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Ultrafast nonlinear optical properties of alkyl-phthalocyanine nanoparticles investigated using Z-scan technique

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We report our results on the femtosecond nonlinear optical studies of alkyl-phthalocyanine nanoparticles dispersed in water and dissolved in chloroform. Nonlinear refractive and absorptive properties were investigated using the closed and open aperture Z-scan techniques. The nonlinear optical coefficients obtained for nanoparticles suspended in water are compared with those dissolved in chloroform, which resulted in simple phthalocyanine solutions. Our studies clearly demonstrate the nonlinear refractive index of nanoparticles to be positive, while that of the nanoparticles in chloroform was negative. Our results and analysis point out a high nonlinearity in the ultrafast domain for both the nanoparticles and solutions indicating their potential in optical signal processing and limiting applications. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3079801]

I. INTRODUCTION

Organic moieties with delocalized π-electron distribution such as porphyrins, phthalocyanines, fullerenes, and other inorganic composites have been extensively investigated over the last decade for their potential applications in all-optical signal processing, switching, and power limiting.[1–18] Particularly, phthalocyanines and their derivatives in solution, thin films, and nanoparticles have been a subject of intensive investigation for specific applications in the fields of photodynamic therapy, solar cells, and nonlinear optical (NLO) applications such as optical switching and optical power limiting.[19–55] It is well established that the optical and other physical properties are enhanced by orders of magnitude with transition from bulk to the nanoparticle form. There are sparse reports on the nanoparticles of phthalocyanines[19–23] and especially studies on their NLO properties. Nitschke *et al.*[19–21] reported NLO studies on zinc phthalocyanine nanoparticles using nanosecond pulses and measured enhanced nonlinear coefficients. Rangel-Rojo *et al.*[23] reported picosecond NLO studies on vanadyl-phthalocyanine nanocrystals in cyclohexane and observed switching of nonlinear absorption from saturable absorption (SA) type at 633 nm to reverse saturable absorption (RSA) type near 580 nm. Wada *et al.*[24] too reported ultrafast nonlinearities in metallophthalocyanine nanoclusters and found an enhancement in the third harmonic generation signal of VoPc(t-bu)$_{1.1}$ (Pc denotes phthalocyanine) thin films.

We have recently been exploring the NLO properties of alkyl and alkoxy phthalocyanines. These are robust molecules with good chemical and thermal stability and which can be easily dissolved in most of the common solvents. Our thorough and methodical investigations focused on the NLO properties in continuous wave, nanosecond, and femtosecond domains. Our goal is to identify, through systematic studies of different phthalocyanines using different pulse durations, the potential molecules for optical limiting and optical switching applications. Our earlier studies on the NLO properties of alkyl phthalocyanines in the femtosecond regime indicated positive nonlinear refractive index and a strong three-photon absorption presence at 800 nm obtained using the Z-scan technique.[5,6] The time-resolved studies performed using degenerate four wave mixing technique using femtosecond pulses suggested a response time for these molecules that is in the sub-100-fs domain and superior figures of merit.[7] Alkoxy phthalocyanines were investigated with nanosecond pulses and those particular studies revealed strong nonlinear absorption in these molecules with one of the highest reported nonlinear coefficients at 532 nm, implying their potential in nanosecond optical limiting applications.[8] Femtosecond NLO properties of alkoxy phthalocyanines in solutions also revealed strong refractive and absorptive nonlinearities.[9] NLO properties of alkyl and alkoxy phthalocyanines were also studied with continuous wave excitation at 633 nm using a He–Ne laser. Interestingly they have proved to be potential molecules in that domain too, possessing one of the highest nonlinear coefficients reported to date.[11,12] These studies assisted us in identifying some of the structure-property relationships. However, a consolidated NLO study using femtosecond, picosecond, and nanosecond pulses will facilitate us in resolving their absolute nonlinear coefficients, origin, and the response time of nonlinearities. Further, comprehensive knowledge of the performance of these molecules in solution, thin film, and/or nanoparticles form is essential to identify the appropriate material for device applications. Herein we present our results on the NLO properties of phthalocyanine nanoparticles [2(3), 9(10), 16(17), 23(24)-tertra-tert-butyl zinc phthalocyanine] at

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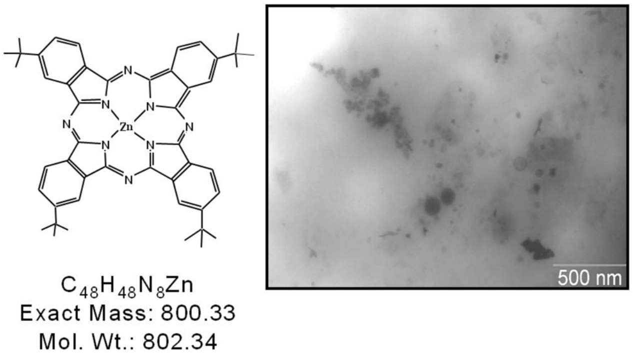
800 nm studied using ~100 fs laser pulses. The nanoparticles remained when dispersed in distilled water, but they dissolved in chloroform, providing a clear solution.

II. EXPERIMENT

Phthalocyanine nanoparticles were synthesized by a modified procedure reported in the literature.[56] About 0.2 g of t-Bu$_4$PcZn was dissolved in 1 l of freshly distilled acetone and left to stand undisturbed overnight to allow the principally inorganic impurities to settle, allowing us to benefit from *purification by sedimentation*. The purity of the remaining supernatant was examined by thin layer chromatography. 200 μl of the acetone solution was injected into 10 ml of vigorously stirred de-ionized water at room temperature. After injection, the aqueous nanoparticle dispersion was irradiated immediately using a microwave oven (LG; 2.45 GHz, 900 W) operating at 560 W for 1 min. The treatment with microwaves is considered to be a homogeneous irradiation of the entire droplet liquid dispersion system formed after reprecipitation. Experimentally this implied that subsequent to injection of the organic solution into water, microwaves were employed to heat the dispersion and hence forced the organic solvent to evaporate rapidly. This rapid evaporation was aimed to prevent aggregation between droplets. The particle size measurement was done by using transmission electron microscopy (TEM). For TEM investigations approximately 2 ml of freshly prepared nanoparticle-water dispersion was dropped onto a Formvar coated copper grid. The water was evaporated under reduced pressure at room temperature. The resulting sample was observed on a Philips Tecnai F12 FEI transmission electron microscope. Experimental details of the standard Z-scan[57] setup are reported elsewhere.[5,6] Briefly, femtosecond pulses were obtained from a chirped pulse amplification system consisting of an oscillator that delivered ~80 fs pulses with a repetition rate of 82 MHz at 800 nm and a regenerative amplifier, which delivered 1 kHz amplified pulses of ~100 fs duration with an output energy of ~1 mJ. The bandwidth of the output was ~11 nm, indicating nearly transform-limited pulses. The pulses were focused using a lens with focal length of 120 mm. The peak intensities used were in the range of 50–500 GW cm^{-2}. Samples were placed in 1-mm glass/quartz cuvettes for all the NLO studies performed.

III. RESULTS AND DISCUSSION

Particle size of the nanoparticles was investigated using the transmission electron microscope and the linear absorption data. Figure 1(a) shows the structure of the zinc phthalocyanine, while Fig. 1(b) depicts the TEM picture of the as-synthesized phthalocyanine nanoparticles. The nanoparticles once dissolved in chloroform resulted in phthalocyanine molecules exhibiting properties similar to those of normal phthalocyanines (herewith referred to as "PcM," implying nanoparticles dissolved in chloroform solution). Phthalocyanines nanoparticles dispersed in water (herewith referred to as "PcN," implying nanoparticles dispersed in distilled water) provided stable and clear colloidal solution. UV-visible absorption spectra of PcN and PcM are shown in Fig. 2. The figure also depicts the absorption spectrum of pure phthalocyanine molecules dissolved in chloroform for comparison. PcM spectra had Q-band redshifted slightly with respect to Pc. For PcN Q-band was quenched compared to PcM and Pc and blueshifted compared to Pc. The intensive green or blue color, characteristic of these phthalocyanine solutions, was found to be much lighter for the nanoparticles because of this Q-band quenching. Shifts in the UV/visible spectra are known to indicate stacking behavior of molecules within an aggregate.[58,59] Czikklely *et al.*[60] reported a series of different arrangements for dye molecules in aggregates, which could be identified by the position of their blue- and redshifted absorption bands. In our case a blueshifted band is observed with respect to the molecular peak. This possibly suggests that this peak represents single molecules, which surround the particle as a shell. The molecular fluorescence spectra of the Q-band in the 600–900 nm region and B-band in the 300–500 nm region are shown in Fig. 3. Chen *et al.*[61] reported emission spectra of Q-band for gallium and indium phthalocyanine compounds, and Wrobel and Boguta[62] reported those for t-Bu$_4$PcZn and (PhS)$_4$PcZn compounds. The emission spectra for PcN and PcM were recorded at excitation wavelengths of 300 and 330 nm, respectively. It is evident that the transition from mo-



(a) **(b)**

FIG. 1. (a) Structure of the phthalocyanine whose nanoparticles were studied. (b) TEM image of the nanoparticles dispersed in water.

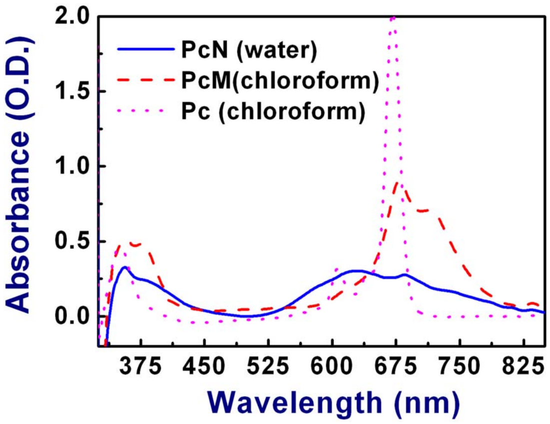


FIG. 2. (Color online) Absorption spectra of PcN in water (solid curve), PcN in chloroform resulting in PcM (dashed curve), and pure phthalocyanine in chloroform (dotted curve).

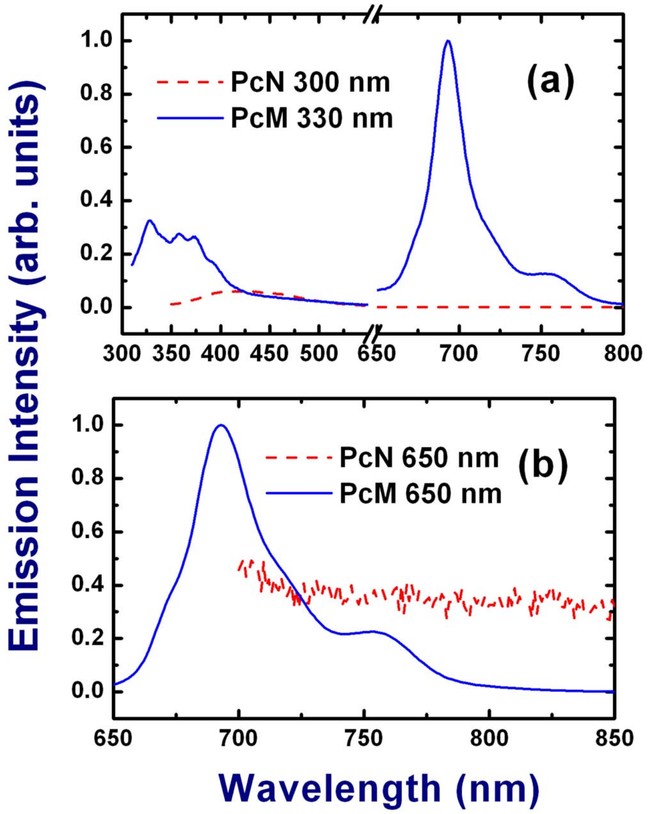


FIG. 3. (Color online) Emission spectra of PcM and PcN (a) excited with 300 and 330 nm, respectively, and (b) excited with 650 nm.

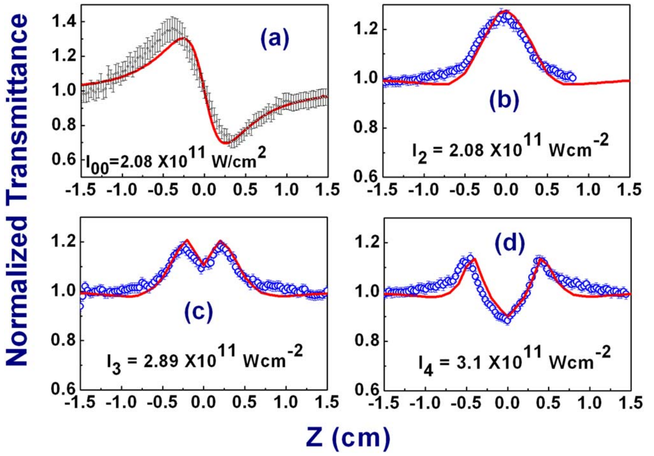


FIG. 4. (Color online) (a) Open aperture Z-scan data (open circles) for PcM in chloroform obtained for an intensity of 2.08×10^{11} W/cm^2. Solid line is the best fit. [(c) and (d)] Open aperture Z-scan curves obtained for PcM at different intensities.

lecular solution to quasi-solid-state nanoparticles for each phthalocyanine is accompanied in all cases by a complete quenching of the Q-band and B-band fluorescence as illustrated in Fig. 3. The fluorescence spectra of PcM exhibited two emission peaks (near 350 and 700 nm), whereas PcN had very weak emission peak (400–450 nm). The observation in PcN is unexpected and could be attributed to impurities, which needs thorough investigation. Fluorescence lifetime measurements for PcM were carried out using a time-resolved spectrofluorometer. The decay observed was monoexponential with a best fit value of ~3.83 ns.

The closed and open aperture Z-scan data recorded for PcN and PcM are presented in Figs. 4 and 5. Error bars indicated in all the figures are indicative of few inaccuracies in the data collection and are from concentration measurements. We also expect errors from fitting procedures, calibration of the neutral filters used, estimation of the focal spot size, and corresponding peak intensities. We anticipate the maximum error resulting from such factors in the evaluated values of nonlinear coefficients to be ~15%. We noticed that PcN exhibited negative nonlinearity in chloroform [Fig. 4(a); peak followed by valley] and positive nonlinearity in water [inset of Fig. 5; valley followed by peak] as revealed by signatures of the closed aperture data. The magnitude of nonlinear refractive index (n_2) evaluated from closed aperture data was $\sim 0.92 \times 10^{-15}$ cm^2 W^{-1} (*negative*) for PcM and $\sim 1.16 \times 10^{-15}$ cm^2 W^{-1} (*positive*) for PcN. Both the scans were recorded for similar concentrations and peak intensities of the pump pulses. It is evident that the magnitude nonlinearity has been *enhanced* by ~30% in the nanoparticle form apart from switching of the sign. However, the *enhancement* was re-evaluated carefully, taking into consideration the contributions from respective solvents. Typically, chloroform and water possess *positive* nonlinearities though the magnitudes are much lower than those of the solutes, and we estimated their contribution to be <5% at intensities used in the experiments. Despite the contribution from solvents we established the nonlinearity of PcN to be higher than that of PcM with an approximate enhancement of magnitude by ~20%. Our earlier studies on various phthalocyanines indicated negative nonlinearity recorded through the closed aperture scans.[5,6,9] There have been earlier reports of sign switching of n_2 in different media.[63–66] Osborne *et al.*[63] reported sign reversal of the n_2 in silver nanocluster–doped soda-lime glasses using 6 ps pulses. Their studies were repeated several times and found the effect of laser exposure (intensity dependence) for the reason in sign reversal. The irreversible changes observed in those studies were caused by a thermal influence produced by highly repetitive pulses. Ganeev *et al.*[65] investigated silicate glasses doped with silver nanoparticles using 55 ps pulses and found the turnaround in

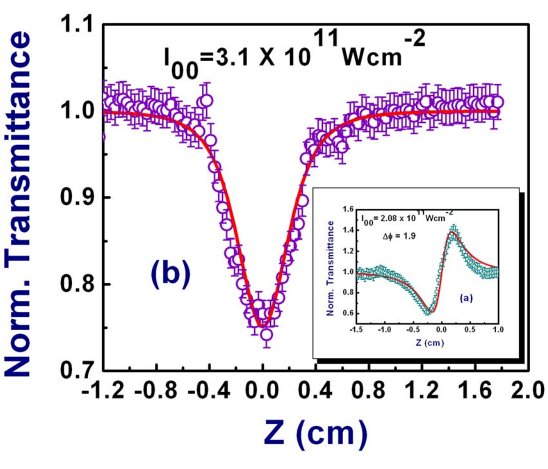


FIG. 5. (Color online) Open aperture data for PcN in water indicating the presence of three-photon absorption. Inset shows the closed aperture data representing positive nonlinearity.

n_2 sign from positive to negative with increasing peak intensities. However, in their case they attributed the reason for this change to interband transitions. Serna *et al.*[66] reported the sign change of both refractive and absorptive nonlinearities in Cu-doped glass with increasing laser intensity, and the mechanism of alteration in the refractive type was found to be a thermally activated enlargement of Cu nanoparticles. In the present case we use femtosecond laser pulses which are 1 ms apart. Thermal diffusion occurs typically in the picosecond to few hundred nanosecond regime. The femtosecond laser pulse possibly encounters an average thermal contribution, which is negative, at the beam waist in addition to the nonlinearity from the nanoparticles. We suppose that the negative nonlinearity observed in both molecular solution and nanoparticles in chloroform solution has a component of this average thermal contribution (also negative). Therefore, the positive nonlinearity observed with PcN has to be larger than the reported value by average thermal contribution from water. We believe that the sign change is primarily due to change in the particle size in water and chloroform.

Figures 4(b)–4(d) show the open aperture Z-scan data recorded for PcM at various peak intensities. The behavior was purely SA type at low intensities as depicted in Fig. 4(b). However, for intensities greater than 2.5×10^{11} W/cm^2 the behavior switched from SA to RSA close to the focus. The RSA dip near focus was further enhanced with increasing intensity [Figs. 4(c) and 4(d)]. We anticipate that at lower intensities the linear absorption dominates and SA is observed, while at higher peak intensities RSA is the dominant mechanism. It is evident from Fig. 4(d) that even at peak intensities of 3.1×10^{11} W/cm^2 the wings of the curve exhibits SA kind of behavior. This kind of effect has prospective applications in optical pulse compression, optical switching, and optical limiting.[65] Similar transition behavior was also reported by Elim *et al.*[67] in their NLO studies on gold nanorods, and they attributed its source to the free carrier absorption. We observed similar complicated nonlinear absorption (switching over from RSA to SA or vice versa) in alkyl phthalocyanines (free base and zinc) in a separate study[9] which suggested a stringent dependence on the peak intensities and concentrations of the sample used. Organic molecules, in general, possess complicated nonlinear absorption mechanism depending on the pulse duration used, peak intensities, solution concentration, lifetimes of the excited states, spectral region of excitation, etc. In the present case a simplistic three-level model was utilized for extracting the nonlinear coefficients (two-photon and three-photon absorptions included) through fits to the experimental data.[68] The lifetime for PcM measured with excitation near 650 nm was ~3.8 ns, similar to that of the pure phthalocyanine in chloroform. The nonlinear coefficients obtained from the best fits are presented in Table I. The value of three-photon absorption coefficient (γ) retrieved from the fits was 8.5×10^{-23} cm^3 GW^{-2}, while the value of two-photon absorption coefficient (β) was 3.5×10^{-12} cm/W. The fits were better when both β and γ were included rather than γ alone. Surprisingly, open aperture Z-scan data of PcN [Fig. 5] illustrated only RSA type and the best fits provided three-photon absorption coefficient (γ) of ~13.5 $\times 10^{-23}$ cm^3 GW^{-2}. Both the data were recorded for similar concentrations in water and chloroform. Significantly, the values reported here (especially for nanoparticles) are averaged for the whole volume. If we take into consideration volume fraction of the nanoparticles, nonlinear coefficients will be enhanced by at least three orders of magnitude. The γ values obtained for PcM are comparable to those obtained for pure alkyl (Zn) phthalocyanine synthesized and were studied separately.[5,6] However, in that particular study we observed only three-photon absorption and not the complex behavior as seen in the present case. This could be explained by the following: (a) slight differences in the absorption spectra for PcM and pure ZnPc, especially in the *Q*-band; (b) the nanoparticles when dissolved in chloroform do not match the properties of ZnPc due to physical/chemical reasons and the chemistry being completely different in the case of nanoparticles; and (c) the concentrations used in that study were lower than the ones used here.

TABLE I. Two-photon absorption coefficients (β), three-photon absorption coefficients (γ), nonlinear refractive indices (n_2), and clamping thresholds of the phthalocyanines excited with 800 nm wavelength, 110 fs pulses.

Solvent/ solution	β (cm W^{-1})	γ (cm^3 W^{-2})	n_2 (cm^2 W^{-1})	Clamping threshold (J cm^{-2})
Water (PcN)	⋯	13.5×10^{-23}	11.6×10^{-16}	0.03
CHCl$_3$ (PcM)	3.5×10^{-12}	8.5×10^{-23}	-9.18×10^{-16}	⋯

Figure 6 depicts the optical limiting curve for PcM and PcN recorded at concentrations of $\sim 10^{-4}M$. It is apparent that the limiting threshold for the nanoparticles is lower than that of chloroform solution. These molecules exhibit strong RSA/three-photon absorption; the limiting mechanism can be accredited to nonlinear absorption. We have not observed any significant scattering from these dispersed solutions which could have influenced the limiting threshold. The limiting threshold (calculated per pulse) was estimated to be ~0.03 J/cm^2 for the nanoparticles. Our recent studies on alkyl and alkoxy phthalocyanines[5–9] provided sufficient evidence that nonlinear absorption in such molecules is critically dependent on concentration of the solutions, peak in-

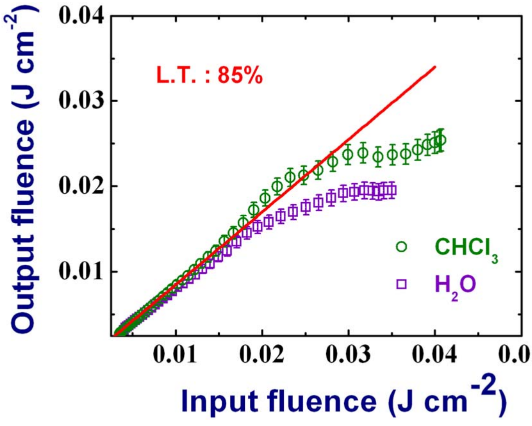


FIG. 6. (Color online) Optical limiting curve obtained for PcM (open circles) and PcN (open squares) dispersed in water and dissolved in chloroform, respectively. Solid line is the linear transmittance curve.

tensities used, and absorbance of the molecules at excitation wavelength. There, possibly, could be saturation of the population in higher excited states at higher peak intensities. Similar saturation effects were observed in pure alkoxy phthalocyanines with femtosecond excitation.[9] We are currently investigating the concentration and intensity dependent nonlinear absorption studies of both PcN and PcM using Z-scan and nonlinear transmission data to ascertain this saturation behavior. There have been few reports on the NLO properties of phthalocyanine nanoparticles in the nanosecond domain, but there is no report in the femtosecond domain. Hence, it is difficult to compare our data even qualitatively with those reported. Through proper tailoring of the nanoparticle size, we expect to further enhance the value of nonlinear refractive index, which could find impending applications in optical signal processing.

IV. CONCLUSIONS

Femtosecond NLO studies of alkyl-phthalocyanine nanoparticles dispersed in water and dissolved in solution were carried out at 800 nm using the Z-scan technique. PcM exhibited negative nonlinearity, while PcN possessed positive nonlinearity, which was disclosed by the signature of closed aperture data. The magnitude of the nonlinear refractive index n_2 was $\sim 0.92 \times 10^{-15}$ cm^2 W^{-1} (negative) for PcM and $\sim 1.16 \times 10^{-15}$ cm^2 W^{-1} (positive) for PcN. Open aperture Z-scan data of PcM revealed SA kind of behavior switching to RSA in SA, whereas PcN exhibited strong and pure three-photon absorption. For the case of PcM the value of three-photon absorption coefficient (γ) retrieved from the fits was 8.5×10^{-23} cm^3 GW^{-2} and the two-photon absorption coefficient (β) was 3.5×10^{-12} cm/W. The measured three-photon absorption coefficient (γ) for PcN, obtained through fitting of the experimental data, was 1.35×10^{-22} cm^3 GW^{-2}. PcN proved to be a good optical limiter in the femtosecond domain with limiting threshold of ~ 0.03 J/cm^2.

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