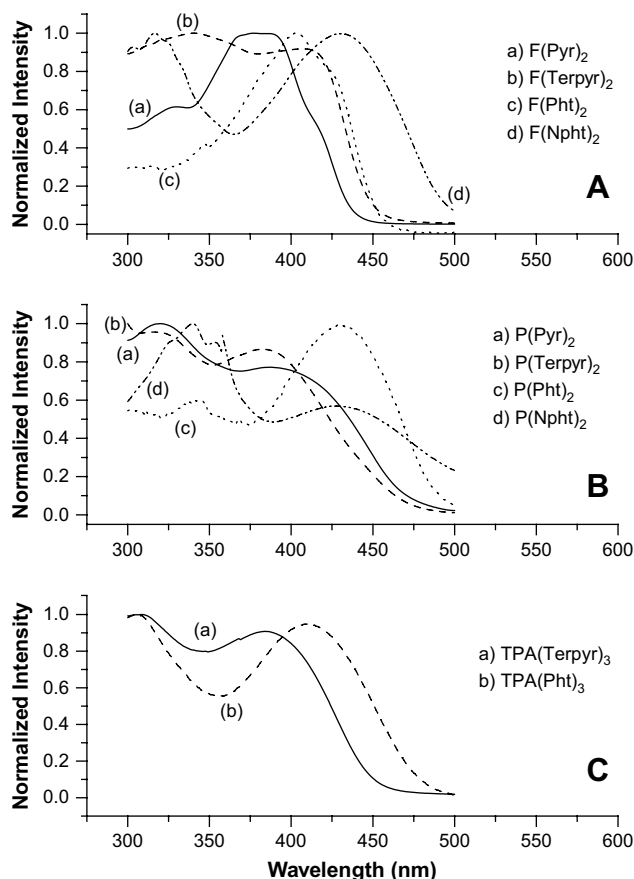


Fig. 2. The absorption spectra of the (A) fluorene, (B) phenylene and (C) tribranched molecules in THF solutions.

Concerning the Φ values summarized in Table 1, the molecules with fluorene core have higher Φ than the corresponding phenylene molecules. This may be attributed to the more planar conformation of the fluorene core compared to the phenylene one. Additionally, in both fluorene and phenylene molecules, Φ decreases when the edge substituents are phthalimide and naphthalimide. Similarly, the tribranched molecule with phthalimide substituent, TPA(Pht)₃, has much lower Φ than TPA(Terpyr)₃ having terpyridine substituent.

Fig. 4 shows the TPA cross sections of the fluorene molecules in THF solutions for different excitation wavelengths. All fluorene molecules exhibit a maximum δ -value at the lowest excitation wavelength, i.e., 750 nm except from F(Npht)₂ which exhibits a maximum δ at 840 nm. This red-shift of the TPA maximum is related to the red-shift of the one-photon absorption of F(Npht)₂ compared to the other fluorene molecules (Fig. 2). The highest δ -value among the fluorene molecules is exhibited by F(Pht)₂ and is equal to 1660 GM. F(Pht)₂ also has a moderate Φ equal to 0.36. F(Npht)₂ has a high δ -value equal to 1160 GM but it exhibits a low Φ equal to 0.15. On the other hand, F(Pyr)₂ and F(Terpyr)₂ exhibit low δ values equal to 180 and 290 GM respectively. However, these molecules have the highest Φ values among the fluorene molecules.

In Fig. 5, the δ values of the phenylene molecules are shown. Molecules P(Pyr)₂ and P(Terpyr)₂ exhibit a maximum δ at 750 nm, P(Pht)₂ at 760 nm and P(Npht)₃ at 840 nm. As in the case of the phenylene molecules, the highest δ -value is observed from the molecule with phthalimide substituent, i.e., P(Pht)₂ and is equal to 1500 GM. P(Npht)₂ exhibits a relatively high δ equal to 725 GM but its Φ is very low. Additionally, the molecules with pyridine and terpyridine substituents, i.e., P(Pyr)₂ and P(Terpyr)₂ exhibit small δ values equal to 200 and 260 GM, respectively.

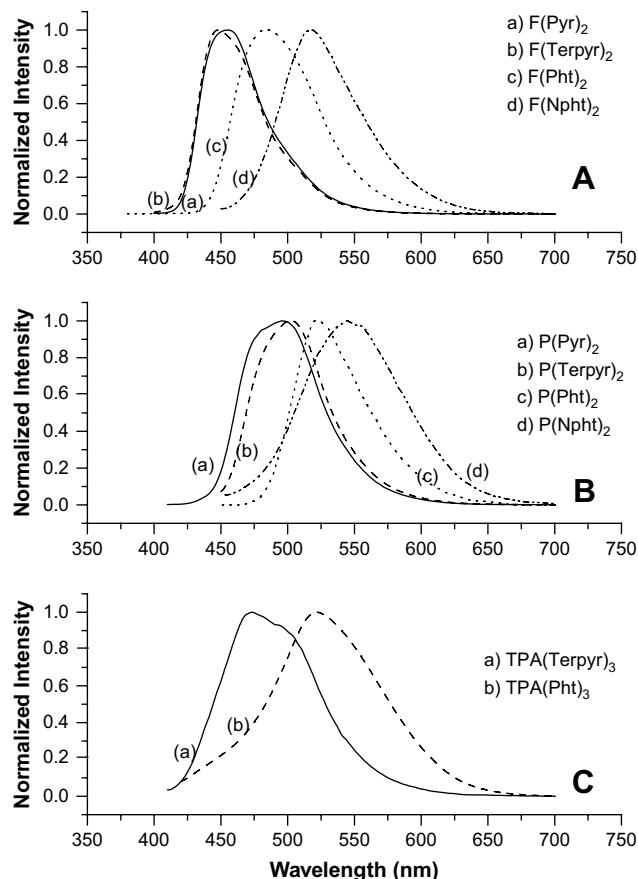


Fig. 3. The fluorescence spectra of the (A) fluorene, (B) phenylene and (C) tribranched molecules in THF solutions.

The maximum δ values of all molecules are summarized in Table 1, together with their TPA action cross section, i.e., the product $\Phi \cdot \delta$. In many cases in the literature, a high δ -value is accompanied by a low Φ . However, in applications like TPA pumped lasing, both high δ and Φ values are needed. Therefore, the TPA action cross sections provide a more complete aspect of the potential use of molecules in certain TPA applications.

Comparing the TPA properties of the quadrupolar molecules, it is concluded that phthalimide and naphthalimide substituents lead to higher δ values than pyridine and terpyridine ones. This could be attributed to the fact that pyridine and terpyridine substituents have a twisted conformation relative to the central core of the molecules. This leads to a shortening of the π -electron delocalization length and to a hindering of effective intramolecular electron transfer. Additionally, this is an indication that phthalimide and naphthalimide are stronger electron-accepting substituents than

Table 1
The photophysical properties and TPA cross sections of the molecules studied

Molecule	λ_{abs} (nm)	λ_{fluor} (nm)	Φ	δ (GM)	$\Phi \cdot \delta$ (GM)
F(Pyr) ₂	386	455	0.54	180	97
F(Terpyr) ₂	407	447	0.51	290	148
F(Pht) ₂	402	484	0.36	1660	598
F(Npht) ₂	431	518	0.15	1160	174
P(Pyr) ₂	388	495	0.35	200	70
P(Terpyr) ₂	383	502	0.42	260	109
P(Pht) ₂	429	522	0.26	1500	377
P(Npht) ₂	426	544	0.07	725	50.7
TPA(Terpyr) ₃	384	473	0.71	100	71
TPA(Pht) ₃	410	522	0.13	1200	156

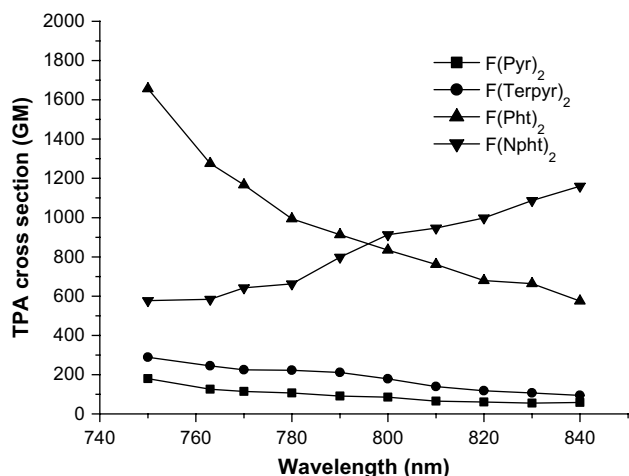


Fig. 4. The TPA cross sections of the fluorene molecules $F(Pyrr)_2$, $F(Terpyr)_2$, $F(Pht)_2$ and $F(Npht)_2$ in THF solutions for different excitation wavelengths. The experimental uncertainty is approximately 10%.

pyridine and terpyridine. Another conclusion is that δ increases when terpyridine is used as substituent instead of pyridine. This increase of δ is equal to 1.6 and 1.3 times for the fluorene and phenylene molecules, respectively, and is related to the strengthening of the acceptor efficiency in the case of terpyridine [18]. Finally, $F(Pht)_2$, having fluorene central core and phthalimide edge substituents exhibits the highest value of δ as well as of $\Phi \cdot \delta$. This means that $F(Pht)_2$ is the most promising molecule for applications like TPA pumped lasing, TPA microscopy, etc. $F(Pht)_2$ is of the general type A- π -A. On the other hand, the corresponding phenylene molecule $P(Pht)_2$ is of the general type A- π -D- π -A since the alkoxy substituents in the central phenylene ring act as electron donors. Although, $P(Pht)_2$ seems to be more suitable for TPA since it can experience intramolecular charge transfer from the center to the edges, $F(Pht)_2$ has the higher δ -value meaning that the fluorene core enhances the TPA. This is possibly due to its planarity and enhanced π -orbital overlapping.

Fig. 6 shows the TPA cross sections of the tribranched molecules. $TPA(Terpyr)_3$ exhibits a maximum δ of only 100 GM at 750 nm while $TPA(Pht)_3$ has a maximum δ of 1200 GM at 840 nm. The red-shift of the TPA maximum in $TPA(Pht)_3$ compared to the $TPA(Terpyr)_3$ is expected since there is a similar red-shift in the

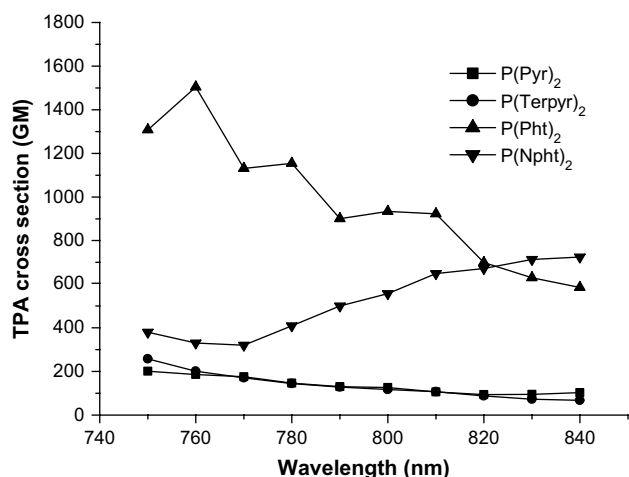


Fig. 5. The TPA cross sections of the phenylene molecules $P(Pyrr)_2$, $P(Terpyr)_2$, $P(Pht)_2$ and $P(Npht)_2$ in THF solutions for different excitation wavelengths.

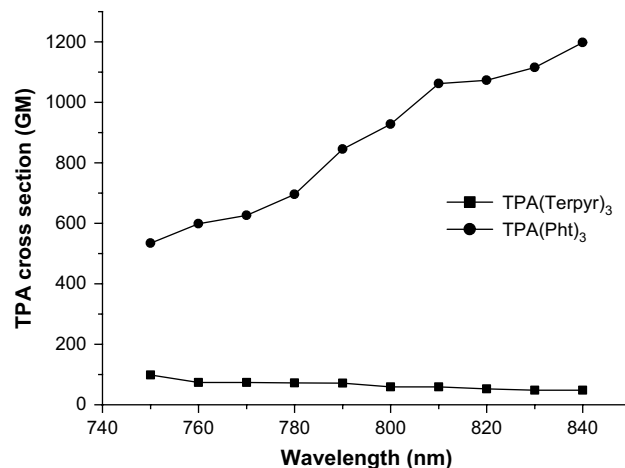


Fig. 6. The TPA cross sections of the tribranched molecules $TPA(Terpyr)_3$ and $TPA(Pht)_3$ in THF solutions for different excitation wavelengths.

one-photon absorption spectra. It should be noted here that a tribranched molecule similar to $TPA(Terpyr)_3$ and $TPA(Pht)_3$ but with naphthalimide substituents at the periphery has also been synthesized and studied concerning TPA. However, it showed very low TPA properties and the results are not presented. Although, $TPA(Pht)_3$ has a relatively low Φ , its TPA action cross section $\Phi \cdot \delta$ is still higher than that of $TPA(Terpyr)_3$. Therefore, as in the case of the quadrupolar molecules, the incorporation of phthalimide substituent in the tribranched molecules constitutes the optimum synthetic strategy to achieve the highest TPA cross section and a reasonable TPA action cross section. As reported by Macak et al. [23] the use of the amino central core breaks the conjugation of the whole molecule. Therefore, the high δ of $TPA(Pht)_3$ may be due to the strong vibronic coupling in this tribranched molecule [23,33].

Finally, it needs to be noted that, in some cases, the highest δ -value of the molecules may not be within the wavelength range of this study. Even higher δ values than those reported here may be found at shorter or longer wavelengths. However, after analyzing our results it is fairly safe to conclude that phthalimide edge substituent enhances δ in both the quadrupolar and tribranched molecules.

4. Conclusions

A series of quadrupolar and tribranched molecules has been synthesized and studied concerning photophysics and TPA in order to determine the optimum synthetic strategy to achieve high TPA action cross section. A TPEF technique using femtosecond pulses was used to determine the TPA cross sections. It was found in all cases that the use of phthalimide edge substituents, playing the role of an electron acceptor, increases the TPA cross sections and gives reasonable fluorescence quantum yields. The quadrupolar molecule $F(Pht)_2$, bearing fluorene central core and phthalimide edge substituents, has shown a TPA cross section of 1660 GM and a TPA action cross section of 598 GM and it was proved as the most suitable for TPA applications among the molecules in this work.

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