Nonlinear Absorption Spectrum in Perylene Derivatives

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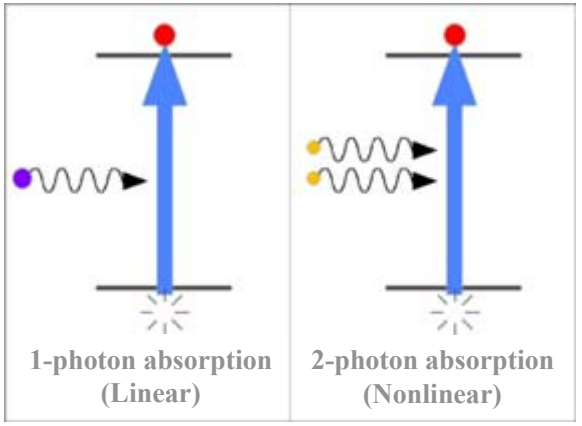
ABSTRACT

Knowledge about nonlinear absorption spectra of materials used in photonic devices is of paramount importance in determining their optimum operation wavelengths. In this work, we have investigated the two-photon absorption (2PA) degenerate cross-section spectrum for perylene derivatives using the Z-scan technique with femtosecond laser pulses. All perylene derivatives studied present large 2PA cross-sections, only comparable to the best ones reported in the literature. The results achieved in the present investigation indicate perylene derivatives as promising materials for two-photon applications.

S. L. Oliveira, D. S. Correa, L. Misoguti, C. J. L. Constantino, R. F. Aroca, S. C. Zilio, C. R. Mendonça, "**Perylene Derivatives with Large Two-photon Absorption Cross Sections for Application in Optical Limiting and Upconversion Lasing**" Advanced Materials, in press (2005).

TWO-PHOTON ABSORPTION

Upon exposure to intense laser pulses, molecules can instantaneously absorb two photons to access an excited state, each of them with half of the energy required to match the electronic transition.



$$\vec{P} = \chi^{(1)}.\vec{E} + \chi^{(2)} : \vec{E}\vec{E} + \chi^{(3)} \vdots \vec{E}\vec{E}\vec{E} + \ldots$$

$$Im\left[\chi^{(3)}\right]$$

$$\alpha = \alpha_0 + \beta\, I$$

β: two-photon absorption coefficient

Such 2PA process has interesting characteristics, with direct consequence for applications:

(i) improved spatial resolution due to the square dependence on the excitation irradiance → 3D optical data storage, micro-fabrication;

(ii) negligible linear absorption at the pumping wavelength, with the resulting increase of penetration depth → photodynamic cancer therapy

TWO-PHOTON ABSORPTION SPECTRUM

Accordingly, a great deal of effort was directed to the development of various design strategies employed to synthesize new two-photon absorbing materials with large 2PA cross-sections (δ) and increase physical and chemical stability.

High optical nonlinearities have been reported in organic materials at specific wavelengths, only recently the dispersion of the nonlinear absorption over a wide spectral range started to be characterized. Such information is important:

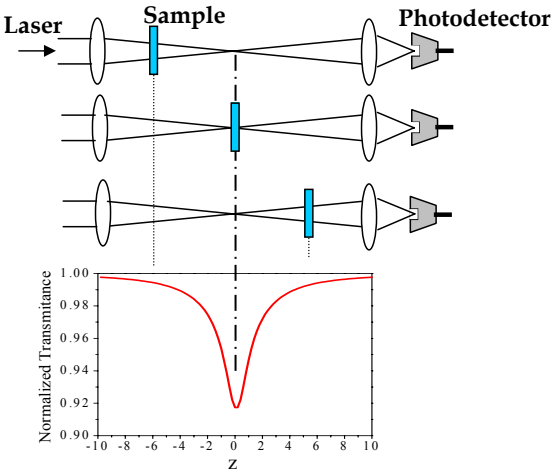
(i) Molecular design strategy of a given nonlinear optical material
(ii) Origin of the observed nonlinearities
(iii) Operation wavelength for a given device

2PA spectrum is obtained from:

- Multi-photon excited fluorescence
- **Open-aperture Z-scan**

} discrete wavelengths, tunable sources

OPEN-APERTURE Z-SCAN



Normalized Transmittance:

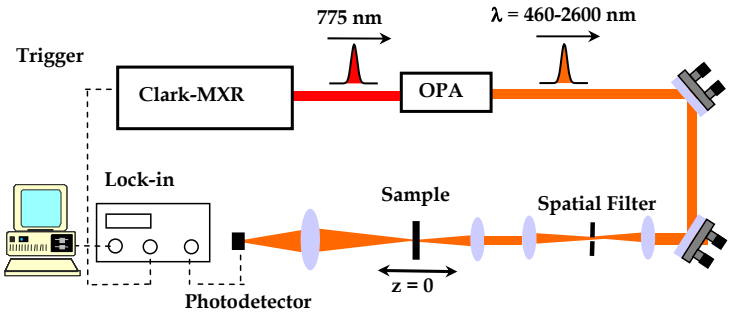
$$TN(z)=\frac{T(z)}{LT}=\frac{1}{\sqrt{\pi}q_0(z,0)}\int_{-\infty}^{\infty}ln\left[1+q_0(z,0)e^{-\tau^2}\right]d\tau$$

Knowing that

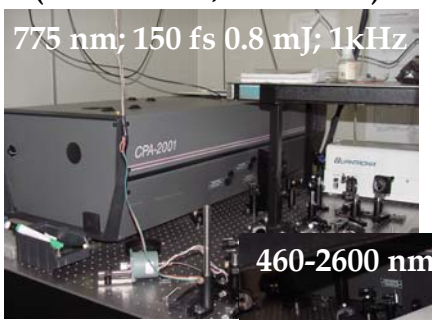
$$q_0(z,t)=\beta I_0(t)L\left(1+z^2/z_0^2\right)^{-1} \qquad \delta=h\nu\beta/N$$

M. Sheik-Bahae et al., *IEEE J. Quantum Electron.* 26, 760-769 (1990).

EXPERIMENTAL SETUP



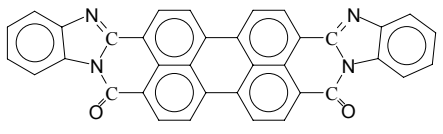
(Clark-MXR, CPA-2001)



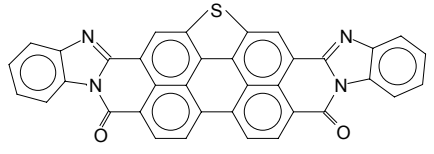
In this context, the present work reports on the degenerate 2PA cross-section spectra of perylene tetracarboxylic derivatives (PTCD) in the spectral range going from the visible to the near infrared.

PTCD are organic dyes, readily available, thermal and chemically stable. The perylene moiety presents remarkable electron donor characteristics, although adding lateral groups the molecule could play the role of electron acceptor or donor. Moreover, their strong absorption and emission in the visible spectral range makes them potential candidates for applications as photoconductors, laser materials, etc.

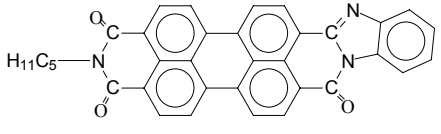
MOLECULAR STRUCTURES



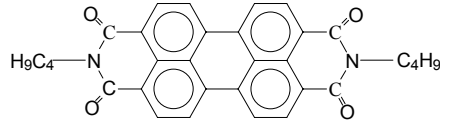
AzoPTCD



Monothio BZP



PazoPTCD



BuPTCD

TWO-PHOTON ABSORPTION CROSS-SECTION

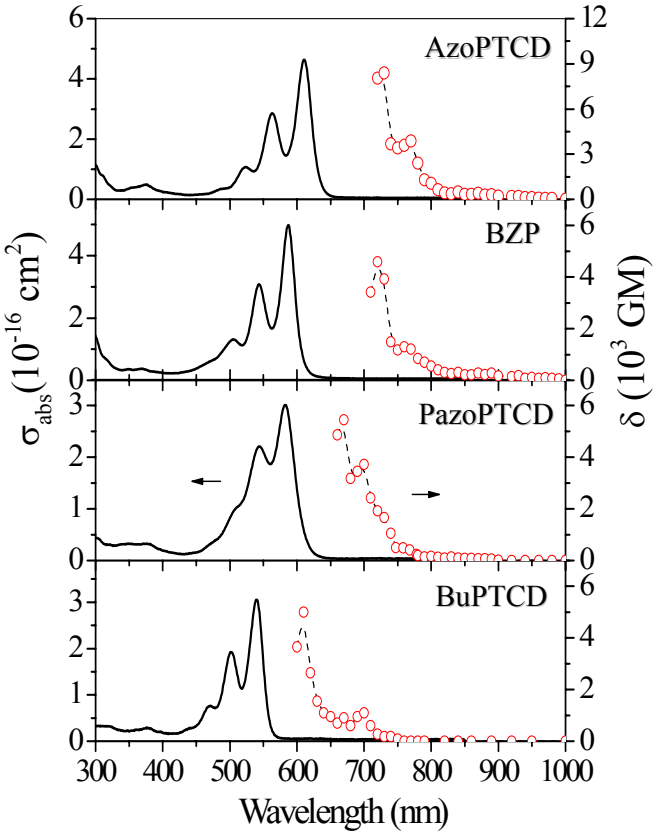


FIG. 1. Linear absorption and degenerate 2PA spectrum of the PTCD materials in a solution with 10% trifluoroacetic acid in dichloromethane.

- PTCD → linear absorption bands (400-660 nm), with the vibronic structure superposed to the π-π* transition.

- High δ values at several excitation wavelengths.

- The increase observed in the 2PA cross-section spectra → resonance enhancement of the nonlinearity ↔ sum-over states (SOS) model, assuming that the π→π* transition gives the major contribution to the virtual intermediate state and that the excited state corresponds the absorption peaks around 350 nm.

FRONTIER MOLECULAR ORBITALS

The molecular geometries were optimized by the AM1 method.

Frontier molecular orbitals were calculated using ZINDO/S (HiperChem 7.5). Configuration interaction (CI) calculations included single excited configurations from the ground state, 24 (occupied) x 24 (unoccupied)

Transition energy ($\Delta E_{linear.abs}$) decreases in a similar way as the π-conjugation length;

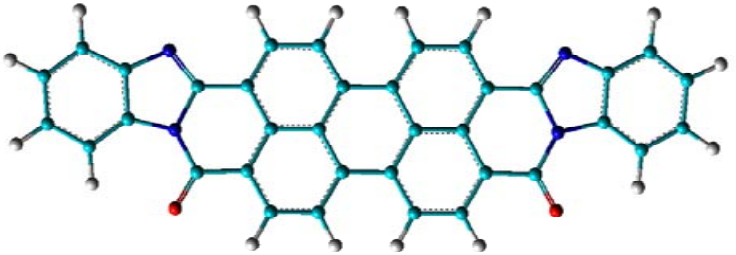
Bathchromic shift are the result of the HOMO → LUMO energy change;

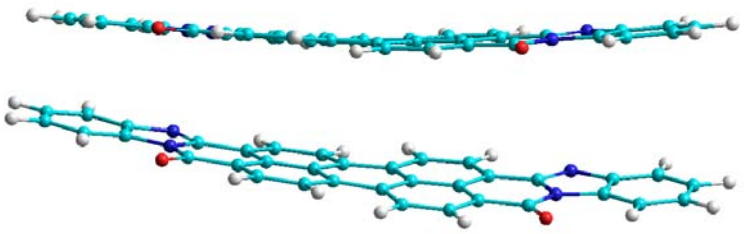
By analyzing the 2PA spectra far from linear absorption edge of the four PTCD derivatives it can be established an unambiguous relation between molecular charge delocalization (conjugation length) and the third-order nonlinear optical response (2PA):

The results suggest that even larger 2PA cross-sections could be obtained by manipulating the perylene derivatives, by positioning donor or acceptor groups symmetrically or by increasing the molecule conjugation length, in agreement with the molecular design strategies proposed in the literature.

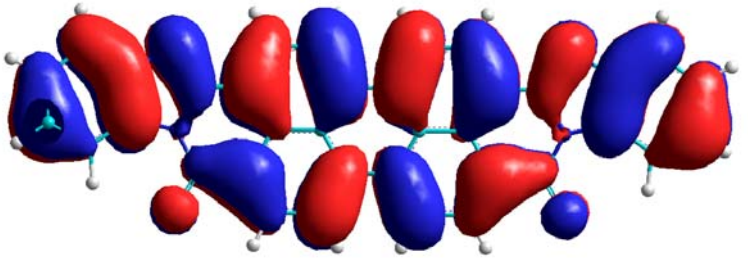
M. Albota, D. Beljone, J. L. Breda, J. E. Ehrlich, J. Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. Marder, D. McCord-Maughon, J. W. Perry, H. Rockel, M. Rumi, G. Subramanian, W. W. Webb, X. L. Wu, C. Xu, *Science* **1998**, *281*, 1653.

AzoPTCD

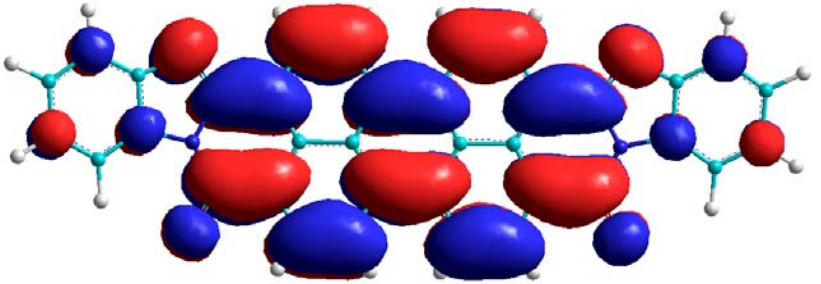




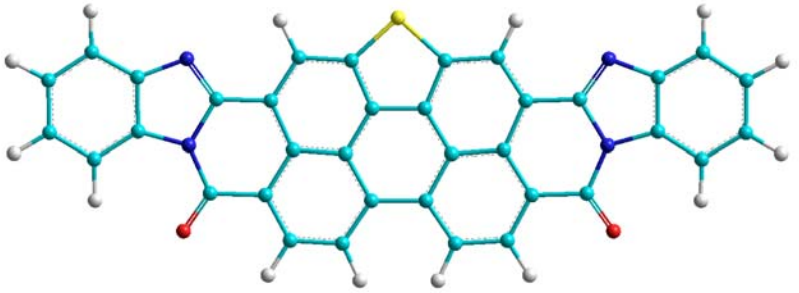
HOMO:

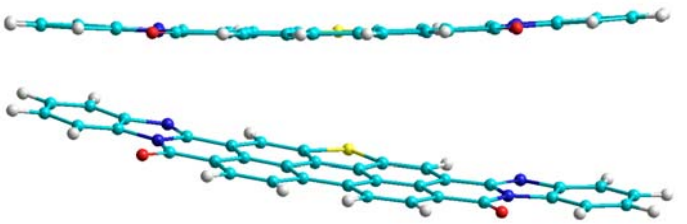


LUMO:



Monothio BZP





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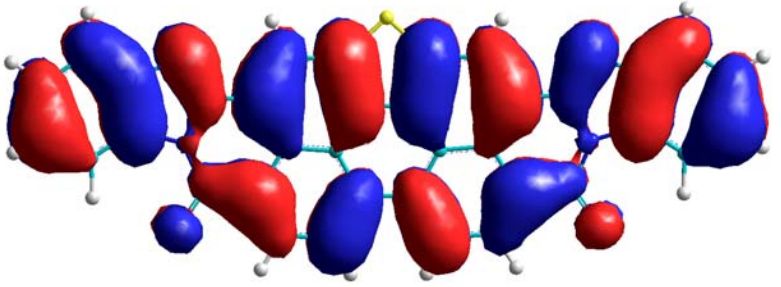

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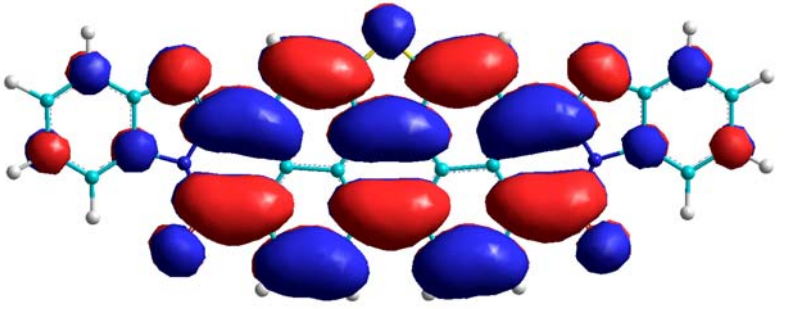
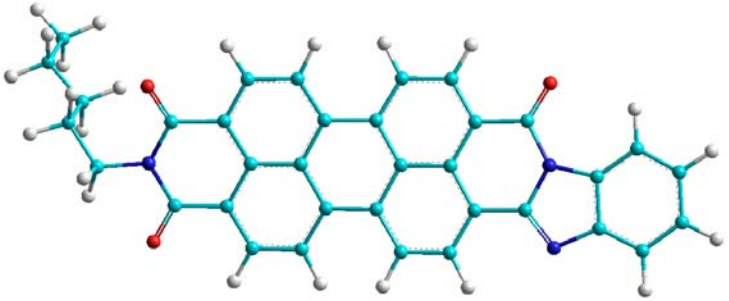
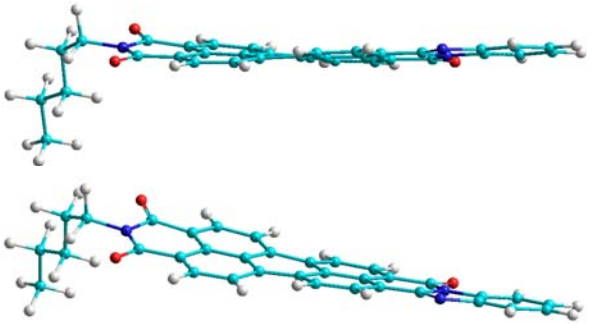


PazoPTCD





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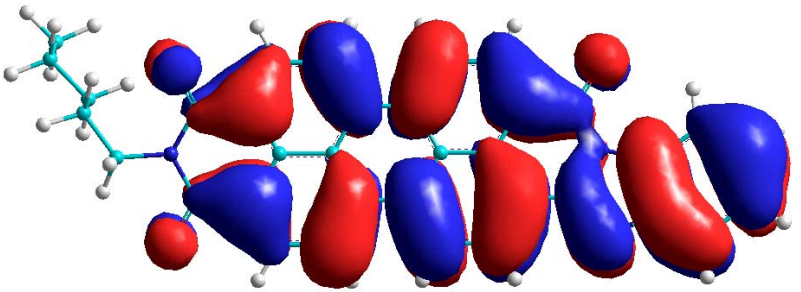

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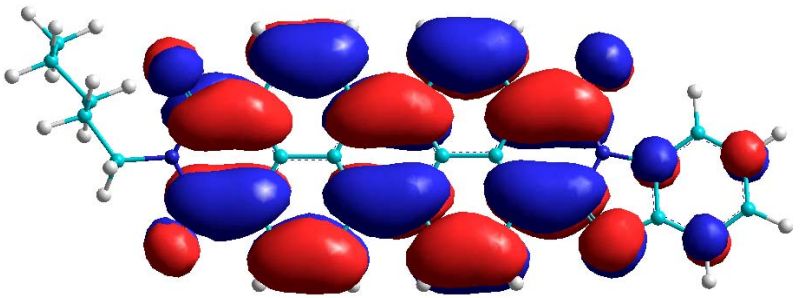
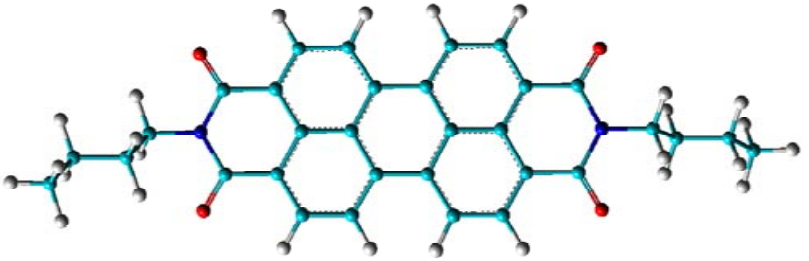
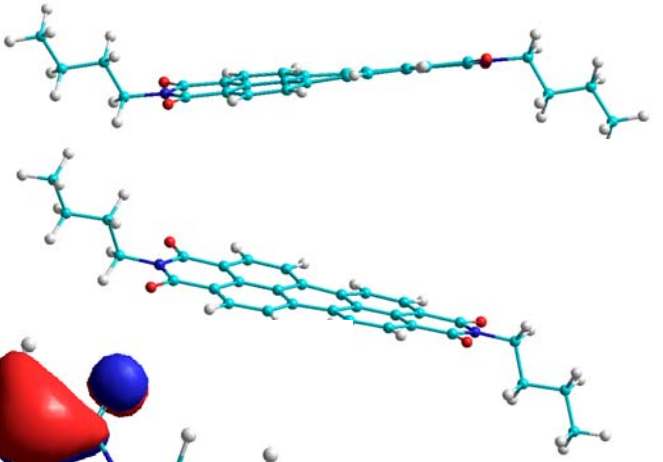


BuPTCD





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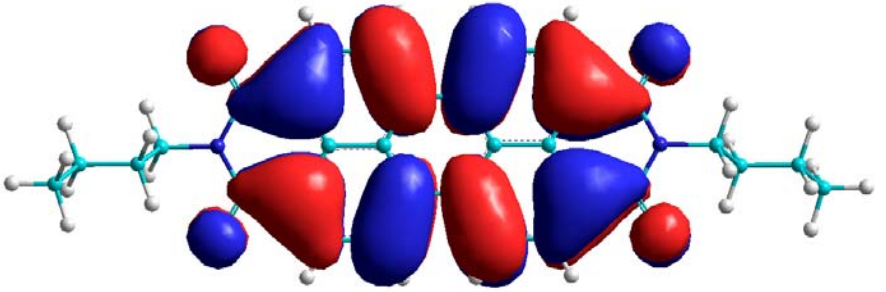

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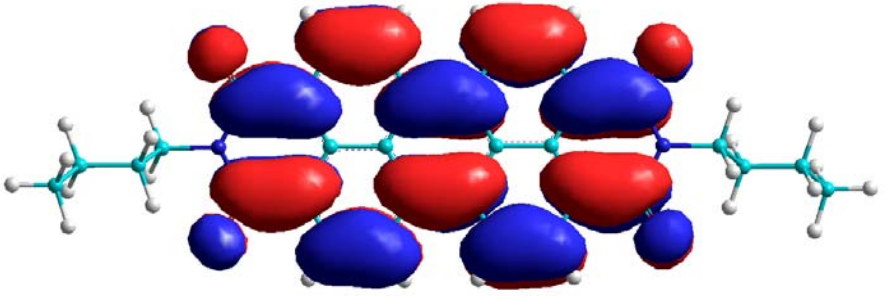

OPTICAL LIMITING

The result shows that PTCD compounds exhibit effective 2PA optical limiting action, which is useful to limit very short pulses, especially at wavelengths near the linear absorption edge.

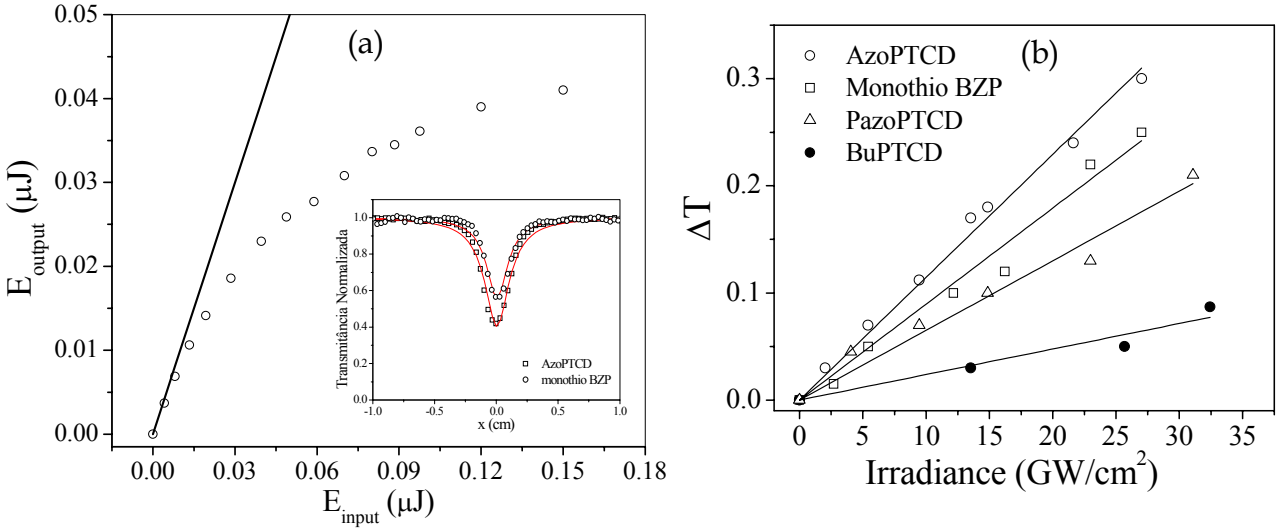

FIG. 2. (a) Output energy as a function of input energy of AzoPTCD (10^{18} molecules/cm^3) in a solution with 10% TFA in DCM and placed in a 2-mm thick quartz cuvette for excitation wavelength at 770 nm. The solid line represents the linear transmittance. The inset shows open-aperture Z-scan signatures for AzoPTCD and Monothio BZP; (b) Transmittance change as a function of irradiance for PTCD derivatives

UPCONVERSION EMISSION INDUCED BY 2PA

A strong two-photon excited fluorescent emission, which is a relevant prerequisite for upconversion lasing, was measured in PTCD for excitation at 770 nm. It should be pointed out that the fluorescence is high enough to be seen by naked eyes.

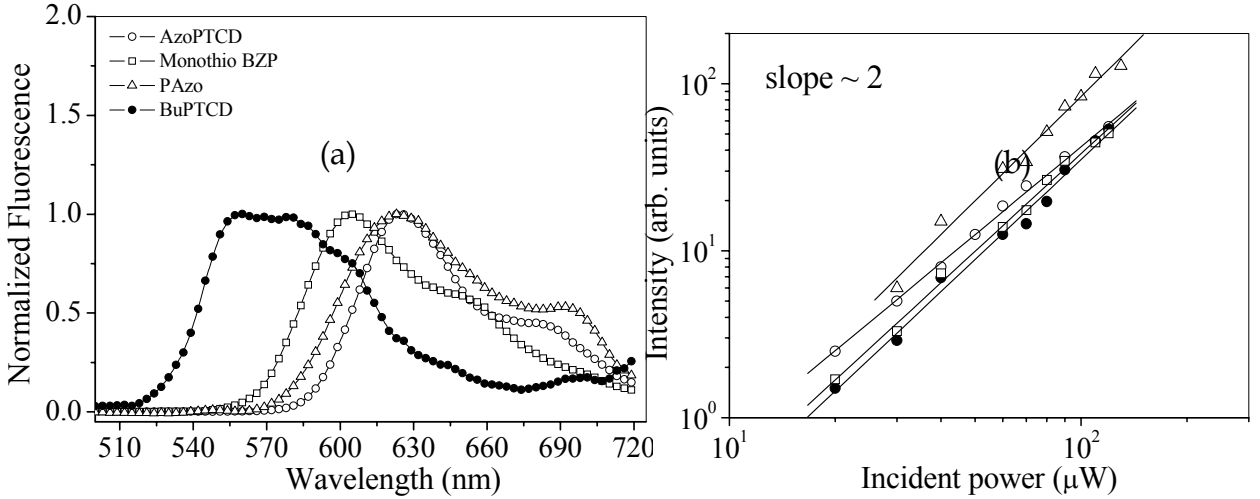

FIG. 3. (a) Normalized two-photon excited fluorescent emission of the PTCD compounds in a solution with 10% TFA in DCM pumped at 770 nm; (b) 2PA fluorescence intensity vs. incident energy.

The observed emission indicates the potential of PTCD to be used as active media for 2PP laser operating at short wavelengths. The efficiency of 2PP lasing in dyes reported so far has been rather low (overall 2PP lasing efficiency smaller than 0.1).

CONCLUSIONS

In summary, large 2PA cross-sections were measured, which are in the same order of the best ones reported for organic compounds specially designed for nonlinear absorption. The results support that 2PA cross-section can be improved by molecular design strategies and the resonance enhancement effect. It is expected that increasing the conjugation and/or adding symmetric donor and acceptor species could further improve the 2PA effect. Results on the transmittance change versus excitation irradiance and the strong two-photon induced fluorescence demonstrate that PTCD compounds are attractive for application in optical limiting and 2PP upconversion lasing.

Acknowledgments

FAPESP

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