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Two-photon absorption related properties of functionalized BODIPY dyes in the infrared range up to telecommunication wavelengths**

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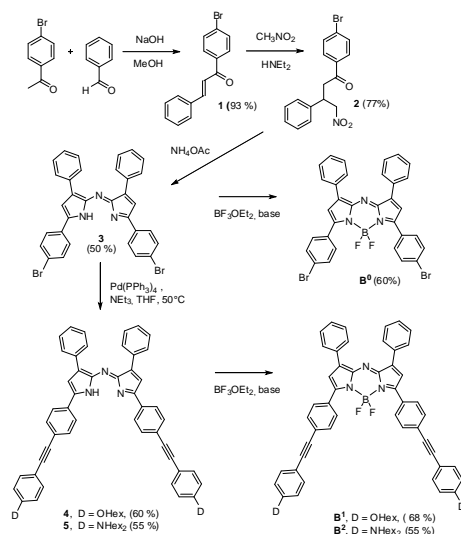
Two-photon absorption (TPA) is a resonant third-order nonlinear optical (NLO) process, in which an electron is promoted from its ground state to an excited state by simultaneous absorption of two photons of half-energy in a focused intense light beam like that generated by a laser source. This phenomenon, theoretically predicted in 1931 by Göppert-Mayer,^[1] has been experimentally evidenced in 1961 in a TPA-induced fluorescence of Eu²⁺ doped CaF₂ crystals under ruby laser irradiation.^[2] Since then, the intrinsic advantages of TPA excitation *i.e.* long wavelength and confocal three-dimensionally (3D) resolved absorption, led to

numerous applications in the fields of material sciences and biology following the availability of tunable laser sources. In particular the development of fs-Ti-sapphire laser triggers numerous studies in the 700-1000 nm spectral range. For instance TPA was successfully involved in the fabrication of microstructures^[3-4] or high density optical memories^[5] with a 3D sub-micrometer resolution, in signal processing or for the design of optical limiting devices devoted to the protection of sensors against laser damages.^[6-7] In life sciences, the long wavelength TPA excitation is located in the biological transparency spectral range (800-1000 nm), and therefore is able to penetrate more deeply biological tissues. Combined with the above mentioned spatial resolution, TPA found exciting applications for bio-imaging using nonlinear microscopy^[8] but also for drug delivery or dynamic phototherapy.^[9] All these applications encouraged the scientific community to design a large variety of chromophores with optimised two-photon cross-section (σ_2) in this 700-1000 nm spectral range, e.g. organic dyes, organometallic or coordination complexes, polymers, dendrimers or nanoparticles and quantum-dots, compiled in a recent exhaustive review.^[10] However, the near infrared (NIR) spectral range has been less studied and in particular the telecommunication wavelengths spectral range (1.3-1.55 μm) where applications in signal processing (optical power stabilization, pulse suppression, optical limiting) are very attractive. Since 2005, under the impulsion of the groups of Marder-Van Stryland and Osuka-Kim, there is a great interest for the design of chromophores exhibiting strong TPA properties in the NIR. Maximal TPA cross-section of ca. 1500 GM at 1.44 μm and 1600 GM at 1.3 μm have been reported for dipolar and quadrupolar squarine type chromophores respectively,^[11-12] whereas nickel(bisdithiolene) complexes^[13] and singlet diradical systems^[14] exhibit significant σ_2 over the entire telecommunication range. On the other hand, numerous fused-, extended- or organized-porphyrin complexes have been reported with very large TPA cross-section ranging from 10^3 up to 10^4 GM.^[15-19] Finally we reported the TPA properties of cyanine-type chromophores (σ_2 of 750 GM at 1450 nm) that present enough solubility to carry out

additional nonlinear transmittance experiments at telecommunication wavelengths.^[20] Herein we report the synthesis, X-rays structures of aza boron-dipyrromethane (BODIPY) NIR dyes functionalized in the α position by donor- π -conjugated systems and their TPA and nonlinear transmittance properties in the 1.2-1.6 μm spectral range.

It is worth noting that BODIPY is a versatile class of chromophores^[21-22] largely studied for its exceptional luminescence properties and used as biomolecular labels, sensors (pH, NO, Hg^{2+} , toxin...) or photonic therapeutic agent.^[21-26] Great efforts have been recently devoted to shift their spectroscopic properties to the NIR spectral range by (i) introduction of electron donating moieties,^[27] (ii) rigidification of the structure^[28] or (iii) replacement of the *meso*-carbon by a nitrogen atom (the “aza”-BODIPY).^[29-31] But surprisingly, whereas water soluble conventional BODIPY dyes featuring low two-photon cross-section were used for two-photon imaging microscopy,^[32-33] these compounds were not fully optimized for TPA applications. To the best of our knowledge, only multichromophoric dyes containing two or three BODIPY units and exhibiting rather modest σ_2 values (75 GM at 990 nm) in the visible were described in the literature.^[34]

The synthesis of the target chromophores **B¹⁻²** (Scheme 1), featuring extended π -conjugated skeleton involves as key step a copper free Sonogashira cross-coupling using $\text{Pd}(\text{PPh}_3)_4$ as catalyst between bromo-functionalized aza-dipyrromethene^[35] and various donor-phenylenethynyl derivative ($\text{D} = \text{OHex}$, $\text{D} = \text{NHex}_2$) followed by classical complexation with boron trifluoride etherate in basic media (Scheme 1). The intermediate synthon **3** and the corresponding complex **B⁰** are prepared using the procedure described by the O’Shea’s group.^[36] Synthetic details and complete characterization are compiled in supporting information. It is important to note that the synthesis of **B⁰⁻²** was carried out at a gram scale and **B²** is enough soluble in chlorinated solvent to envisage further nonlinear transmittance experiments.^[20]



Scheme 1. Synthesis of chromophores.

Crystals of **B**⁰ suitable for X-ray diffraction analysis were obtained by slow diffusion of diethylether into a dichloromethane solution. As already observed for other aza-BODIPY dyes,^[31,35,37-38] the structure (Figure S1 in supporting informations) shows three very planar central fused rings and four twisted peripheral phenyl groups (twist angle of 12-43°); the boron atom lies in an almost perfect tetrahedral environment and the C-N bond lengths between bridging nitrogen N2 and the two pyrroles C4 and C5 are identical (1.322(3) and 1.326(3) Å, respectively), showing the conjugated nature of the chromophore.

All the linear and nonlinear properties were studied in dichloromethane solution and are summarized in Table 1. Absorption spectrum (Fig.1) of **B**⁰ is characteristic of aza-BODIPY with an intense sharp transition ($\omega_{1/2} = 1270 \text{ cm}^{-1}$) exhibiting a shoulder at higher energy. The extended π -conjugated **B**^{1,2} compounds present transitions whose red shift increases with the strength of the donor group ($\Delta\lambda = 37$ and 87 nm for **B**¹ and **B**², respectively). It is worth noting that this shift is accompanied by a significant broadening of the absorption band ($\omega_{1/2} = 2850 \text{ cm}^{-1}$ for the amino derivative).

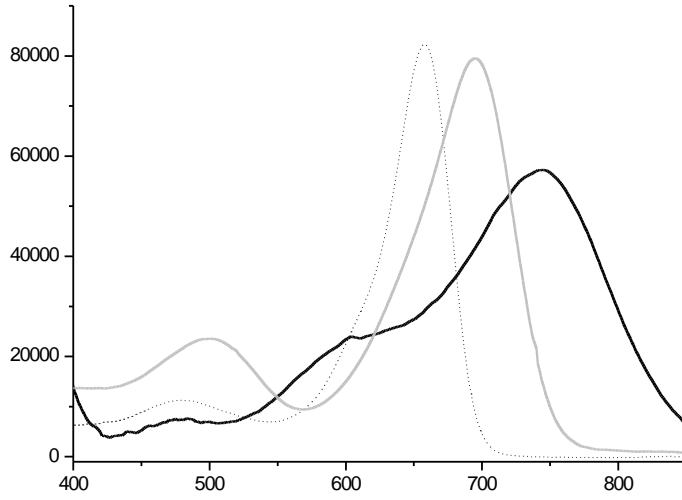


Figure 1. Absorption spectra of **B⁰** (dashed), **B¹** (gray) and **B²** (bold).

Open aperture Z-scan measurements were performed in the 1200-1600 nm spectral range using a fs-optical parametric amplifier pumped by a Ti:sapphire source. At such short pulse duration (130 fs), only TPA process is considered and the propagation equation can be simplified as:

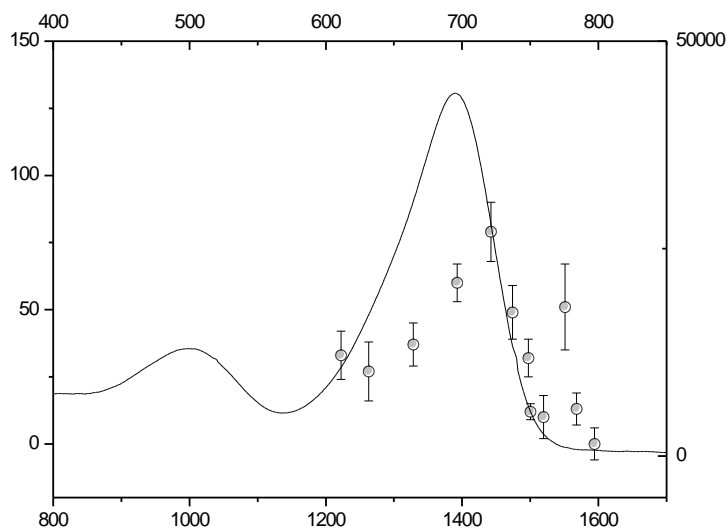
$$dI/dz = -\alpha_2 I^2 \quad (1)$$

where I represents the light intensity, z the propagation axis and α_2 the TPA coefficient. As described previously,^[20] the α_2 coefficient can be determined from the molecular two-photon cross-section σ_2 by:

$$\sigma_2 = h\nu\alpha_2/N \quad (2)$$

Carrying these fs-Z-scan experiments at various wavelengths allowed the determination of the TPA spectra of **B^{0,1,2}** over the entire 1200-1600 nm spectral range (Fig.2). As expected for non-centrosymmetric compounds, each TPA spectrum matches the wavelength doubled linear one, indicating that the same transition is one- and two-photon allowed. At these wavelengths,

the unfunctionalized **B**⁰ chromophore does not present any TPA response in the contrary of the donor- π -conjugated substituted systems **B**^{1,2} (Table 1). Whereas **B**¹ presents a rather small NLO activity, **B**² shows significant σ_2 values (around 600 GM) over the broad 1300-1450 nm spectral range. Furthermore, at lower wavelength, a significant increase is observed with a maximal two-photon cross-section σ_2^{max} of 1070 GM at 1220 nm. This value is close to that of cyanine compounds^[20] and in the same order of magnitude than that of dipolar or quadrupolar derivatives.^[11,12]



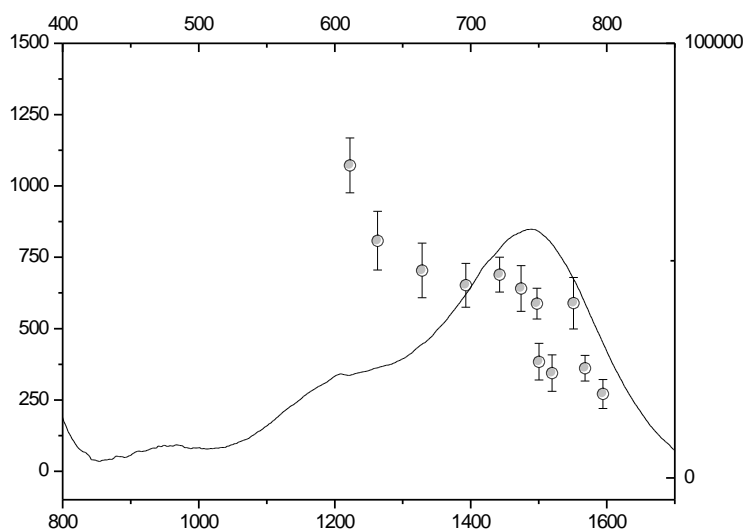


Figure 2. TPA spectra measured by fs Z-Scan method (filled circle) and linear absorption spectra in upper abscissa (—) for **B¹** (up) and **B²** (bottom).

In addition to the high solubility, exceptional thermal stability (T_{d10} about 360 °C) and the large scale availability of **B²** allowed to perform nonlinear transmittance experiments in the telecommunication spectral range. Such experiments were carried out for **B²** at highly concentrated solution ($c = 0.1 \text{ Mol.L}^{-1}$) using a ns-OPO pumped by a frequency tripled Nd:YAG laser source.^[20] Over the 1350-1500 nm range, the nonlinear transmittance curves vs. the laser fluence present characteristic nonlinear transmission properties; this behavior is illustrated at 1350 nm in Figure 3: a good transmission is observed at low energy ($T > 0.9$), whereas beyond the nonlinear transmission threshold observed for a fluence of 0.7 J.cm^{-2} , the laser beam intensity is strongly attenuated up to 60% at a fluence of 7 J.cm^{-2} . Due to the longer pulse duration (7 ns), the simulation of the experimental curves based only on a TPA process failed (blue line, Figure 3) and a higher order effect related to a three-photon absorption, such as a TPA induced excited state absorption (ESA) was taken into account.

Consequently, as already observed in the NIR for cyanine dyes^[20] or in the visible,^[39-40] the propagation equation (1) becomes

$$dI/dz = -\alpha_2 I^2 - \alpha_3 I^3 \quad (3)$$

where α_3 is the three-photon absorption coefficient. Numerical resolution of (3), for temporally and spatially gaussian incident pulses and using the TPA coefficient previously measured by fs-Z-scan, allowed the determination of a α_3 coefficient of 620 cm³.GW⁻² at 1350 nm (Table 1). This value corresponds to a two-fold increase compared to that of cyanine dyes measured in the same condition of concentration (230 cm³.GW⁻² at 1520 nm).^[20] This enhancement, which cannot be interpreted only by a stronger TPA efficiency, could be explained by a strong ESA contribution. This is illustrated in Figure S1 in supporting informations by the comparison of the spectral distribution of α_2 and α_3 between 1350 and 1500 nm: α_3 decreases from 600 to 300 cm³.GW⁻², while α_2 remains nearly constant.

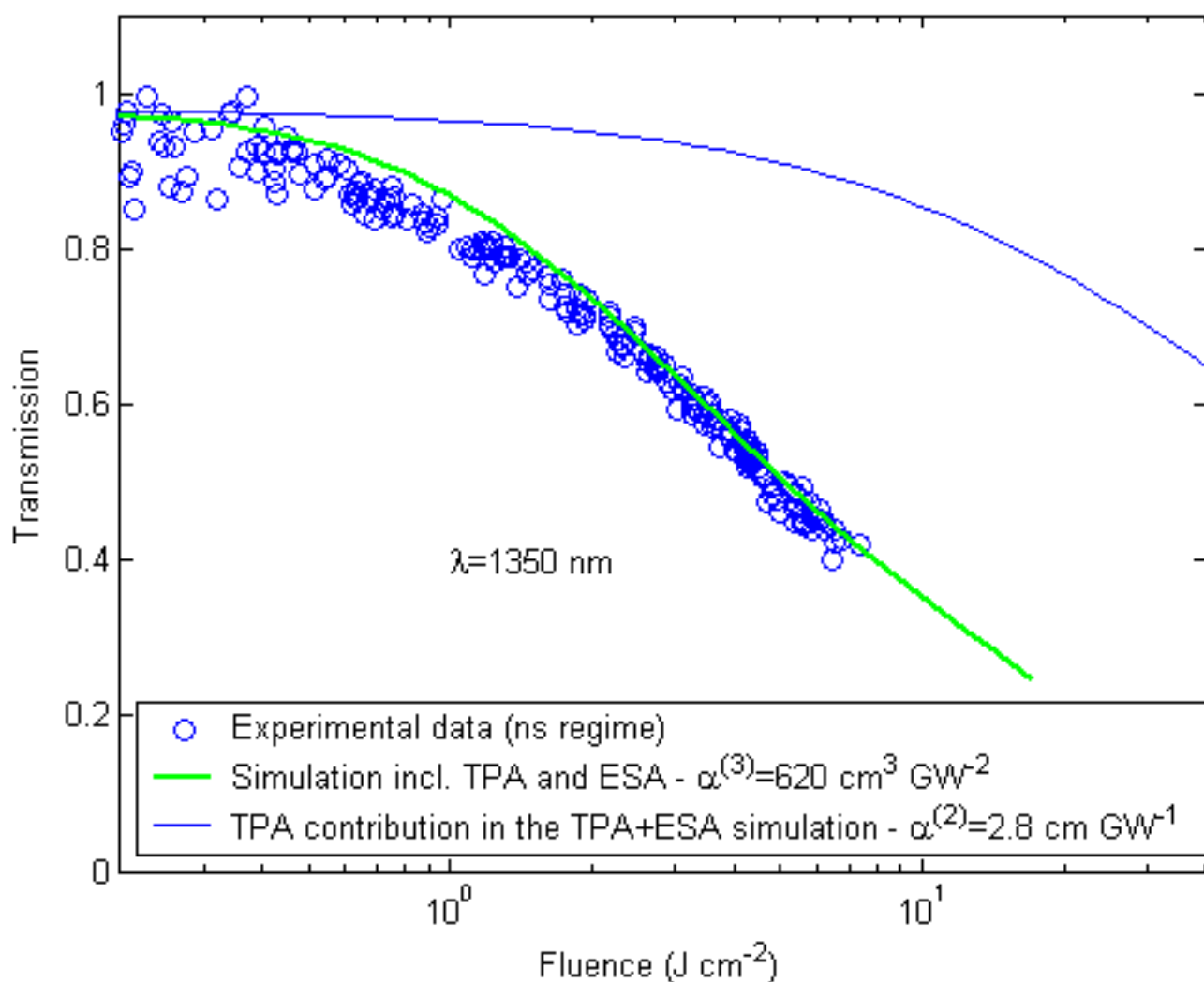


Figure 3. Transmittance variations with the laser fluence in a DCM solution of **B**² at a concentration of 106 g.L⁻¹; experimental data points (blue circle), theoretical simulation using complete model including TPA and ESA contribution (green), including only the TPA contribution within this latter hypothesis.

In conclusion, this study clearly underlines the high potentialities of functionalized aza-BODIPY dyes for TPA related applications in the telecommunication spectral range and in particular for nonlinear transmission. The versatile nature of this class of chromophores opens the way for a fine chemical engineering in order to optimize the TPA properties in the NIR by

additional functionalization of the β position or by rigidification of the lateral π -skeleton for example.

Experimental

[CCDC- 668638 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

[Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-...]

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