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Efficient ultrafast optical limiting using single walled carbon nanotubes functionalized noncovalently with free base and metalloporphyrins

Jyotsana Gupta,^{1,a)} C. Vijayan,^{1,b)} Sandeep Kumar Maurya,² and D. Goswami²

¹*Department of Physics, Indian Institute of Technology, Madras, India*

²*Department of Chemistry, Indian Institute of Technology, Kanpur, India*

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The present work is on the linear and third order nonlinear optical properties of single walled carbon nanotubes functionalized noncovalently with free base porphyrin and a metalloporphyrin separately. The functionalized carbon nanotubes (CNTs) are soluble in dimethylformamide, and the microscopic images show that the porphyrin molecules are attached to the surface of the CNTs. The interaction between CNTs and porphyrins is noncovalent and probably due to π - π interaction as both CNTs and porphyrins have π -electron rich structures. The samples exhibit large ultrafast nonlinear absorption as evident from the open aperture z-scan studies performed using mode-locked Ti:Sapphire femtosecond pulses at 780 nm. The mechanisms of optical nonlinearity of the functionalized CNTs appear to be two photon absorption along with nonlinear scattering with a small contribution from saturable absorption, whereas nonfunctionalized CNTs are known to exhibit saturable absorption. The value of the nonlinear absorption coefficient for the CNTs functionalized with the free base porphyrin is one order smaller than that for CNTs functionalized with metalloporphyrin. Efficient low threshold ultrafast optical limiting is demonstrated for both types of functionalized CNTs. © 2011 American Institute of Physics. [doi:10.1063/1.3587178]

I. INTRODUCTION

Single walled carbon nanotubes (SWCNTs) are promising materials for device applications in areas such as optoelectronics and photovoltaics in view of their unique structural, mechanical, and electronic properties.^{1,2} However, insolubility of these carbon nanotubes (CNTs) in common solvents has been a serious problem, and several schemes are being devised to address this issue. Several research groups have succeeded in making CNTs functionalized by attaching various functional groups such as polymers,³ porphyrins,⁴⁻⁶ and dyes⁷ through either covalent or noncovalent bonding. Noncovalent bonding is simpler than covalent bonding to obtain functionalized CNTs (*f*-CNTs) due to certain structural features of CNTs.⁸ Noncovalent bonding is possible by π - π interaction, Van der Waals forces, electrostatic interaction, etc, and this approach does not normally create any change in the intrinsic electronic structure of CNTs. Porphyrins are conjugated organic compounds, which have a wide applicability in medicine, optics, electronics, and many more fields.⁹ We used porphyrins (free base and metalloporphyrin) to functionalize SWCNTs as the product is generally expected to possess many of the intrinsic properties of the porphyrin such as luminescence and biocompatibility.

There is a lot of scope for *f*-CNTs as useful materials in nonlinear optics, optical communication, optical power limiting, and optical data processing.¹⁰ Developing efficient optical limiters to protect sensitive detectors and eyes from

high power laser radiation, particularly in the ultrafast regime, is an emerging area of research.

Porphyrin shows very good optical nonlinearity dominant by reverse saturable absorption (RSA), two photon absorption (TPA), or higher excited state absorption (ESA).^{9,11} The surfaces of the various semiconductor and metal nanoparticles are decorated with porphyrin molecules, and these are also promising materials for optical limiters due to large RSA in the visible even near-infrared wavelength range.^{9,12} A large optical limiting effect has been observed in the case of PVK-modified SWCNTs due to the photoinduced electron transfer.⁴ However, electropolymerized thin films of Fe³⁺ 5,10,15,20-tetrakis-(4-hydroxytetraphenyl) porphyrins shows enhanced optical nonlinearity dominant by TPA.¹³ Several groups have been exploring nanocomposites as efficient limiting materials with optimal parameters of limiting such as limiting threshold, response time, and wide wavelength range,^{2,14-17} invoking the different mechanisms of optical nonlinearity in nanohybrid materials. Materials such as CNTs and *f*-CNTs with various chromophores and molecules have been shown to have excellent optical limiting behavior with a broadband response from visible to infrared optical region. The physical mechanisms of optical nonlinearity responsible for optical limiting depend on the nature of the attached molecules used for functionalization of CNTs.^{4,18-21} The SWCNTs suspended in water on exposure to femtosecond pulses have been found to exhibit negative cubic nonlinearity and saturable absorption.¹⁷ However, CNTs functionalized covalently with porphyrins show enhancement in the optical limiting behavior, without damaging the one-dimensional structure of CNTs.^{4,17} On the other hand, noncovalent functionalization

^{a)}Electronic mail: jyotsana.gupta@gmail.com.

^{b)}Electronic mail: cvijayan@physics.iit.ac.in.

is procedurally simpler and yet makes it possible to alter the optical properties of the SWCNTs. The nonlinear optical response of *f*-CNTs is found to incorporate mechanisms of ultrafast nonlinear absorption associated with the porphyrin, an aspect that has not been explored much in the literature.

II. EXPERIMENTAL DETAILS

The chemical method used to functionalize CNTs with porphyrin is very simple.⁸ In the current report, we used SWCNTs (obtained from the Department of Metallurgical and Materials Engineering of our institute) functionalized with metal-free 5,10,15,20-tetraphenylporphyrin (TPP, generally known as free base porphyrin) and iron tetraphenylporphyrin (FeTPP) obtained in powder form from Central Leather Research Institute (CLRI), Chennai, India. The following procedure is adopted to suspend the CNTs and the porphyrins in dimethylformamide (DMF). Two milligrams of TPP is mixed with 1 mg CNTs, and the mixture is vigorously stirred with 10 ml DMF for 8 to 10 h followed by 2 h of sonication. The extra insoluble CNTs are removed by 1 h centrifuging at 1600 g (3500 rpm). The collected solid is again suspended in DMF for mild sonication (5 min). The final solution of functionalized CNTs with TPP (*f*-CNTs-TPP) is found to be stable for a few months. A similar procedure is followed to obtain functionalized CNTs with FeTPP (*f*-CNTs-FeTPP). One to two drops of the solutions of functionalized CNTs are dropped onto a carbon-coated copper grid (300 mesh) for few seconds, and the extra solution soaked off with a filter paper for preparing the samples for high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). HRTEM and SEM images of the sample are obtained using a 200 keV JEOL 3010 and FEI Quanta 200 microscope, respectively.

Optical absorption and fluorescence spectra are recorded by JASCO spectrometer. Nonlinear optical response is studied using the *z*-scan technique,²² where a laser beam is focused into a 1 mm cuvette by a convex lens (focal length, 20 cm) to create a spatial variation of intensity. Nonlinear optical absorption and refraction of both *f*-CNTs are done at 780 nm with 120-fs pulses from a mode-locked Coherent Mira Ti:Sapphire laser (model 900 F) at a repetition rate 76 MHz. We used frequency optimized mechanical chopper (MC1000 A, Thorlabs) with 50% duty cycle to control the thermal issues related to high repetition rate femtosecond laser.²³

III. RESULTS AND DISCUSSION

The porphyrins TPP (Figs. 1(a) and 1(b)) and FeTPP (Figs. 1(c) and 1(d)) are observed to be attached with the surface of the CNTs as shown in HRTEM and SEM images. In the figure, 1(a) and 1(c) are HRTEM images and 1(b) and 1(d) are SEM images. The images clearly show that SWCNTs are attached with molecular clusters of the porphyrins, seen as dark clusters. The optical absorption spectra (Figs. 2(a) and 2(b)) of the *f*-CNTs-TPP and *f*-CNTs-FeTPP (solid lines) are compared with those of undoped DMF suspension of CNTs (dashed line), TPP and FeTPP (dotted lines), respectively. The spectra of the *f*-CNTs are remark-

ably different from that of undoped CNTs (dashed line), which actually do not have any feature in the visible region. On the other hand, the spectra contain the features of the porphyrins used for functionalization. There is no significant change in the Soret and the Q bands apart from an overall increase in optical density, which indicates that the interaction between CNTs and the porphyrin is noncovalent in the case of functionalization with either TPP or FeTPP. It has been reported that the noncovalent functionalization of CNTs by different dyes and ink molecules does not result in any major change in the optical absorption spectrum of the CNTs,^{5,7,24} whereas covalent bonding is known to make significant broadening and shifts in the absorption spectrum after functionalization of CNTs.⁴ The noncovalent bonding can be due to π - π or Van der Waals interaction between CNTs and the porphyrins.⁸

We studied the nonlinear optical properties of *f*-CNTs-TPP, *f*-CNTs-FeTPP, and the individual porphyrin separately. Figures 3(a) and 3(b) show the open aperture *z*-scan trace for FeTPP porphyrin and *f*-CNTs-FeTPP, respectively, at three different input powers where the intensity of the transmitted light is plotted as a function of the sample position (*z* in mm). The experimental data points and the theoretical fit (based on Sheik-Bahae formalism²²) are shown as open circles and solid lines, respectively. The transmission coefficient $T(z)$ is defined by the Eq. 1,

$$T(z) = \sum_{m=0}^{\infty} \left[(-q_0)^m / (m+1)^{3/2} \right], \quad (1)$$

$$q_0 = [\beta I_0 L_{eff} / (1+x^2)], \quad (2)$$

$$L_{eff} = [1 - \exp(-\alpha L)] / \alpha, \quad (3)$$

where β is the nonlinear absorption (NLA) coefficient, I_0 is an on-axis electric field intensity at the focal point in absence of the sample, L is sample thickness, $x = z/z_0$, z_0 is Raleigh range ($= \pi \omega_0^2 / \lambda$), and ω_0 (23.64 μ m) being the minimum spot size or beam waist at the focal point. The wavelength (λ) of the laser in overall experiment is 780 nm. The general shapes of the curves indicate strong nonlinear absorption and the data fit quite well with the theoretical model. In the case of FeTPP, the values of the NLA coefficients are 8.42×10^{-9} cm/W at 89 mW, 8.69×10^{-9} cm/W at 92.9 mW, and 8.93×10^{-9} cm/W at 94.8 mW as determined by theoretical fitting in each case. In the case of *f*-CNTs-FeTPP, the corresponding values are 2.82×10^{-9} cm/W at 89 mW, 3.59×10^{-9} cm/W at 91 mW, and 7.81×10^{-9} cm/W at 93 mW, respectively. Figure 4(a) shows the open aperture *z*-scan trace for *f*-CNTs-TPP at three different input powers. The NLA coefficients are 3.21×10^{-8} cm/W at 89 mW, 2.68×10^{-8} cm/W at 91 mW, and 2.02×10^{-8} cm/W at 93 mW as determined by theoretical fitting.

The typical mechanism of optical nonlinearity in CNTs suspension is known to be predominantly saturable absorption.²⁵ In an earlier work, Mhuircheartaigh *et al.* reported on the nanosecond nonlinear response of porphyrin-attached CNTs and attributed the highlighted the role of on saturation of the accessible energy levels under high-intensity pumping.²⁶ However, reverses saturable absorption was reported

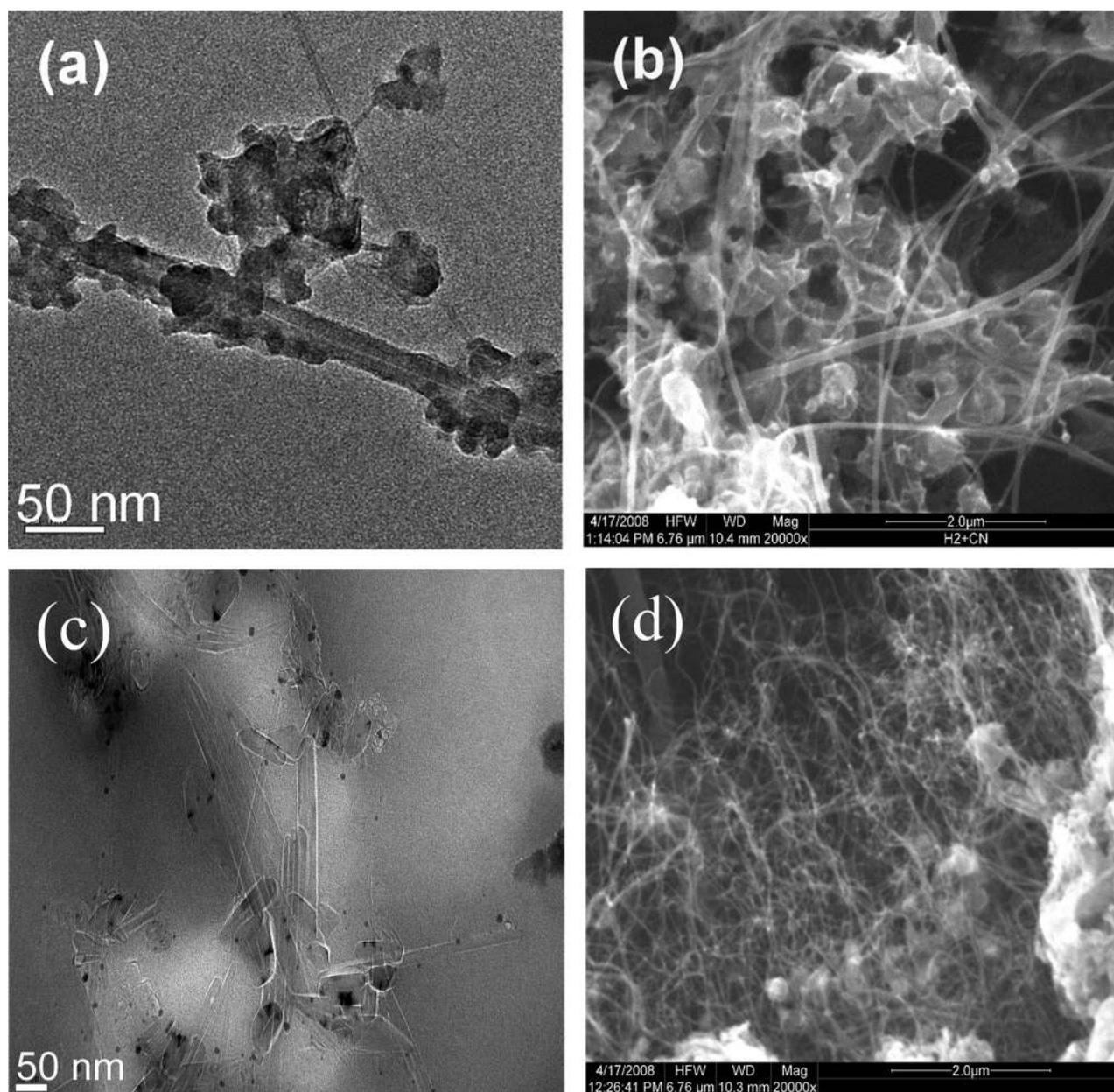


FIG. 1. HRTEM and SEM images of CNTs functionalized with TPP ((a) and (b)) and FeTPP ((c) and (d)), respectively.

by Liu *et al.* in covalent functionalized SWCNTs.²⁰ Different mechanisms are known to be operative depending on the nature of the sample and the laser pulse width used. It is known that a mechanism such as RSA, the value of NLA coefficient β would decrease with an increase in input power because of the saturation of RSA,²⁷ while it will remain unchanged if the mechanism of nonlinearity is TPA.²⁷ The values of β in Fig. 3(a) are found to be more or less the same in the case of the porphyrin at the three different values of input power, and hence the present results support the earlier observation in literature that the mechanism in porphyrin is likely to be TPA.¹³ The small amount of “wing” structures in the z-scan traces are to the occurrence of saturable absorption. However, the interpretation is not straightforward in the case of an increase in the value of β with input power as is observed in the present work in the case of *f*-CNTs-FeTPP, shown in Fig. 3(b). The dependence on input power could be due to

the influence of nonlinear scattering on nonlinear absorption in the high-power regime.²⁰

The nonlinearity of the free base porphyrin TPP has been studied, and the dominant mechanism is known to be RSA, probably caused by porphyrin degradation due to local heating effects in the solution.¹² The open z-scan trace for *f*-CNTs-TPP obtained in the present work is shown in Fig. 4(a). The three different curves are obtained for three different values of input power. The differences in the results are not much and hence the mechanism of nonlinearity appears to be TPA. This is feasible as the solutions do not have much optical absorption at 780 nm, the wavelength of the laser used, whereas, there is strong absorption in the Soret band region of 390 nm.

The β value of *f*-CNTs-TPP is one order larger than that of the *f*-CNTs-FeTPP; this can be attributed due to the difference between free base of porphyrin and metalloporphyrin.²⁸ There is a considerable amount of delocalization of the

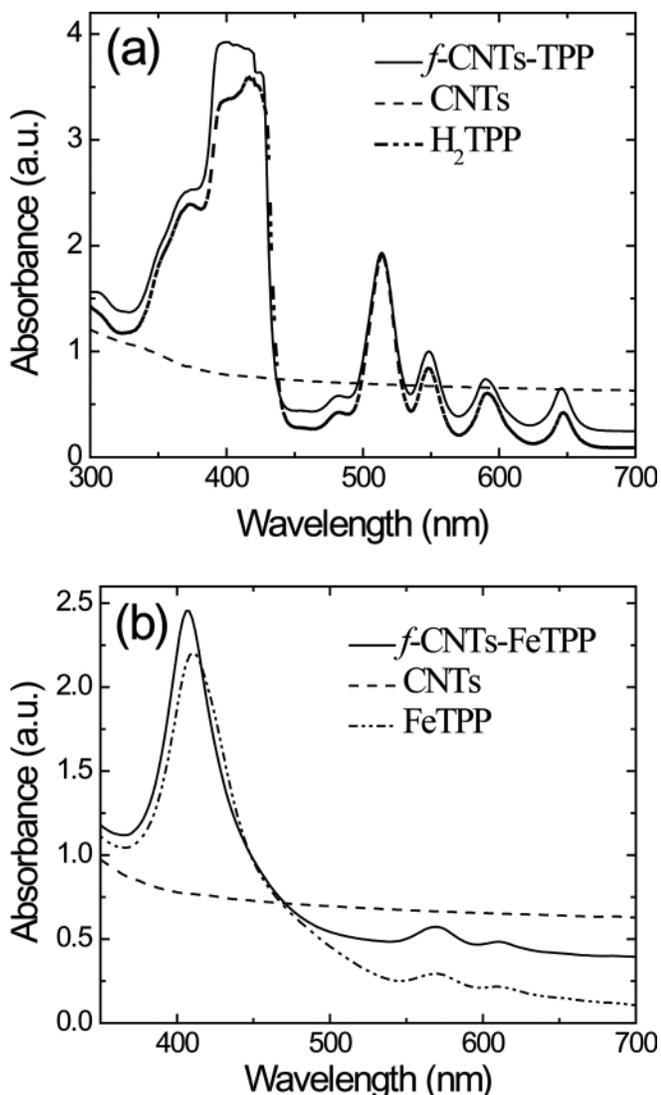


FIG. 2. Optical absorption spectrum of *f*-CNTs-TPP (a) and *f*-CNTs-FeTPP (b), functionalized CNTs (solid line), TPP and FeTPP (dotted line) and undoped CNTs (dashed line).

electron cloud in free base porphyrins, whereas the metal ion in the metalloporphyrin is rigidly bonded with the four nitrogen atoms in the porphyrin ring, resulting in a lower extent of delocalization.²⁸ This leads to a stronger π - π interaction between the CNTs and the free base porphyrin in comparison with the case of the metalloporphyrin. This could be the reason for the enhanced nonlinearity of the CNTs functionalized with the free base porphyrin. A frequency optimized mechanical chopper²³ is employed to avoid thermal effects arising from the large repetition rate.

Figure 4(b) shows the optical limiting curve where the normalized transmittance is plotted as a function of the input fluence. The open and closed circles show *f*-CNTs-TPP and *f*-CNTs-FeTPP, while solid lines are a theoretical fit. The fluence is defined as $F_{Pulse} = E_{Pulse}/(\pi\omega(z)^2)$ with E_{Pulse} is the single pulse energy and $\omega(z)$ is the radius of the propagation Gaussian pulse as a function of position z . The incident fluence at which the transmittance falls to half of the linear transmittance defined as the limiting threshold. The limiting threshold value of *f*-CNTs-TPP and *f*-CNTs-FeTPP are

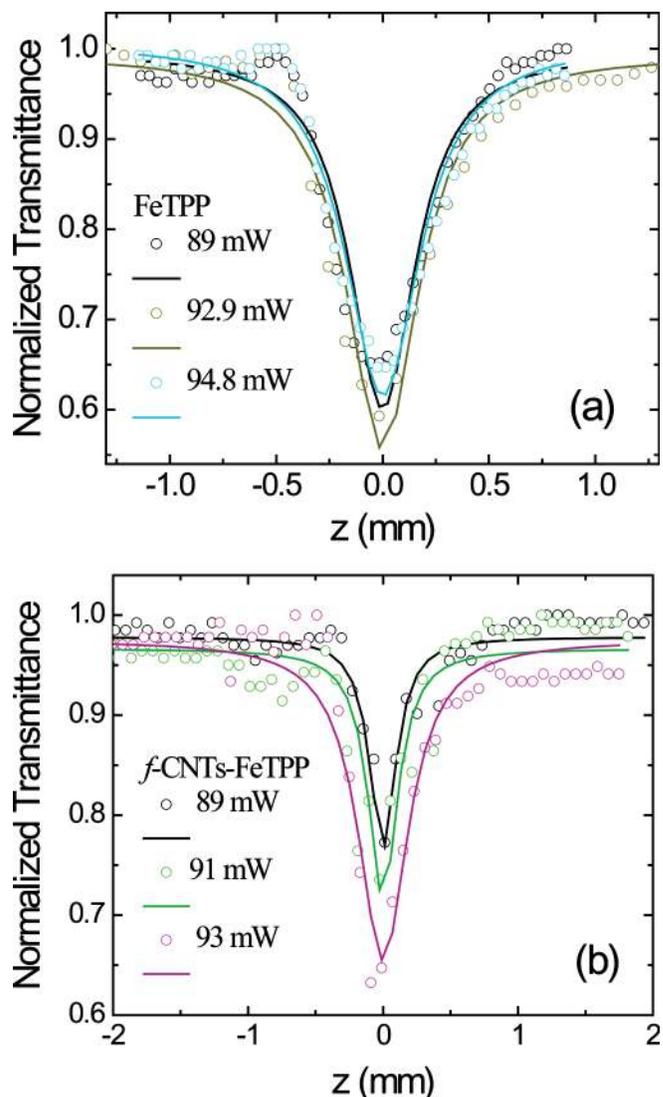


FIG. 3. (Color online) Open-aperture z-scan trace of (a) FeTPP and (b) *f*-CNTs-FeTPP at different input power. Experimental points represent as black, golden, and cyan circles correspond to 89, 92.9, and 94.8 mW power, respectively, in the case of FeTPP porphyrin (a), while black, green, and magenta circles correspond to 89, 91, and 93 mW power in the case of *f*-CNTs-FeTPP (b), respectively. The solid line is a theoretical fit to the experimental data.

1.23×10^{-4} J/cm² and 1.38×10^{-4} J/cm², respectively. In both cases, limiting threshold is better than the available benchmark material such as SWCNTs-TPP, C₆₀, and pure SWCNTs.^{4,29} Involvement of charge-separated excited states arising from photo-induced electron transfer between the porphyrin as donor and the CNTs as acceptor has been proposed as the mechanism of enhancement of optical limiting performance in an earlier report on nanosecond optical limiting with covalently functionalized CNTs.^{4,30} The femtosecond excitation in the present work can lead to the involvement of higher excited states in this process; this would contribute to the enhancement of nonlinear absorption and limiting threshold.

Generally, in the nanosecond pulse regime the nonlinear scattering (such as Mie scattering) is the most common nonlinear mechanism for optical limiting in nanomaterials. Mie scattering plays a role if the size of the particle is comparable

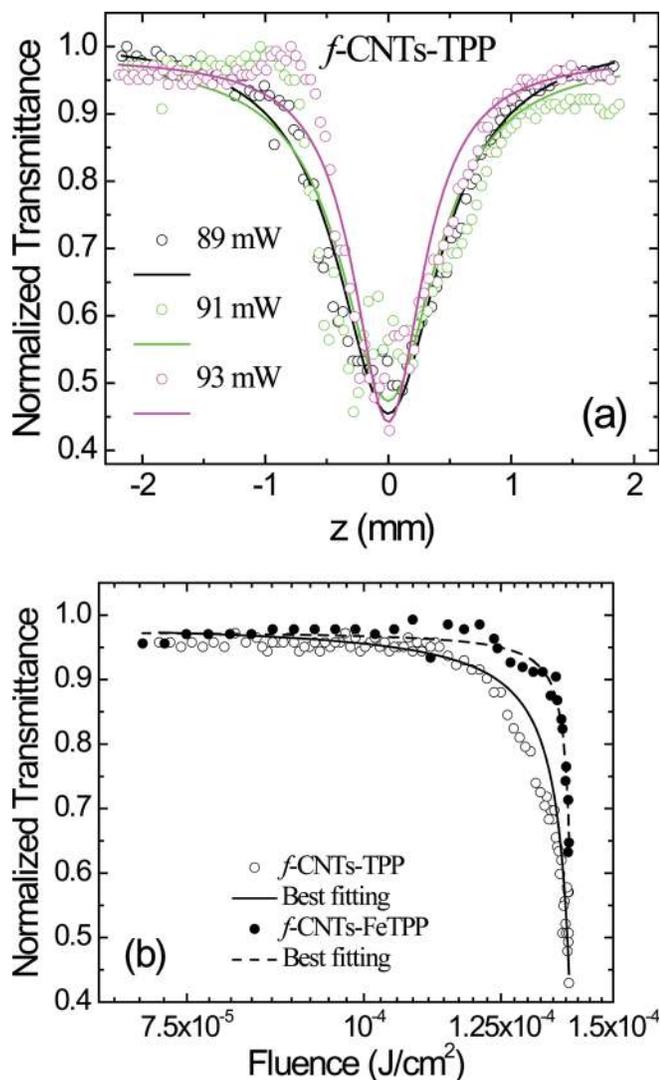


FIG. 4. (Color online) (a) Open-aperture z-scan trace of *f*-CNTs-TPP at different input power. Experimental points represent as black, green, and magenta circles correspond to 89, 91, and 93 mW power, respectively, whereas the solid line is a theoretical fit to the experimental data. (b) Optical limiting curve of functionalized CNTs with TPP (open circles) and FeTPP (closed circles), whereas the solid line is a theoretical fit to the experimental data.

to or larger than the wavelength of the light. However, the mechanism is likely to be different in the case of shorter pulse excitation.³¹ Only a few reports exist on the ultrafast nonlinear optical response of functionalized CNTs. Kamaraju *et al.* observed TPA to be the dominant mechanism for nonlinear absorption in CNTs suspensions in the femtosecond regime.¹⁷ Several reports exist on optical limiting experiments with functionalized CNTs in the nanosecond regime with different values of limiting thresholds.^{2,4,14,17,18,20,24,26} The present observation of *f*-CNTs in the femtosecond regime with the porphyrins is of significance from the point of view of designing efficient and versatile optical limiters with ultrafast response.

IV. CONCLUSION

We have synthesized the soluble CNTs functionalized noncovalently with free base porphyrin as well as a metalloporphyrin and investigated their linear and nonlinear optical

properties. Analysis of the data from TEM, SEM, and optical absorption spectroscopy indicates that the interaction between CNTs and porphyrins is likely to be due to π - π or Van der Waals interaction rather than covalent binding in our samples. Strong nonlinear absorption is observed in the functionalized CNTs. Theoretical fitting of the z-scan data indicates that the mechanisms of nonlinearity involve TPA along with nonlinear scattering and saturable absorption to some extent. Both *f*-CNTs show ultrafast optical limiting with very low threshold values compared to C₆₀ and nonfunctionalized CNTs. The enhancement of nonlinear absorption and optical limiting on functionalization can be attributed to the different mechanism of the nonlinearity, which involve higher excited states in the case of femtosecond excitation of *f*-CNTs. Noncovalent functionalization, though chemically much simpler than covalent functionalization, alters the optical properties of the SWCNTs and makes it possible for the nanocomposite to exhibit mechanisms of nonlinearity normally associated with the molecule used for functionalization. The interesting nonlinear optical properties of these materials and ultrafast response render them as attractive candidate materials with immense scope for device applications in optoelectronics and photonics.

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