

Supporting Information

Unveiling the Molecular Structure and Two-photon Absorption Properties Relationship of Branching Oligofluorenes

**Leandro H. Zucolotto Cocca^{a,*}, André Gasparotto Pelosi^a, Luis M. G. Abegão^b,
Rafael de Q. Garcia Jean-Christophe Mulatier^d, Delphine Pitrat^d, Cyrille
Barsu^d, Chantal Andraud^d, Cleber R. Mendonça^a, Marcelo G. Vivas^c and Leonardo
De Boni^{a,*}**

^a Photonics Group, Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

^b Grupo de Fotônica, Instituto de Física, Universidade Federal de Goiás, 74690-900, Goiânia, GO, Brazil

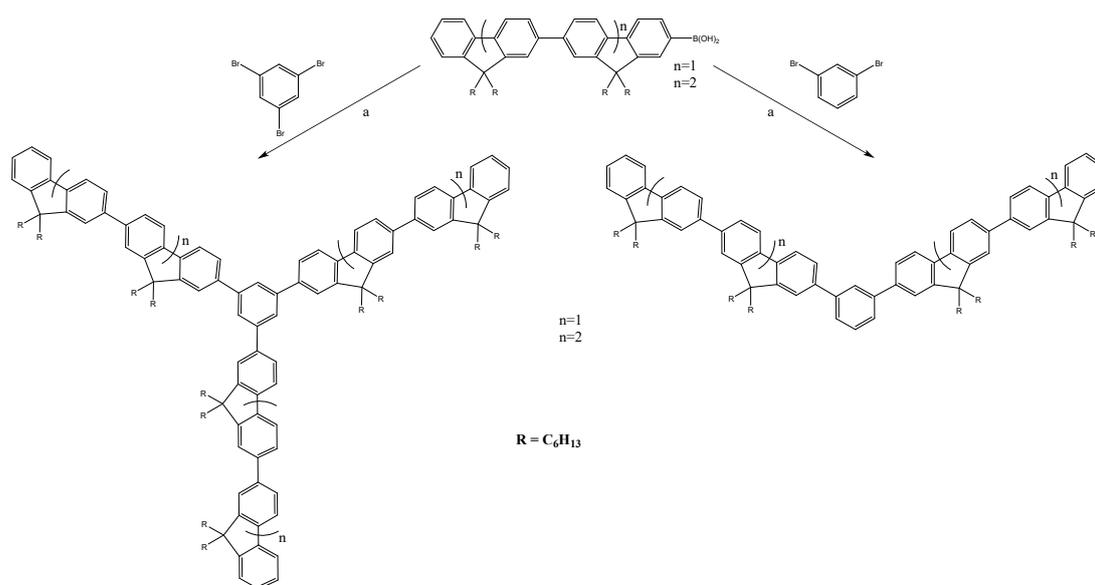
^c Laboratório de Espectroscopia Ótica e Fotônica, Universidade Federal de Alfenas, 37715-400 Pocos de Caldas, MG, Brazil

^d ENSL, CNRS, Laboratoire de Chimie UMR 5182, 46 allée d'Italie, 69364 Lyon France

* Author to whom correspondence should be addressed: leandro.cocca@usp.br and deboni@ifsc.usp.br

1 Synthesis

V and Y shape molecules were prepared following a convergent approach based on Suzuki coupling using halogenated cores and corresponding linear oligomers bearing a boronic acid function (Scheme 1), while the synthesis of halogenated moieties was described previously [1,2].



Reagents and conditions: a) $\text{Pd(PPh}_3)_4$, $\text{Na}_2\text{CO}_3\text{aq. (1M)}$, Toluene, 48 h, 100 °C

Scheme 1: V and Y shape molecules synthesis

Table 1: Summary of the synthesis conditions of V and Y shape molecules.

Molecule	Halogenated core	Boronic acid	Yield
V-Bis	1,3-dibromobenzene	$n = 1$	74%
V-Tri	1,3-dibromobenzene	$n = 2$	57%
Y-Bis	1,3,5-tribromobenzene	$n = 1$	58%
Y-Tri	1,3,5-tribromobenzene	$n = 2$	61%

2 Linear and nonlinear optical measurements

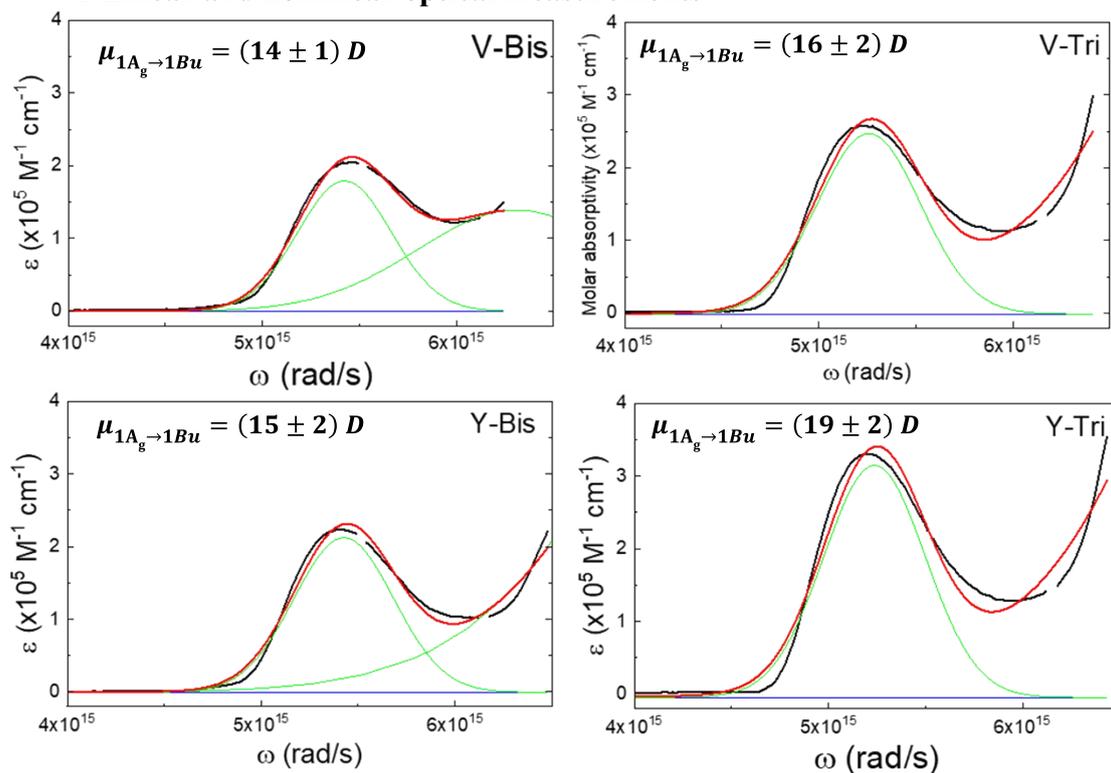


Figure S11: Molar absorptivity (black lines) and Gaussians decompositions (green lines) for transition dipole moment determination. The inset of each graph shows $\mu_{1A_g \rightarrow 1B_u}$ values.

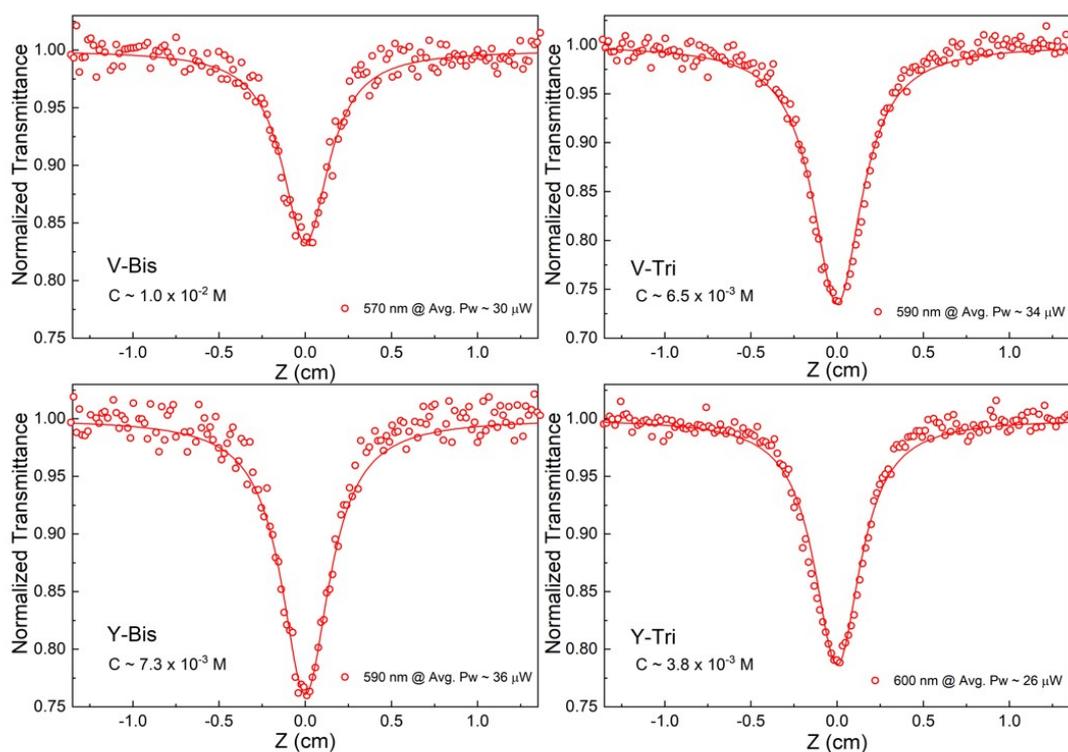


Figure S12: Z-Scan technique experimental data (Red circles) and theoretical adjustment (red line) for oligofluorenes.

3 Femtosecond white-light transient absorption measurements

To guarantee that all dynamics of the transient absorption signal were considered, the data of all four molecules in the two spectral regions were analyzed with a Global Analysis (GA) algorithm. In this algorithm [3], each exponential decay is convoluted with a Gaussian Instrument Response Function (IRF). Additionally, the coherent effect is simulated with the sum of a Gaussian function with its first and second derivatives, with the same time constant of the IRF and the amplitudes of each component determined within the GA fitting. This is done to account for the cross-phase modulation, two-photon absorption, and other effects that may occur when the pump and probe overlap temporally at the sample [4]. Adding more Gaussian derivatives to the coherent effect modeling led to the overfitting of the data in the region of time zero.

As discussed in the main text, no dynamics beyond the fluorescence lifetime were observed. Suppose the values of fluorescence lifetime are used as input to the Global Analysis algorithm. In that case, the time constant of a second exponential tends to be a value much greater than the observation time ($\gg 10$ ps). Alternatively, it can also tend to a value under the time resolution of the IRF, meaning that only one time constant and a coherent effect are sufficient for explaining the data. The hypothesis of the coherent effect being responsible for the signal variations close to time zero was confirmed by varying the White-light continuum (WLC) region that was being monitored by the spectrometer. This variation allowed a change in the coherent artifact to be observed, as is exemplified by Figure SI3, which shows the Transient absorption trace for the same wavelength (680.5 nm) under different WLC conditions.

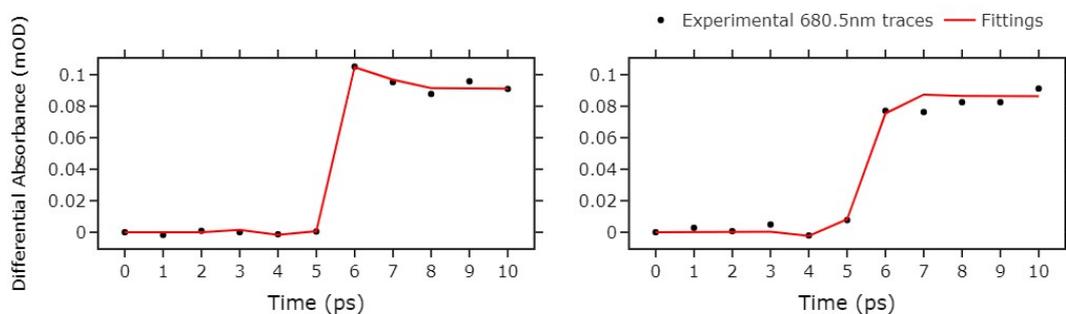


Figure SI3: Two TA measurements taken with different conditions of the WLC reveal a distinct, coherent artifact due to different coherent interactions between the pump and probe. The FWHM of the IRF was fit to 1.6 ps in this trace.

4 Fluorescence Quantum Yields measurements

Fluorescence quantum yield (Φ) measurements were performed using the Brouwer Method [5] employing the following equation:

$$\phi = \phi^{ref} \times \frac{\int_{\lambda_0}^{\lambda_f} F(\lambda)}{\int_{\lambda_0}^{\lambda_f} F_{ref}(\lambda)} \times \frac{f_{ref}}{f} \times \frac{n^2}{n_{ref}^2} \quad \text{Eq. S1}$$

in which the index *ref* is associated with the reference sample. $F(\lambda)$ is the fluorescence emission spectrum that was integrated overall emission range ($\lambda_0 \rightarrow \lambda_f$), f is defined as $f = 1 - 10^{-A(\lambda_{ex})}$, in which $A(\lambda_{ex})$ is the absorbance of the sample at the excitation wavelength and n is the refractive index of the solvent. Both solutions (the reference and the studied compounds) were placed in a quartz cuvette with an optical path of 1 cm and with a concentration of 10^{-6} M. The fluorescence quantum yield of the reference sample is named 3c in Ref. [6].

5 Fluorescence lifetime measurements

The fluorescence lifetimes determination was carried out using femtosecond laser pulses (Pharos light conversion) with pulses of approximately 200 fs with wavelengths of 343 nm and a 300 Hz repetition rate. The laser beam reaches the sample (cuvette with 2mm optical pathway), and the PL is collected at 90° with respect to the incident beam, which is captured through the telescope and an optical fiber coupled to the spectrometer to measure the PL. Owing to the fluorescence lifetime being of the order of the experiment resolution (500 ps), we employed a mathematical convolution ($I_{measured} = I_{real} * IRF$) to eliminate any interference of the experiment in the determined fluorescence lifetime. In the expression above, $I_{measured}$ refers to the fluorescence emission signal (experimental data in Figure SI4), I_{real} is related to the actual fluorescence decay (which is related to fluorescence lifetime, the theoretical curve in Figure SI4), and IRF is the instrument response function (reference, inset of Figure SI4). In view of determining the IRF we collected a reference signal using an empty quartz cuvette.

Figure SI4 exhibits the fluorescence signal (I_{measured} -black circles), the reference (IRF-black squares inset graphs), and the theoretical fitting (red lines). Inside each graph also is shown the determined fluorescence lifetimes.

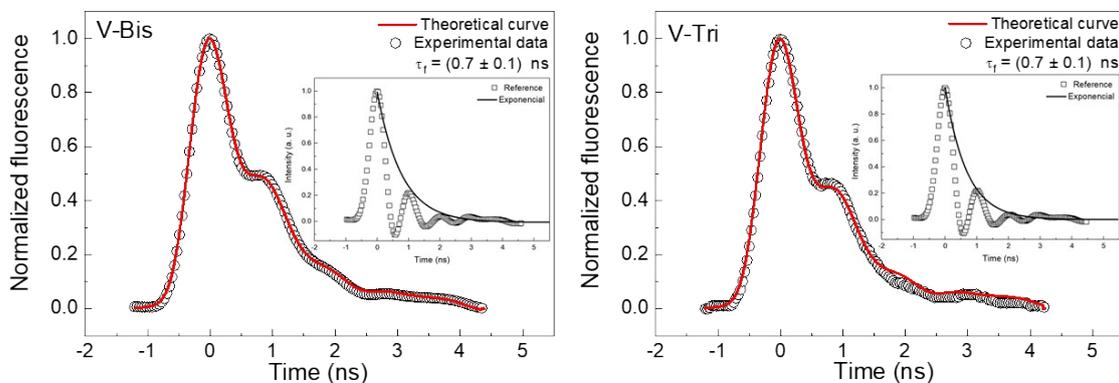


Figure SI4: Fluorescence lifetime determination for V-Bis and V-Tri. The black circles represent the fluorescence decay and red lines represent the theoretical fitting employed to determine the τ_f . Inside the graphs are shown the IRF (Black squares) and the τ_f values.

References

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