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

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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, $\delta$, 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 alcoxy-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 $\delta$ values. $\delta$ 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 $\delta$-value of 1200 GM was found.

## 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, $\delta$ [12,13].

It is nowadays well known that the incorporation of electron donating groups, D, (like amino and alcoxy) and electron accepting groups, A, (like cyano, pyridine and benzothiazole) in $\pi$-conjugated organic molecules can lead to a great enhancement of $\delta$. Thus, dipolar, D-$\pi$-A and quadrupolar molecules, D-$\pi$-A-$\pi$-D or A-$\pi$-D-$\pi$-A, have been synthesized and studied experimentally [5,8,10,14–17] and theoretically [18]. Another strategy to obtain large $\delta$ 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 $\pi$-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 $\delta$, 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 $\delta$ [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 $\delta$ 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

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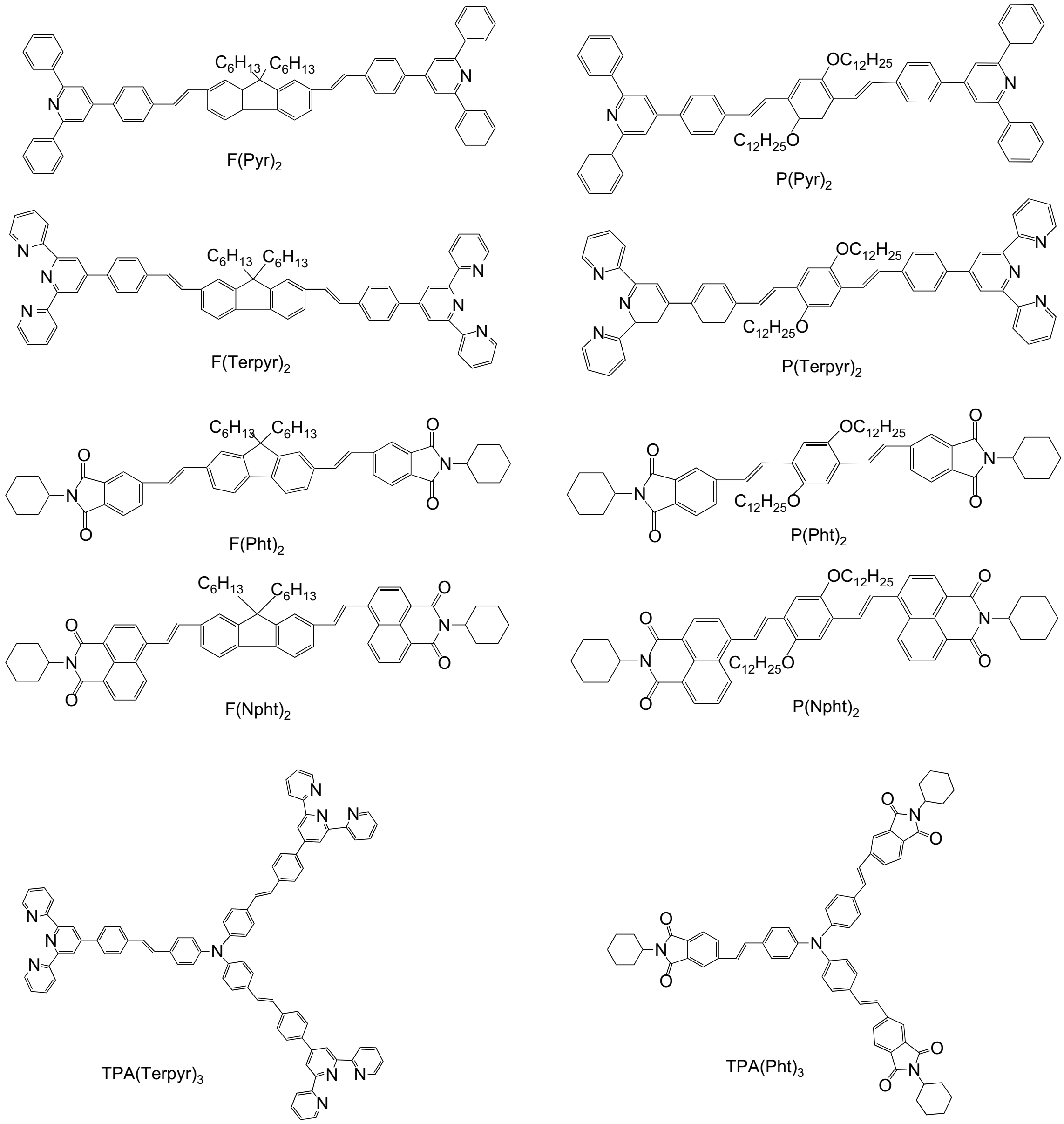
a high fluorescence quantum yield. With this in mind, we report, in this paper, the photophysical and TPA properties of a series of new quadrupolar and tribranched molecules. The quadrupolar molecules bear various electron accepting edge substituents and two different central cores namely fluorene- and alcoxy-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 alcoxy-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 alcoxy 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 intramolecular charge transfer from the core to the periphery.



F(Pyr)$_2$ P(Pyr)$_2$

F(Terpyr)$_2$ P(Terpyr)$_2$

F(Pht)$_2$ P(Pht)$_2$

F(Npht)$_2$ P(Npht)$_2$

TPA(Terpyr)$_3$ TPA(Pht)$_3$

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