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Perylene Derivatives with Large Two-Photon-Absorption Cross-Sections for Application in Optical Limiting and Upconversion Lasing**

By Samuel L. Oliveira,* Daniel S. Corrêa,
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We report on the degenerate two-photon absorption (2PA) spectra of perylene tetracarboxylic derivatives (PTCDs), bis(benzimidazo)perylene (AzoPTCD), and bis(benzimidazo)thioperylene (Monothio BZP), obtained by means of the Z-scan technique with femtosecond laser pulses. The results show that these materials possess exceptionally high 2PA cross-sections. At 750 nm, for instance, AzoPTCD and Monothio BZP present 2PA cross-sections of $3400 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ and $1170 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$, respectively. In addition, the 2PA saturation behavior observed as the laser irradiance increases and the strong two-photon-induced fluores-

cence suggest that PTCD compounds may be attractive candidates for applications in optical limiting and two-photon pumped (2PP) upconversion lasing.

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. Such a 2PA process has interesting characteristics with direct consequences to applications including: i) improved spatial resolution owing to the square dependence on the excitation irradiance; ii) negligible linear absorption at the pumping wavelength, with a resulting increase of penetration depth, particularly in biological tissues; and iii) very fast temporal response. The advantages of the 2PA mechanism have been explored in numerous studies leading to promising applications, such as 2PP frequency-upconverted lasing, optical limiting, fluorescence excitation microscopy and imaging, three-dimensional optical data storage and lithographic microfabrication, and photodynamic therapy.^[1–8] Accordingly, a great deal of effort has been directed to the development of various design strategies to synthesize new two-photon absorbing materials with large 2PA cross-sections (δ) and to increase physical and chemical stabilities. Most of the recently developed two-photon absorbers are organic compounds.^[2,5,9–15] Here, we investigate the possibility of using PTCD dyes as materials with high nonlinear optical absorption. PTCDs are organic dyes, readily available and thermally and chemically stable. The perylene moiety presents remarkable electron-donor characteristics,^[16,17] although on adding lateral groups, the molecule can play either an electron-acceptor or -donor role. Moreover, their strong absorption and emission in the visible spectral range makes them potential candidates for applications as organic semiconductors, photoconductors, and laser materials.^[16–22]

Although high optical nonlinearities have been reported in organic materials at specific wavelengths, only recently has the dispersion of the nonlinear absorption over a wide spectral range begun to be characterized.^[2,5,7,13–15,23–26] From an applications point of view, such information is important in formulating a molecular design strategy for a given nonlinear optical material. In this context, the present work reports on the degenerate 2PA cross-section spectra of AzoPTCD and Monothio BZP solutions in the spectral range from the visible to the near infrared. The optical properties of PTCD derivatives identify them as a new class of stable and efficient two-photon absorbers with promising characteristics for applications in two-photon-excited fluorescence and optical limiting.

AzoPTCD and Monothio BZP derivatives, the molecular structures of which are presented as insets to Figures 1a,b, respectively, have electronic absorption bands spanning the 400–660 nm spectral range, with the vibronic structure superposed on the π – π^* transition that is characteristic of the PTCD chromophore.^[27,28] However, they are transparent in the near-infrared region, as seen in Figure 1. It should be pointed out that at the concentration levels used in this investigation, no aggregation was detected.

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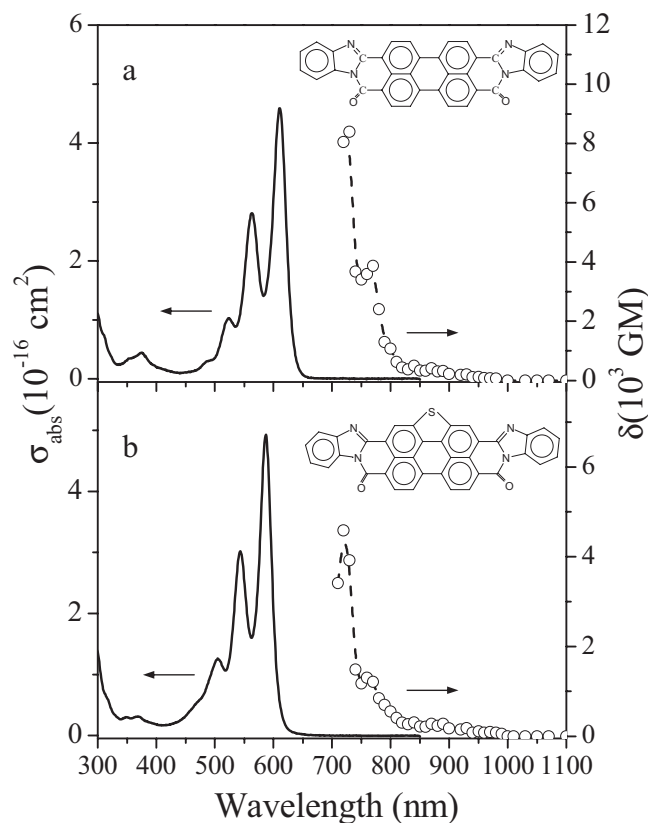


Figure 1. Linear σ and degenerate δ 2PA spectrum of a) AzoPTCD and b) Monothio BZP in a solution with 10 vol.-% TFA in dichloromethane. Insets: the respective molecular structures. (GM: Göppert Mayer units.)

The δ values for PTCd dyes were determined using open-aperture Z-scan measurements,^[29,30] with laser pulses from an optical parametric amplifier pumped by a Ti:sapphire chirped pulse amplified system, delivering 150 fs pulses at 775 nm with a 1 kHz repetition rate. Typical 2PA Z-scan signatures for AzoPTCD and Monothio BZP at 770 nm (non-resonant condition) are included in Figure 2b. The solid lines represent theoretical fittings obtained with the expression proposed by Sheik-Bahae et al.^[30] Similar Z-scan curves were also obtained for other pump wavelengths in order to determine their δ values (not shown).

The 2PA cross-section spectra for PTCd compounds are shown in Figure 1 (open circles). It can be seen that these derivatives exhibit high δ values at several excitation wavelengths. For instance, the δ value at 710 nm for bis[(diarylamino)styryl]benzene with covalently attached sulfonium groups, which has been proposed as a two-photon-activated photoacid generator, is 690 GM ($1 \text{ GM} \equiv 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$),^[5] while the δ value for AzoPTCD at 720 nm is around 8000 GM. At 740 nm, we found a δ value of 3680 GM, which is among the highest 2PA cross-sections observed for organic compounds. In addition, the value of $\delta = 1064 \text{ GM}$ achieved for AzoPTCD at 800 nm is similar to that obtained for 1,3,5-tricyano-2,4,6-tris(vinyl)benzene derivatives, which have been established as very efficient 2PA materials.^[23] Therefore, the results indicate

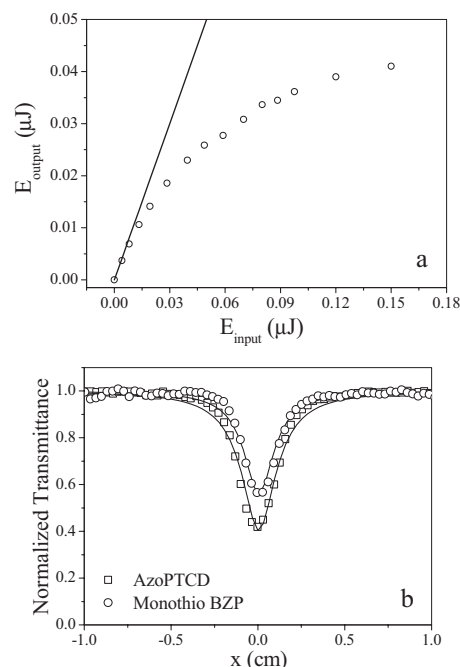


Figure 2. a) Output energy as a function of input energy for AzoPTCD ($10^{18} \text{ molecules cm}^{-3}$) in a solution with 10 vol.-% TFA in dichloromethane, placed in a 2 mm thick quartz cuvette with excitation at 770 nm. The solid line represents the linear transmittance. b) Open-aperture Z-scan signatures for AzoPTCD and Monothio BZP at 770 nm. The solid lines represent the theoretical fittings obtained using Equation 2.

that the PTCd derivatives studied here are promising materials for photonic devices based on 2PA processes, such as optical limiters and 2PP lasers. The monotonic increase observed in the 2PA cross-section spectra at wavelengths below 800 nm can be attributed to the resonance enhancement of the non-linearity, in agreement with the resonant denominator in the sum-over-states (SOS) model,^[11,31,32] assuming that the $\pi \rightarrow \pi^*$ transition (corresponding to the peak of the absorption band around 550 nm) provides the major contribution to the virtual intermediate state and that the excited state corresponds to the absorption peaks around 350 nm. Regarding the molecular strategy to obtain materials with efficient two-photon cross-sections, our results suggest that even larger 2PA cross-sections could possibly be obtained by manipulating the perylene derivatives, by positioning donor or acceptor groups symmetrically, or by increasing the molecule conjugation length, in agreement with molecular design strategies proposed in the literature.^[11]

In order to evaluate the potential applications of these compounds, optical limiting measurements were performed. Figure 2a shows the optical limiting effect of AzoPTCD obtained at 770 nm. Similar optical limiting results were also achieved for Monothio BZP using the same experimental setup. This result shows that PTCd compounds exhibit effective 2PA optical limiting action, which is useful to limit very short pulses, in the wide wavelength range from 730 to 900 nm, especially at wavelengths near the linear absorption edge.

Furthermore, chromophores with intense 2PA processes can be applied in 2PP lasers, where gain can be extracted from the bulk of the material. In this way, a strong two-photon-excited fluorescent emission, which is a relevant prerequisite for upconversion lasing, was measured in PTCs for excitation at 770 nm. The upconversion spectra for AzoPTCD and Monothio BZP are shown in Figure 3a, where the maximum intensities occur around 600 and 620 nm, respectively. These curves were truncated around 730 nm to eliminate the excitation

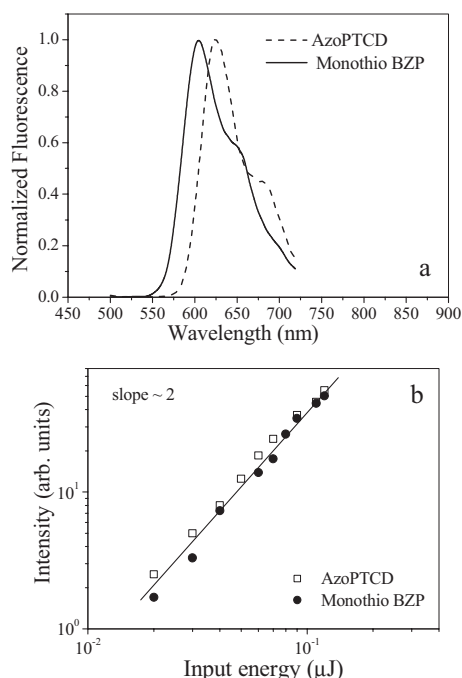


Figure 3. a) Normalized two-photon-excited fluorescent emission of AzoPTCD and Monothio BZP in a solution with 10 vol.-% TFA in dichloromethane pumped at 770 nm. b) Two-photon-excited fluorescence intensity as a function of the incident energy for AzoPTCD and Monothio BZP at 770 nm excitation wavelength.

wavelength. It should be pointed out that the fluorescence is high enough to be seen by the naked eye.

A square dependence of the two-photon-excited fluorescence intensity versus pumping irradiance was observed when the excitation irradiance was far below the process saturation, as expected when the 2PA mechanism is responsible for the upconverted emission (Fig. 3b). The observed emission indicates the potential of PTCs to be used as an active media for 2PP lasers operating at short wavelengths. It is important to point out that the overall efficiency of 2PP lasing in dyes reported has been low, and thus the PTC dyes are interesting materials for investigation.^[33] Some investigations have reported overall 2PP lasing efficiency smaller than 0.1.^[1,34,35]

In summary, the experimental degenerate 2PA cross-section of PTC derivatives was determined. Large 2PA cross-sections were measured (for instance, 8000 GM at 720 nm for AzoPTCD), which are of the same order as the best reported

values for organic compounds specially designed for nonlinear absorption.^[5,23] The results confirm that 2PA cross-sections can be improved by molecular design strategies and the resonance enhancement effect. For future work it is expected that increasing the conjugation and/or adding symmetric donor and acceptor species may further improve the 2PA effect in PTC derivatives. The present report opens new opportunities for the potential application of PTC molecules with uniquely large 2PA cross-sections in two-photon imaging and sensitization. Results on the transmittance change versus excitation irradiance and strong two-photon-induced fluorescence demonstrate that PTC compounds are attractive for application in optical limiting and 2PP upconversion lasing.

Experimental

Samples: Samples of AzoPTCD and Monothio BZP were obtained from Xerox Research Center of Canada (XRRc). Their molecular structures are shown in the inset of Figure 1. Since perylenes are insoluble in organic solvents, solutions were prepared with 10 vol.-% trifluoroacetic acid (TFA) in dichloromethane and placed in a 2 mm thick quartz cuvette to carry out the linear and nonlinear optical measurements.

Spectroscopic Measurements: The concentration of PTC derivatives used for nonlinear optical measurements were around 10^{-3} mol L⁻¹, while the UV-vis absorption spectra were obtained with concentrations of the order of 10^{-5} mol L⁻¹ using a Varian spectrophotometer model Cary 50. Nonlinear optical measurements were carried out using the Z-scan technique, which is a simple and sensitive method to determine the 2PA coefficient β . The details of the Z-scan technique experimental setup is described elsewhere and hence only a brief explanation is given here [29,30]. This method consists basically of moving the nonlinear sample through the focal plane of a focused Gaussian beam and monitoring the changes in the far-field intensity pattern. For pure absorption nonlinearity, the light field induces an intensity dependent absorption,

$$\alpha = \alpha_0 + \beta I \quad (1)$$

where I is the laser-beam irradiance, and α_0 and β are the linear and nonlinear absorption coefficients, respectively. For a positive β value, far from the focus position, only the linear transmittance contributes to the signal, while in the vicinity of the focus, the intensity increases and the nonlinear absorption process generates a dip in the transmittance. By monitoring the transmittance change as the sample is scanned through the focal position, one is able to determine the β coefficient. Under non-resonant conditions, the absorption Z-scan signature presents a decrease in the transmittance, characterizing a 2PA mechanism. This procedure generates an absorption Z-scan signature, and the magnitude of the nonlinear process can be extracted from it. The open-aperture Z-scan transmittance change can be found by time integrating the transmitted power to give the normalized energy transmittance, assuming a temporally Gaussian pulse [30]

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

where

$$q_0(z,t) = \beta I_0(t)L \left(1 + z^2/z_0^2 \right)^{-1} \quad (3)$$

and L is the sample thickness, z_0 is the Rayleigh length, z is the sample position, and I_0 is the pulse irradiance. Thus, once the open aperture measurement is performed, the β coefficient can be found unam-

biguously from fitting Equation 2 to the experimental data. The 2PA cross-section δ is determined by means of the expression

$$\delta = hv\beta/N \quad (4)$$

where N is the number of molecules per cm^3 and hv is the excitation photon energy. Usually, δ is expressed in Göppert Mayer (GM) units, in which $1 \text{ GM} \equiv 1 \times 10^{-50} \text{ cm}^4 \text{ s nm}$, using an optical parametric amplifier (TOPAS, from Light Conversion) pumped by 150 fs pulses at 775 nm, delivered by a commercial Ti:sapphire chirped pulse amplified system CPA-2001 from Clark-MXR Inc., operating at a 1 kHz repetition rate. The full width at half maximum (FWHM) pulse duration was 120 fs, and the spatial profile of the laser beam presented a Gaussian distribution. The beam waist size and pulse irradiance were determined via Z-scan measurements on fused silica (1.2 mm) [36]. The transmitted signal was monitored using a simple silicon positive intrinsic negative (PIN) photodetector coupled to a lock-in amplifier.

Two-photon-induced fluorescence measurements from 500 to 730 nm were carried out using the same laser system described above operating at 770 nm. The emission was dispersed by a monochromator and collected by a standard photomultiplier coupled to a lock-in amplifier. 2PA fluorescence emission intensity versus incident intensity was performed by changing the laser power with polarizers. Optical limiting measurements were carried out with the pump laser beam from the above-mentioned laser at 770 nm focused on a 2 mm thick quartz cuvette. The pump intensity was controlled with the same attenuator used in the fluorescence measurements. All measurements were performed at room temperature.

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Novel Nanopyramid Arrays of Magnetite**

By Fei Liu, Peijiang Cao, Huairuo Zhang, Jifa Tian, Congwen Xiao, Chengmin Shen, Jianqi Li, and Hongjun Gao*

Highly ordered magnetic metal nanowire arrays have been the focus of nanofabrication and nanotechnology for their potential applications in high-density storage and magneto-

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