Nonlinear spectroscopy of novel borondipyrromethenes complexes

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Borondipyrromethanes (BODIPYs) are promising molecules for applications in optics because of their fluorescence quantum yields, low self-aggregation and the capacity of receiving a wide range of substituents for tuning their spectroscopic profiles. However, BODIPYs usually present low two-photon absorption cross-sections (σ_{2PA})[1], which diminishes their capabilities of being used in photonics applications. Increasing the conjugation length and adding donor and acceptor groups to the BODIPYs core have been shown to improve σ_{2PA} of up to 400 GM[2].

Here, we study the σ_{2PA} spectra of seven novel BODIPY[3] with different acceptor and donor groups, using the open-aperture Z-Scan[4] from 470 to 1200 nm, and apply sum-over-states (SOS) to model the data. Figure 1 shows the linear absorption, σ_{2PA} and the SOS fit for two of the studied molecules. Quantum chemical calculations were used to obtain the transition wavelength and maxima σ_{2PA}, as shown in Table 1.

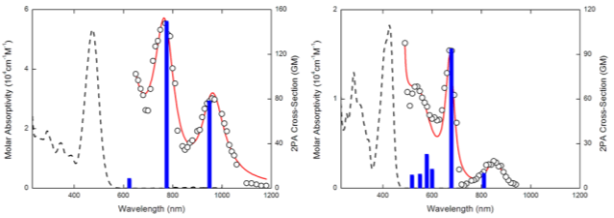

Fig. 1: Linear absorption (dashed line) and σ_{2PA} (circles), as well as the SOS fitting (continuous line) for two of the studied molecules (**VII** and **V** respectively). The bars represent the states calculated through quantum chemistry.

	λ_{2PA} Calc.	σ_{2PA} Calc.	λ_{2PA} Meas.	σ_{2PA} Meas.
II	578.0	195.4	580	70
III	543.7	284.4	550	119
IV	597.1	319.2	590	156
V	678.1	1117.4	670	93
VI	775.9	2405.2	770	148
VII	985.8	2467.9	990	198

Table 1: Maxima σ_{2PA} measured and calculated.

The differences between the σ_{2PA} occur mainly due to the groups added to the BODIPY core. Molecule **II**, which presents the lowest σ_{2PA}, has a F acceptor group, which is weaker than the other added groups, such as Br (Molecule **III**), NO_2 (Molecule **IV**) and H_3CO (Molecule **V**). Molecules **VI** and **VII** present the highest σ_{2PA} due to an addition of a Benzene-NMe_2 arm, which increases both, the conjugation length and the inter-charge transfer, collaborating for larger nonlinear effects. Since all σ_{2PA} were higher than 50 GM, the proposed BODIPYs succeeded in increasing the average nonlinear properties in relation to previous ones.

References

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